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The 14th International Conference

AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES



Proceedings

Dubrovnik, Croatia / 6-10 October 2003

PROCEEDINGS OF

The 14th International Conference
"AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES"

Publisher
Croatian Air Pollution Prevention Association

For publisher:
Vladimira Vadjić, Ph.D.

Editor in Chief:
Krešimir Šega, Ph.D.

Reviewers:
Prof. Marko Šarić, Ph.D.
Prof. Fedor Valić, Ph.D.

Design of front page:
Antun Paunović

Printed by:
MTG-Topgraf, Velika Gorica, Croatia

Edition:
300 copies

ISBN 953-6609-03-7

CIP - Katalogizacija u publikaciji
Nacionalna i sveučilišna knjižnica, Zagreb

UDK 504.3.054(063)
INTERNATIONAL Conference "Air Quality - Assessment and Policy at Local, Regional and Global Scales" (14 ; 2003 ; Dubrovnik)
The 14th International Conference "Air Quality - Assessment and Policy at Local, Regional and Global Scales", Dubrovnik, 6-10 October 2003 : proceedings / <editor in chief Krešimir Šega>. - Zagreb : Croatian Air Pollution Prevention Association, 2003.

ISBN 953-6609-03-7

I. Onečišćenje atmosfere — Zbornik

430930064

Croatian Air Pollution Prevention Association (CAPPA)

International Union of Air Pollution Prevention and Environmental Protection Associations (IUAPPA)

The 14th International Conference

"AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES"

Proceedings

Dubrovnik, 6-10 October, 2003

UNDER THE AUSPICES OF:

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Ministry of Environmental Protection and Physical Planning

Ministry of Science and Technology

Croatian Chamber of Economy

Mayor of the city of Dubrovnik, Dubravka Šuica

ORGANIZERS:

Croatian Air Pollution Prevention Association (CAPPA)

International Union of Air Pollution Prevention and Environmental Protection Associations (IUAPPA)

CO-ORGANIZERS:

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TABLE OF CONTENTS

Plenary sessions

Williamson T
LIMIT VALUES IN EUROPEAN AIR QUALITY POLICY: EMERGING ISSUES **21**

Seifert B
EXPOSURE ASSESSMENT - THE WAY BEYOND AIR QUALITY ANALYSIS **29**

Schwela D, Hakkinen P, Papameletiou D
CONSUMER PRODUCTS AND INDOOR AIR QUALITY: AN EMERGING ISSUE AND OPPORTUNITY **41**

Medina S, Mücke H G, Plasencia A
AIR POLLUTION AND HEALTH: A EUROPEAN INFORMATION SYSTEM TO ASSESS THE HEALTH IMPACT AIR POLLUTION (THE APHEIS PROJECT) **49**

Amann M
LINKAGES AND SYNERGIES OF GLOBAL, REGIONAL AND LOCAL EMISSION CONTROLS **55**

Round Table on Emission Trading in Greenhouse Gases and Air Quality in Europe

Dell'Anno P
EMISSION TRADING: GENERAL PRINCIPLES OF THE PROPOSAL FOR DIRECTIVE COM/2001/058 ..... **63**

Emissions and Control

Amara G, Brusca S, Clasadonte M T, Lanzafame R, Matarazzo A

TECHNO-ECONOMIC ANALYSIS OF AN INNOVATIVE PROJECT FOR THE PRODUCTION OF ENERGY FROM WASTE THERMO-DESTRUCTION 71

Benstead T J, Evans R J D

CATALYTIC CONTROL OF EMISSIONS FROM STATIONARY SOURCES 81

Evans R J D

THE EMISSIONS MANAGEMENT SECTOR: RESPONDING TO THE NEEDS OF A NETWORK OF CITIES..... 89

Karvosenoja N, Johansson M, Kupiainen K

SIZE-FRACTIONED PARTICULATE MATTER EMISSIONS IN FINLAND IN 1990-2020..... 97

Longhurst J W S , Beattie C I , Chatterton T J, Woodfield N K

MANAGING THE IMPACT OF VEHICLE EMISSIONS IN URBAN AREAS FOR THE PURPOSE OF LOCAL AIR QUALITY MANAGEMENT 105

Sato A, Ichikawa Y

ESTIMATION OF NO_x EMISSIONS RELEASED FROM THE COGENERATION SYSTEMS IN URBAN AREA 113

Sciacca S, Fallico R, Ferrante M, Campo M, Pesce P, Cutello P

RECOVERY OF NOT DANGEROUS SPECIAL WASTES FOR THE PROTECTION OF THE ATMOSPHERE AND ENERGETIC SAVING..... 119

Senante E, Galtier L, Békaert C, Lambolez-Michel L, Decottignies V, Budka A

ODOURS MANAGEMENT AT WASTE TREATMENT FACILITIES: ODOUR SOURCES, ODOUROUS COMPOUNDS AND CONTROL MEASURES 123

Spigno G, Pagella C, M D Fumi, De Faveri D M

HEXANE CONTAINING WASTE GASES: EXPERIMENTAL DATA AND MODELLIZATION OF A FUNGI BIOREACTOR 129

Sporenberg F, Suder S
INTEGRATED ENVIRONMENTAL MANAGEMENT SYSTEMS BASED ON MEASUREMENT TECHNIQUES 137

Avirović G, Vešligaj A and Maren M
GREENHOUSE GASES EMISSION FROM FERTILIZER PRODUCTION 145

Aurer Jezerčić I A, Gelo A, Čolja D
EMISSION MEASUREMENTS FROM CREMATION FURNACE 153

Kopjar D, Barbalić N, Mačković D
REASONABLE LIMITATIONS OF AIR POLLUTANT EMISSION FROM THE EXISTING HEP's THERMAL POWER PLANTS 161

Pašalić G, Mikšik Z
PARTICLE EMISSION MEASUREMENT FROM CEMENT FURNACE STACK 173

Paskalev Z, Apostolova D
USE OF GAUSSIAN PLUME MODEL TO CALCULATED THE EFFECTIVE DOSES RECEIVED FROM THE POPULATION AROUND NPP "KOZLODUY" 183

Monitoring and Measurement

Allegrini I, Costabile F, De Santis F, Ianniello A
AREA SATURATION MONITORING OF ATMOSPHERIC POLLUTANTS BY MEANS OF PASSIVE SAMPLERS AND DIFFUSION DENUDERS 193

Bešlić I, Šega K, Bencetić Klaić Z
THE INFLUENCE OF WEATHER TYPES ON SUSPENDED PARTICLE CONCENTRATIONS 201

Borghese A
BROADBAND EXTINCTION SPECTROSCOPY TECHNIQUE FOR REMOTE SENSING OF AIR POLLUTION 207

Cattaneo C, Palanca A, Zolezzi M, Rovatti M
MONITORING OF MERCURY AND OTHER HEAVY METALS DEPOSITION IN SAVONA (ITALY) **215**

Fischer G, Jäckel G, Albrecht A, Kämpfer P
ANALYSIS OF AIRBORNE MICROORGANISMS IN THE SURROUNDING OF COMPOSTING FACILITIES **223**

Fumarola G, Gambadoro A, Zerbo A, Clasadonte M T
CHARACTERIZATION OF THE BACKGROUND CONCENTRATION IN AN INDUSTRIAL AREA **231**

Butković V, Cvitaš T, Kezele N, Klasinc L, Šorgo G
TROPOSPHERIC OZONE IN CROATIA **239**

Kovač E, Kezele N, Cvitaš T, Klasinc L
PHOTOCHEMICAL POLLUTION INDICES – AN ANALYSIS OF 12 EMEP STATIONS **247**

Leu H G, Chien H C, Fu J S, Jang C C
ADVANCED AIR QUALITY MODLEING ASSESSMENT IN TAIWAN .. **255**

Herceg Romanić S, Krauthacker B, Milanović Z
PCBs AND PCDD/Fs IN ZAGREB AMBIENT AIR SAMPLES BETWEEN 1997 AND 2001 ..... **261**

Kwokal Ž, Branica M
GASEOUS MERCURY SPECIES IN THE POLLUTED PART OF THE KAŠTELA BAY (EASTERN ADRIATIC COAST) **267**

Kwokal Ž, Branica M
THE PRESENCE OF TOTAL GASEOUS MERCURY IN THE OPEN-AIR AND THE ATMOSPHERE OF SOME ELECTROCHEMICAL LABORATORIES **273**

Mamane Y, Yossef O, Melamed E
SOURCE APPORTIONMENT OF COARSE AND FINE PARTICLES IN THE HADERA URBAN AREA ALONG THE EAST MEDITERRANEAN COAST **279**

Matarazzo A, Clasadonte M T, Zerbo A
OZONE ANALYSIS WITH DOMINANCE BASED ROUGH SET APPROACH IN A HIGH-RISK ENVIRONMENTAL AREA **287**

Labazan I, Krstulović N, Milošević S
TRACE GAS DETECTION BY CAVITY RING-DOWN SPECTROSCOPY **297**

Picer M, Holoubek I, Klánová J, Kohoutek J
CHLORINATED HYDROCARBONS IN THE ATMOSPHERE AND SURFACE SOIL IN THE AREAS OF THE CITY OF ZADAR AND MT. VELEBIT – CROATIA **303**

Primerano P, Catalfamo P, Corigliano F, Di Pasquale S, Arrigo I
THE IMPACT OF ACID DEPOSITIONS WITH SANDSTONE AND GRANITE BODIES **311**

Schultz E, Ronneberger O, Burkhardt H
AUTOMATED MICROSCOPIC RECOGNITION OF ATMOSPHERIC PARTICLES IN AMBIENT AIR SAMPLES **319**

Senante E, Békaert C, Decottignies V, Galtier L
ASSESSMENT OF AIR QUALITY AT WASTE MANAGEMENT ACTIVITIES: STRATEGIES OF SAMPLING **325**

Števulová N, Eštoková A, Šenitková I
MONITORING AND CHARACTERISATION OF INDOOR PARTICULATE MATTER **331**

Yuan C S, Lin Y C, Lee C G
A FEASIBILITY STUDY ON USING ATMOSPHERIC VISIBILITY AS AN ALTERNATIVE AMBIENT AIR QUALITY INDICATOR FOR METRO KAOHSIUNG, TAIWAN **339**

Borovečki D, Gliha Z, Šojat V
QUALITY CONTROL IN PRECIPITATION ANALYSIS **347**

Čačković M, Šega K, Vađić V, Hršak J, Bešlić I, Šoljić Z
METALLIC AND ACIDIC COMPONENTS IN HIGH-RISK PARTICLE FRACTION IN ZAGREB AIR **351**

Hršak J, Čačković M, Kalinić N, Balagović I
DEPOSITION OF ACIDIC COMPONENTS AND HEAVY METALS IN ZAGREB IN 1999-2001 ..... **361**

Marović G, Senčar J, Šega K, Bešlić I

TOTAL BETA ACTIVITY IN THE AIR AND WET FALLOUT IN RELATION WITH SUSPENDED PARTICULATE MATTER CONCENTRATIONS 369

Pepeljnjak S, Šegvić M

SEASONAL VARIATION OF AIRBORNE MOULDS IN CONTINENTAL AND MEDITERRANEAN PARTS OF CROATIA (2002) 377

Šišović A, Vadjić Ž, Šega K, Bešlić I, Vadjić V

WINTER AND SUMMER PAH MASS CONCENTRATIONS – COMPARISON BETWEEN PM_{10} AND $PM_{2.5}$ PARTICLE FRACTION MEASUREMENTS 385

Šojat V, Hrabak-Tumpa G, Gelo B, Borovečki D, Gliha Z

NO_2 LEVELS IN CROATIAN AIR FROM 1992 TO 2001 393

Tomić T, Periš N, Barač A

EMISSION INFLUENCE FROM CEMENT PLANTS ON CONCENTRATIONS OF THALLIUM IN DEPOSITED MATTER IN THE AREA OF KAŠTELA BAY 403

Vasilić Ž, Drevenkar V, Bešlić I, Šega K

ORGANOCHLORINE PESTICIDES AND PCB CONGENERS IN SUSPENDED PARTICULATE MATTER COLLECTED IN ZAGREB ... 409

Žužul S, Pehnec G, Čačković M, Vadjić V

SEASONAL VARIATIONS OF OZONE MASS CONCENTRATIONS IN THE AIR OF ZAGREB 417

Global and Regional Environment

Bartlett T, Vardoulakis S, Williamson T

A PRACTICAL PERSPECTIVE ON LOCAL AIR QUALITY MANAGEMENT IN THE UK 425

Biamino W, Gambadoro A, Sesia V, Trivero P, Zerbo G

ATMOSPHERIC POLLUTION MAP IN A WIDE INDUSTRIAL AREA: MONITORING AND FORECASTING BY MEANS OF GROUND-BASED REMOTE SENSING DATA 433

Calabrò G, Currò P
POLICIES AIMED AT IMPROVING AIR QUALITY IN URBAN AREAS **441**

Chang C M, Chang L N, Kuo K T, Lu S C
THE IMPACT OF CURRENT TREND OF CLIMATE CHANGE ON AIR POLLUTION POTENTIAL IN TAIWAN **449**

Di Lorenzo A
TRANSPORT, ENERGY AND ENVIRONMENT: THE ROLE OF NATURAL GAS **459**

Fabiano B, Currò F, Cazzola D, Palazzi E, Pastorino R, Del Borghi M
A STUDY ON RISK ASSESSMENT OF ROAD TUNNEL FIRES BY FULL-SCALE AND LABORATORY TESTING **467**

Hart G S, Rosenberger J
CANADA'S INVOLVEMENT WITH POLLUTANT RELEASE AND TRANSFER REGISTERS (PRTRs) IN LATIN AMERICA AND THE CARIBBEAN **475**

Kadikis N, Vasiljeva T, Lyulko I
DEVELOPMENT OF AIR MONITORING STRATEGY IN LATVIA **481**

Möller D, Bierman M, Wieprecht W, Acker K, Kalass D, Hofmeister W, Tian-Kunze X
NEW INSIGHTS INTO ATMOSPHERIC HYDROGEN PEROXIDE UNDER POLLUTED AND REMOTE INFLUENCE **489**

Moon K C, Ghim Y S, Bae G N, Lee S B, Kim Y P
SHIPBOARD MEASUREMENTS OF LONG-RANGE TRANSPORTED AIR POLLUTANTS OVER THE YELLOW SEA **499**

Murlis J
AIR POLLUTION IN ITS SOCIO-ECONOMIC CONTEXT: A PRODUCT FOCUSSED POLICY FOR THE FUTURE **509**

Pandžić K
UPPER-AIR WIND ROSES FOR THE WESTERN CROATIA **517**

Santoprete G, Tarabella A
USE, MATERIALS, ENVIRONMENTAL EFFECTS AND PERSPECTIVES OF GEOTHERMAL ENERGY 523

Sun E J
MONITORING OF CHINA SAND STORM PARTICLES WITH PETRI DISH AND GALSS SLIDE IN SHELTER 533

Vardoulakis S, Bartlett T, Fisher B E A, Delmas V, Deacon A
REGIONAL STRATEGIES AND CROSS-BORDER CO-OPERATION TO CONTROL OZONE POLLUTION 543

Impacts

Day RJ
PUBLIC PERCEPTIONS OF AIR POLLUTION AND ITS EFFECTS IN NORTH LONDON, UK 555

Fallico R, Ferrante M, Fiore M, Costantino G, Pesce P, Cutello P
PROFESSIONAL EXPOSURE TO BENZENE: COMPARISON BETWEEN BIOCHEMISTS' INDICES AND FREQUENCIES OF SCE "SISTER CHROMATID EXCHANGES" 563

Ferrante M, Fallico R, Fiore M, Pesce P, Cutello P
METILTERBUTILETHER: AN EMERGENT PROBLEM IN ATMOSPHERIC POLLUTION 569

Galtier L, Békaert C, Decottignies V, Senante E
DUSTS AND NOISE MEASUREMENT IN A HOUSEHOLD WASTE SORTING PLANT AND CORRECTIVE MEASURES: A REAL-SCALE STUDY 573

Merkord J, Kröning G, Weber H, Hennighausen G
TOXICITY OF DIBUTYLTIN DICHLORIDE (DBTC) IN RATS 579

Reichert T, Fitz S, Anshelm F, Gauger T, Schuster H, Droste-Franke B, Friedrich R
DOSE-RESPONSE-FUNCTIONS FOR POLYMER WEATHERING: A CONTRIBUTION FOR THE MAPPING OF AIR POLLUTION EFFECTS 587

Ribeiro H
AIR POLLUTION IN AN AREA OF SÃO PAULO, BRAZIL: HEALTH EFFECTS ON CHIDREN **601**

Roussel I, Dechenaux J, Shadkowski C, Muls E
A MULTICENTRIC STUDY OF PERSONAL EXPOSURE: WHAT LESSON? **607**

Sciacca S, Ferrante M, Pesce P, Nicolosi D, Scuderiand E, P Cutello
THE VOLCANO Mt ETNA: FIRST APPRAISAL ON THE HEALTH EFFECTS OF VOLCANIC-ASH **615**

Šenitkova I
INDOOR AIR QUALITY - CHEMICAL POLLUTANTS **621**

Kalinić N, Hršak J, Vadjić V, Lambaša-Belak Ž, Mihelčić V, Perković B
AIRBORNE FLUORIDE CONTAMINATION OF SOIL AND VEGETATION **629**

Šegvić M, Cvetnić Z, Pepeljnjak S
AIRBORNE FUNGI IN NATURALLY VENTILATED AND AIR-CONDITIONED INDOOR SPACES AND OUTDOOR AIR IN ZAGREB (June, 2002) **639**

Air Quality Studies

Barbalić N, Marijan G
NEW EU VERSUS CROATIAN AIR QUALITY STANDARDS **649**

Brulfert G, Chaxel E, Chemel C, Chollet J P
NUMERICAL SIMULATION OF AIR QUALITY IN CHAMONIX VALLEY, USE OF DIFFERENT CHEMISTRY INDICATORS **661**

Bigg M G
THE FUTURE OF INDUSTRIAL EMISSION REGULATION IN THE UK AND EUROPE **669**

Giugliano M, Grosso M, Lonati G
THE ATMOSPHERIC FINE PARTICULATE IN LOMBARDY (ITALY) **677**

Lee J Y, Yi S M and Kim Y P

DRY DEPOSITION FLUXES OF PARTICULATE PAHS AT THREE SITES AT KOREA IN 1999 685

Longhurst J W S , Beattie C I , Chatterton T J, Woodfield N K

IMPROVING AIR QUALITY THROUGH LOCAL AIR QUALITY MANAGEMENT. A CRITICAL REVIEW OF BRITISH EXPERIENCE AND PRACTICE 691

Marques M C, Carrilho C L, Lourenço J M, Gaspar R M

AIR POLLUTION DISTRIBUTION ON TEMPORAL AND SPATIAL SCALES FOR NORTHERN PORTUGAL URBAN AREA OF CHAVES 699

Meskal N

IMPROVED POINT SOURCE INVENTORY - DEMONSTRATION OF THE NEW REPORTING SOFTWARE FOR CONSOLIDATED REPORTING OF CRITERIA AND TOXIC EMISSIONS 707

Nećak J, Jelavić V

EVALUATION OF THE AIR QUALITY STATE IN THE REPUBLIC OF CROATIA WITH NATIONAL ACTION PLAN 715

Premec K

TOTAL OZONE AND UV-B RADIATION OVER CROATIA 727

Sparacia S, Milazzo A, Saija G

KEY ENVIRONMENTAL RESOURCES IN STRATEGIC ENVIRONMENTAL CONTROL OF THE FIRM 735

Sparacia S, Milazzo A, Ciraolo L

GLOBAL DEVELOPMENT OF THE ENVIRONMENTAL VALUE CHAIN AND STRATEGIC ENVIRONMENTAL CONTROL 745

Sparacia S, Milazzo A, Ciraolo L

STRATEGIC ENVIRONMENTAL CONTROL 753

Šega K, Beslić I, Šišović A, Čačković M, Škrbec A

SILAQ PROJECT - CROATIA 761

Špirić Z, Vađunec J, Ferenčić M, Brezovec M, Borovec M, Vađić V, Bašić F, Mesić M, Seletković Z, E Srebočan, Pompe-Gotal J

ECOLOGICAL MONITORING IN GAS FIELD MOLVE 769

Thunis Ph, Cuvelier C

CITYDELTA: A MODELLING INTER-COMPARISON EXERCISE IN 8 EUROPEAN CITIES 777

Vadjić V

AIR QUALITY IN CROATIA MONITORING AND CATEGORIZATION AT REGIONAL SCALE 783

Weber R O, Gehrig R, Fischer A

PARTICLE NUMBER CONCENTRATIONS FROM RURAL TO URBAN SITES IN SWITZERLAND 793

Plenary Sessions

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Dubrovnik, CROATIA 6-10 October 2003

LIMIT VALUES IN EUROPEAN AIR QUALITY POLICY: EMERGING ISSUES

T Williamson*

ABSTRACT

This paper will analyse the essential elements of the current system of air quality regulation in Europe as it has evolved over the past few decades, and assess how well it achieves its ultimate aims, directed at both the individual and society more broadly, of:

1. Preventing exposure to pollutants in the ambient air at concentrations considered likely to cause harm, and
2. Achieving the highest level of human and environmental protection in the most cost-effective manner.

The paper focuses mainly on health and air quality as the principal concerns of the Clean Air For Europe (CAFE) programme.
The pressures which are impacting on the system are analysed, and three main components are identified:

- New and emerging health evidence, undermining thresholds and emphasising chronic impacts;
- Differential improvements in air quality, both within and between Member States; and
- Widespread predicted non-compliance with a number of key limit values.

The general conclusion is that current controls, based on a system of Air Quality Limit Values set out in the Air Quality Framework Directive (96/62/EC) and subsequent "Daughter" Directives, may not on their own be the optimum vehicles for delivering the greatest standard of overall health protection. Alternative and

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supplementary systems are offered and it is suggested that the European Commission consider the development of an explicit enforcement policy for the current system as an interim measure, while research and development work is undertaken on the alternatives.

INDEX TERMS

INTRODUCTION

The control of air pollution in Europe takes a number of different forms, each designed to address different aspects of the problem. These include:

- Emission controls, e.g. the Large Combustion Directive (2001/80/EC), the National Emission Ceilings Directive (2001/81/EC), industrial emission control through IPPC.
- Product controls, e.g. the Auto-Oil Programme.
- Exposure limits, although these are currently not common other than for health and safety purposes within workplaces.
- Ambient concentration limits, e.g. the Air Quality Framework Directive (96/62/EC) and subsequent "Daughter" Directives[2].

It is this latter category with which this paper is directly concerned, taking the view that, in terms of human health effects, ambient concentrations are currently the lead element in policy development.

There are a number of key features of the Air Quality Limit Value (AQLV) system as currently defined in EU legislation, which have been responsible for shaping the policy response by Member States.

The first is that they are set for single pollutants, i.e. each pollutant has its own AQLV, to be achieved in its own timescale and with its own tolerance limit. This makes for a system which is relatively simple and easily understood, but ignores the fact that pollutants are rarely generated singly and that different pollutants will also produce common symptoms in populations. The second feature is that they apply in all places and at all times where human exposure is likely (generally urban areas). The third feature, that compliance is mandatory, further reduces the level of flexibility available, but also clearly adds a greater incentive to comply. The policy inevitably becomes one of "hot-spot" elimination regardless of the scale of the hot-spot and the number of people exposed (with the exception of ground level ozone).

[2] 1st daughter directive (SO_2, NOx, PM_{10}, and lead) - 99/30/EC; 2nd daughter directive (CO and benzene) - 2000/69/EC; 3rd daughter directive (ozone) – 2002/3/EC.

CHANGING EVIDENCE

Clearly, there are circumstances where limit values are the most appropriate policy tool for driving improvements in air quality. In broad terms, these are where an identified pollutant exists routinely at levels above those thought to give rise to significant health (or other) effects, in most or all areas (or at least the majority of urban areas). Furthermore, this pollutant should have multiple, diverse sources and a variety of possible control techniques should be available. This was the situation across Europe in the early to mid 1990s when the current systems in both the UK and EU were developed. Air quality has improved markedly across Europe since the Air Quality Framework Directive was adopted in 1996.
However, a number of issues have emerged which raise questions about the future effectiveness of limit values as the sole regulating mechanism for air quality, principally:

1. *Health evidence*. Health evidence has increasingly come from epidemiological rather than clinical studies, resulting in two important shifts. Firstly, there is a greater understanding of chronic effects which has tended to shift the focus onto long term pollutant concentrations rather than episodic peaks. Secondly, these studies have tended to undermine the concept of a threshold of effects, implying that a health benefit can be shown for a reduction in concentration wherever it occurs and from whatever level.
2. *Differential improvement of air quality*. The varying characteristic of each Member State has meant that progress on improving air quality has occurred at different rates. There has always been a gap between what is "challenging" for different Member States, and there is some evidence that this gap has increased over time. The expansion of the Union over the next few years will tend to exacerbate this problem.

There is further pressure being brought to bear on the current system through projected non-compliance with the key AQLVs for NO_2, PM_{10} and ozone. While a low level of non-compliance is inevitable if a system is to be "challenging", the predictions are thought to apply to a large number of Member States, quite possibly the majority with regard to NO_2. Evidence of this in the UK has recently emerged,[3] but is certainly not confined here. Widespread non-compliance such as this threatens to undermine the credibility of the system.

The Need for Change

From the preceding discussion, the question arises as to whether the system of air quality limit values currently in place delivers what is expected, i.e. the maximum health benefit for the population in the most effective manner?

[3] Air Quality Expert Group; Nitrogen Dioxide in the UK (Draft for Comment); DEFRA; May 2003; http://www.defra.gov.uk/corporate/consult/aqeg-no2/index.htm

To achieve further improvements in air quality, at least two fundamental changes of approach should be considered:

1. Future policy must be directed at reducing exposure to those pollution issues with the greatest health impact; and
2. New techniques must be developed to address the impact of measures on air toxicity rather than specific pollutants.

The greatest impact of measures to reduce long-term exposure to 'chronic air toxics' (pollutants such as PM and carcinogens) which have a chronic effect upon mortality is achieved by targeting actions that have the greatest impact upon the exposure of the largest number of people. In this, consideration also ought to be given to the combination of regulations on indoor and outdoor air. Reducing exposure at pollution hotspots at which relatively few individuals are exposed will be much less effective in health (benefit) terms.
The limit values approach is designed to protect those people exposed to an unacceptable risk of health impacts by poor air quality. The assumption is that those who live in areas where pollutant levels are below the limit values are not at risk (or at least an acceptable risk). Chronic effects and the lack of thresholds tend to disable this assumption, but do not necessarily run counter to the basic concept.

Short Term Options

To properly address these concerns, the current system may therefore need to be adjusted or supplemented in some way. There are a number of easily available policy solutions which could be used to relieve the pressure on the system in the short term. All have been used by the EU in the past, both in relation to air pollution and in other environment fields. The most obvious candidates for such short term solutions are relaxation of the AQLVs, some form of derogation, or the partial or total conversion of limit values to guide values. This latter option could be used to set, for example, a guide value for roadside locations with a strict limit value for background locations.
There is the danger, however, that by simply "tweaking" the system, its credibility is undermined, the level of complexity is increased and it moves away from the original policy objective.

ENFORCEMENT POLICY

One of the most pressing problems facing the current system is the widespread predicted exceedances of some of the AQLVs (PM_{10}, NO_2, and O_3). All three of the short term options shown could be proposed as ways of relieving this pressure, but they all weaken it to a greater or lesser degree and should therefore be seen as undesirable, certainly in the longer term.
An alternative approach would be for the Commission to develop an explicit enforcement policy for AQLV non-compliance, looking beyond simple strict liability

to how far Member States had taken all reasonable steps to comply. The burden of proof that they had done all that was reasonable to comply would need to rest with Member States and it should be backed up by a high level of scrutiny by the Commission, or by independent assessors, to test the veracity of the evidence. It should be made clear to Member States what is expected of them and the details of the scrutiny process. For preference, the policy should be developed in close consultation with key stakeholders. An enforcement policy developed along these lines would serve two functions, beyond acting as an incentive for Member States to take what action they can to comply with the regime as it currently stands. Firstly, it would help supply the Commission with data on the true extent of the air quality problem in Europe, and actions available to address it. Secondly, it would allow some time to research and develop more robust ways of improving the performance of the current system over the longer term.

LONG TERM SOLUTIONS

In order to secure the further air quality improvements needed to protect the health of the population, new approaches will need to be considered. This is a view which is emerging from a number of different sources as the performance of the current system is being reviewed. For example, the UK Government's Air Quality Expert Group concluded that "*a more flexible and holistic approach to air quality management might deliver more effective control strategies.*"[4]

Arguably, numerically expressed requirements cannot be avoided within any regulatory system. One attraction of the limit value approach is their relative ease of application and low level of scrutiny required to ensure compliance. The current approach, or something analogous to it, will need to be retained as a "backstop" to address grossly polluted areas and to prevent such areas from developing. What should be sought is a system which will supplement and extend the current regime to address the problems of inherent variation, a lack of effect thresholds, chronic health effects, and the inevitable trade offs between different pollutants with differing priorities.

This section describes two complementary approaches – gap closure and total air index - which could be developed to fit this supplementary role. They are not offered as finished solutions, but as a start point for further research.

1. Gap Closure

The objective of this approach is to reduce total population exposure, thereby maximising the public health benefits of actions to improve air quality, particularly where background concentrations tend to make up a large proportion of the total, as is the case for particulate matter. It relies on the progressive closure of

[4] Air Quality Expert Group; Nitrogen Dioxide in the UK (Draft for Comment); DEFRA; May 2003; http://www.defra.gov.uk/corporate/consult/aqeg-no2/index.htm

the gap between the "natural background" concentration and the current population weighted exposure.
The gap-closure target could be defined for each Member State, based either on the basis of a percentage reduction or an absolute concentration reduction, e.g. a 30% reduction by 2010 or a 2mg/m^3 reduction by 2010. The former would probably be more equitable between countries. The gap closure approach could be operated on the basis of monitoring and/or modelling of concentration values, or it could be used to develop emission reduction targets, so as to parallel the National Emissions Ceiling (NEC) Directive approach. An alternative would be to adopt stepped targets over shorter timescales.
The starting point is to define a *'natural' exposure concentration* and a *population-average 'current' exposure concentration.* The 'current' population-average exposure concentration will be determined essentially by the urban background concentration, with the population-weighted average being strongly influenced by concentrations in the larger urban areas.
The 'natural' background could be determined by monitoring, coupled with source apportionment. A separate 'natural' background would be required for each agglomeration, although an average could be applied over a reasonably large area.

2. Total Air Index

(a) Combined Risk

In addition to concentration, the problems of exposure to any pollutant are a function of:

- The range of health impacts caused by it;
- The probability of experiencing each of those health impacts per unit exposure;
- The severity of each impact.

An overall risk rating for any pollutant could thus be derived by summing the product of probability and severity across all impacts of that pollutant. At specific locations the total risk faced from air pollution would be calculated as the sum of the exposure-weighted risk ratings across all pollutants.
Various reviews provide listings of the health effects associated with different pollutants combined with risk factors linking concentration to response. Severity can be measured in either physical terms (e.g. using the DALY, disability adjusted life year, approach) or in economic terms, both of which approaches have been accepted by policy makers. The biggest problems for such an analysis would be that the effects of different pollutants are known to varying degrees, and the confidence in quantifying risk is also variable. However, the same could be said of any approach that seeks to identify acceptable standards.
A distinct strength of this method is that it would provide an explicit rationale as to why some effects and some pollutants end up being considered more important than others. In terms of persuading public opinion this is likely to be more powerful

than alternatives where the rationale for preferring action against one pollutant over another remains implicit.
Risk ratings for individual pollutants could be used to set objectives in terms of overall risk reduction beyond current concentration standards. This approach could have a very significant benefit in terms of improving the cost-effectiveness of future pollution control. It would need to be backed up with extensive information from monitoring and modelling, but these data are already being generated under existing legislation.

(b) Combined Toxicity

An alternative, and possibly simpler, approach to combined risk would be to use the toxicity of combined pollutants more directly. Whilst considerable uncertainty exists, the impact of different incremented reductions of different pollutants with chronic effects are now emerging. This enables a combined chronic air toxicity (CAT) index to be developed:

$$CAT = [A]X + [B]Y + [C]Z + \text{etc.}$$

where [A] = concentration of pollutant A (e.g. PM_{10}); X = impact on life expectancy per unit of pollutant A (e.g. $\mu g/m^3$ PM_{10}); [B] = concentration of pollutant B; Y = impact on life expectancy per unit of pollutant B; etc.
This index could be more transparent to the public than a combined risk approach and could be modified periodically as scientific understanding improved. The index would enable measures to improve air quality to be targeted at pollutants of greatest effect. Under current knowledge, the emphasis would be biased towards PM_{10} and ozone, which agrees very well with the stated policy aims of the CAFE programme. It would also enable the combined effect of improvements to air quality for several pollutants to be more adequately quantified and costed.

CONCLUSIONS

Current air quality legislation in Europe, i.e. the system of mandatory air quality limit values for pollutants of concern, has achieved much in the last decade. Set within the wider framework of legislation and policy on air pollution, it is clear that the European Union has developed a comprehensive and rigorous framework which is now being set into a more coherent strategy through the CAFE process. However, the system is coming under increasing pressure and widespread exceedances of some of the AQLVs are predicted. Also, the system may not in fact be performing its function of achieving the best possible health outcome for the population in the most cost effective manner. Furthermore, some of the basic assumptions which lie behind the AQLVs, e.g. that thresholds of effect exist, are being undermined. While there are short term adjustments which can be made to the system, these are not likely to be satisfactory in the longer term, and may result in the credibility of the system being seriously damaged.

What is needed is a revised regime whereby gross pollution is dealt with by the traditional approaches, including limit values, while overall exposure levels are addressed through a supplementary system. This supplementary system could consist of targets based on a gap closure approach, and/or indices of total air risk or toxicity. The process of moving from the current system, reliant on the use of AQLVs as the principle policy driver, to one which uses AQLVs in conjunction with a supplementary approach will need careful management and will take some time. The first step in this transition, aside from the development of an explicit enforcement policy for the current system, would be to conduct further research into the detailed operation and viability of both the gap closure and total air index approaches. The next step would be to monitor the performance of the indices in real time, publishing the results alongside more traditional indicators, with the final step being the incorporation of the chosen index into the legislative framework.

APPENDIX A

Acknowledgements

This paper was developed by NSCA following discussion with, and using contributions from, the following:

Christer Ägren	Swedish NGO Secretariat on Acid Rain
Greg Archer	Carbon Trust
George Barrett	PowerGen
Tim Brown	NSCA
Dr. Andrew Farmer	Institute for European Environment Policy
Dr. Nigel Haigh	Institute for European Environment Policy
Mike Holland	EMRC
Prof. Duncan Laxen	Air Quality Consultants
Prof. Jim Longhurst	University of the West of England
Richard Mills	NSCA
Steve Moorcroft	Casella Stanger
Dr. John Murlis	University College London
John Rea	Department for Environment, Food and Rural Affairs
John Spiers	Royal Commission on Environmental Pollution
Dr. Martin Williams	Department for Environment, Food and Rural Affairs
Tim Williamson	NSCA

The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

EXPOSURE ASSESSMENT - THE WAY BEYOND AIR QUALITY ANALYSIS

B Seifert*

ABSTRACT

Ambient air pollution has been, and still is, monitored at fixed-site monitoring stations. However, it is clear that people spend their day at places sometimes far away from such sites if they are outdoors, or even not at all outdoors. Thus, fixed-site monitoring does not reflect real exposure to air pollutants. As a consequence, science has developed tools for exposure assessment by either personal monitoring or modelling taking into account the time spent in the various microenvironments and the pollutant concentration in these microenvironments. An even more advanced procedure is probabilistic exposure assessment in which the deterministic "point estimate" is replaced by a probabilistic approach using frequency distributions of the parameters involved in the exposure model. As usual, policymakers are slowly following these scientific developments.

KEYWORDS

Exposure, probabilistic exposure assessment, personal sampling, indoor air

INTRODUCTION

The determination of the concentration levels of pollutants in the air has been for years, and still is, the major preoccupation of many if not all, participants of this conference. It is only by measuring these levels that we can fulfil the needs that result from either legal requirements or research activities. Examples of the two different aspects are the check of compliance with air quality regulation and the support of studies on health effects of air pollutants, respectively.

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However, especially in the case of studies to assess the health impact of air pollution, we have come to know over the years that measuring the concentration of an air pollutant at one or several sites will not give us sufficient information. In fact, despite a large number of studies, the real extent of the health impact of many air pollutants, particularly when they occur at lower concentration levels, is still somewhat unclear. One of the reasons may be that using concentration data from fixed site monitoring stations in health effects studies is not appropriate. In fact, we all know that the air at such sites is not the one that people participating in health effects studies breathe all day long.
To overcome these difficulties, the concept of exposure assessment has been introduced. In this paper, starting from the definition of exposure, it will be explained to what extent this concept is a useful complement of classical air quality analysis.

THE DEFINITION OF EXPOSURE

In 1991, the US National Academy of Science published a report in which exposure was defined in the following way: "Exposure occurs when there is contact at a boundary between a human and the environment with a contaminant of a specific concentration for an interval of time; the units are concentration multiplied by time." (NAS, 1991).
Usually, this definition is expressed by the mathematical relationship given in Equation 1, where ΔE is the exposure of an individual to a pollutant concentration C during a specific time period Δt.

$$\Delta E = C \cdot \Delta t \qquad (1)$$

This definition describes one special type of exposure, namely the "integrated exposure" (Georgopoulos and Lioy, 1994). It has the drawback that it "filters out", as Ott (1995) has put it, information that is important for health risk assessment. In fact, the author has given a very impressive example of the problems associated with the use of Equation 1. Suppose two children playing with electricity for one hour, each of the two "exposed" to 600 "Volt · minutes". Child 1 is supposed to receive a constant potential of 10 V over the entire period of 1 hour, while child 2 experiences an equally constant, but much lower level of 1 V for the first 59 minutes, and then a sudden 540 V peak. It is evident that although the exposure is mathematically identical, child 1 would be in good health, whereas child 2 would be dead.
In a similar way, in air pollution, it would make an important difference if air containing 5 mg carbon monoxide/m^3 is breathed over 24 h, leading to 120 mg/m^3 · h, or if the same exposure of 120 mg/m^3 · h is the result of inhaling air for just 10 minutes that contains 720 mg/m^3 carbon monoxide/m^3.
Another problem with Equation 1 is that the resulting unit "concentration multiplied by time" is a bit confusing. The way out of the problems is to define exposure at some instant of time as the "joint occurrence of two events: (1) the

pollutant of concentration *C* occurs at a particular location in space at a particular time, and (2) the person is present at the same time and location in space" (Ott, 1995). It is important to always remain aware of these boundary conditions if the term "exposure" is used instead of the term "concentration", which is the case frequently.

The contact with pollutants can occur via the various media, air, water, soil, and food. The resulting exposure can be called "total exposure". One of the earliest large-scale exposure studies in which this term was used was the Total Exposure Assessment Methodology (TEAM) study (Wallace, 1987). However, this study when it was carried out first, considered only air as an uptake medium.

Today, it becomes more and more common practice to use the term "aggregate exposure" if exposure to one specific pollutant across the various media is meant. Following a definition given by US-EPA (2001), which is based on earlier work (ILSI, 1998), aggregate exposure refers to "*the amount of a chemical available at the biological exchange boundaries (e.g., respiratory tract, gastrointestinal tract, skin) for all routes of exposure".* Thus, within an aggregate exposure assessment all relevant routes of exposure are analysed. In fact, in real life, exposures from different pathways cannot be considered as independent events. Rather, they occur as a series of sequential or simultaneous events that are linked in time and place. It depends on the characteristics of the pollutant which of these routes plays the dominant role, or a role at all.

In the context of this paper, only the exposure from air will be considered, with "aggregate air exposure" denominating exposure from both outdoor and indoor air. The indoor air compartment can be subdivided further into homes, workplaces, schools, kindergartens, restaurants, passenger cabins of cars, busses and aircrafts, etc. Equation 1 then becomes Equation 2 according to which the time spent in the various microenvironments is taken into consideration. In this equation, "*i*" refers to the different microenvironments considered, and t_i is the time fraction spent in microenvironment *i* which shows concentration C_i.

$$E = \sum_i C_i \cdot t_i \qquad (2)$$

WAYS TO DETERMINE AIR EXPOSURE

There are two important ways to determine total air exposure, one is by *measuring*, and the other is by *modelling*. For the measurement case, personal sampling is the magic word: the person under study is provided with a personal sampler which has to be carried on the person or at least as close as possible over the entire 24 h of the day. Since this is cumbersome for a study participant, the modelling approach is being used as an alternative. In this case, total air exposure is calculated taking into account the time spent in the various microenvironments (indoors and outdoors) and the concentrations known to be present in these

microenvironments. If the uptake of a pollutant via air is calculated a person's breathing rate should also be considered in addition to the pollutant concentration that is governed by time and location. For example, activities like running, slow walking, working at a desk, and sleeping all cause different breathing rates (Spier et al., 1992).

Personal sampling provides a concentration level that represents integration over the concentration levels in all compartments visited by the person during the 24-h (or longer) measurement period and, thus, cannot detect the individual contribution of any compartment. In contrast, the modelling procedure permits to assess the contribution to total air pollutant exposure in each of the microenvironments. This kind of source apportionment can be of great help to decide what measures should be given preference in controlling pollutant concentrations.

It should be noted that the concept of total air exposure has important roots in the country where this conference takes place. In fact, it was in a paper published more than 25 years ago that Mirka Fugaš of the hosting Institute for Medical Research and Occupational Health described the indoor/outdoor situation for sulphur dioxide, lead and manganese. As is mentioned in the paper, the exposures calculated from data collected indoors and outdoors data demonstrate "the importance of adjusting the health related monitoring programme to the actual exposure pattern of the citizens" (Fugaš, 1975).

A more recent example of a study to experimentally assess exposure of people to volatile organic compounds (VOC) is the German Environmental Survey (GerES). GerES is a large-scale population study carried out in Germany repetitively (Seifert et al., 2000). In the 1990/92 round (GerES II), personal sampling for some 70 VOC was done on 113 adults using badge-type passive samplers. The individuals had been selected at random among the total study population of 2500 (Hoffmann et al., 2000). Using additional information obtained from questionnaires, multivariate regression analysis permitted to quantify the major sources of personal exposure to various VOC. As an example, it was found that the most important determinant of benzene exposure was exposure to environmental tobacco smoke indoors.

Another interesting example is related to exposure to toluene. The time spent daily on reading newspapers and magazines explained 10 % of the variance. This reflects the off gassing of toluene from printed matter, which is caused by the use of toluene as a solvent for print colours. It is clear that such exposure-related information cannot be obtained from a monitor installed outdoors.

In a recent publication on exposure to $PM_{-2.5}$ which describes the results of a model approach (Burke et al., 2001), it has been stated that the microenvironment "indoor-residential" had the greatest influence on total air exposure to $PM_{-2.5}$, compared to the other microenvironments considered, namely outdoor and non-residential indoor (office, school, store, restaurant, bar, in-vehicle). The outdoor compartment as such was found to make a *direct* contribution of around 5 % on

average. Another 35 % was due to an *indirect* contribution via infiltration of outdoor air into indoor spaces. Thus, about 60 % of the total air exposure to $PM_{-2.5}$ would not be influenced by control measures taken to reduce outdoor air $PM_{-2.5}$ levels. For non-smoking homes only, the calculated ratio was about 50 % : 50 %.

OUTDOOR AIR MONITORING AND EXPOSURE

In the early days of air pollution abatement much attention was paid to the control of emissions from industrial activities. Combustion-generated pollutants were on top of the list, and these were represented by the "classical" air pollutants, sulphur dioxide, nitrogen oxides, carbon monoxide, and suspended particulate matter. In contrast, traffic then played a less important role. Consequently, monitoring sites were generally installed close to industrial sources, and in most countries much fewer sites were established to provide information about what we now call the urban environment.

Although this has changed with the growing importance of traffic as a source of air pollution, there is still the question about the meaning of the outcome of studies of health effects of air pollutants that use monitoring data from sites that are not installed where people really live and stay for longer periods of time.

A first step into clarifying the situation was to provide reliable information on where people spend their time and what they are doing all day long. The most widely quoted information of this kind is in the publication of Szalai (1972), which tabulates data on about 25,000 people in 12 countries. With the advances of knowledge in this field, more differentiated information has become available. The data all show what everyone knows from common observation: we are not staying next to a fixed site monitoring station for 24 hours, very likely we do not even stay there for a few minutes per day. Information on human activity patterns has been obtained in the USA from a 2-year large-scale probability-based telephone survey, the National Human Activity Pattern Survey (NHAPS) carried out from 1992 to 1994 (Klepeis et al., 2001). The publication also summarises the development of studies on human activities starting from the early work of Lundberg et al. (1934), and concludes that 87 % of the total time of the day are spent indoors. From the data given and those of other studies referred to in the paper one can derive the following 60/20/10/10 rule of thumb: an average person spends about 60 % of the day's 24 hours at home, 20 % in other indoor environments (e.g., workplace, school, shops, theatres), 10 % in transit, and 10 % in outdoor air. This, clearly, is a very rough rule, but it has the advantage of being easier to remember than more precise numbers.

The importance of personal sampling for correct exposure assessment becomes especially visible in studies on suspended particulate matter. For example, Williams et al. (2000a) performed personal, indoor and outdoor measurements in 21 elderly persons living in a retirement facility in Baltimore. The study subjects spent about

95 % of their time indoors. Mean $PM_{-2.5}$ levels were 13.0, 10.0, 9.4, and 22.0 $\mu g/m^3$ for personal sampling, inside apartment sampling, central site in the building, and outdoor site (11 km from the building), respectively. The difference between personal and indoor concentrations is explained by what is called the "personal cloud" around the individual. The existence of such concentration gradient, which has first been described by Rodes et al. (1991), is supported by findings of Luoma and Batterman (2001) who concluded that occupant activities increased the concentration of particles of 5-25 μm diameter by up to 10 $\mu g/m^3$ in the vicinity of the activity. Also, there seems to be an influence of particle size on the relationship between personal, indoor and outdoor concentrations. This influence may be one of the reasons why the personal/outdoor ratio for $PM_{-2.5}$ was reported to be <1 by Williams (2000a) while the respective ratio for PM_{-10} was found to be >1 by Janssen et al. (1998). In their study on 37 adults, these authors found a mean outdoor PM_{-10} concentration of 42 $\mu g/m^3$ whereas the mean personal concentration was 62 $\mu g/m^3$. The median Pearson's R case was 0.50, and 0.71 if days with exposure to tobacco smoke were excluded. In an earlier study with $PM_{-3.5}$ samplers Spengler et al. (1985) had found much lower correlations between personal and ambient sampling. Correlation coefficients did not exceed 0.28 and were dependent on the smoking status of the study participant.

The results of Williams et al. (2000a, 2000b), together with those of others (e.g., Lioy et al., 1990), support the evidence that for an individual indoor and personal PM concentrations can differ substantially from the concentration measured at the nearest fixed site outdoors. However, on a population average good correlations have been observed, e.g., $r = 0.89$ in the Baltimore study (Williams et al., 2000b). These good correlations support the use of ambient PM measurements as exposure surrogate in epidemiological time series studies (Janssen et al., 1998; Rojas-Bracho et al., 2000; Sarnat et al., 2000; Williams et al., 2000a; Williams et al., 2000b). On the other hand, few studies have addressed the question whether ambient long-term PM concentrations predict long-term personal PM well. This is due partly to the logistical complications involved in measuring personal PM over long periods of time. Analyses conducted within the European EXPOLIS study have suggested that long-term ambient PM concentrations predict the population average of a series of personal $PM_{-2.5}$ measurements well (Jantunen et al., 2002).

UNCERTAINTY IN EXPOSURE ASSESSMENT

Exposure assessment is subject to uncertainty. Uncertainty refers to the lack of knowledge about specific factors in contrast to variability, which represents the true heterogeneity that is inherent to a factor. For example, there is variability among humans due to genetic differences or lifestyle, variability in time of pollutant concentrations on a daily or a seasonal basis, or variability in the time-activity pattern among different people depending on age, sex and geographical

location. An important element of uncertainty is the so-called parameter uncertainty that refers to, e.g., measurement errors (US-EPA, 1992). Measurement errors can be decreased to some extent by selecting a more appropriate measurement method or better quality control. While uncertainty can sometimes be reduced through further study, variability cannot. However, variability can be characterised better.

One of the possibilities to deal with uncertainty is sensitivity analysis. In sensitivity analysis, one of the variables is changed while the others are kept constant, and the effect of the change on the result is determined. This helps detect the variable that has the greatest influence on exposure.

If total air exposure of an individual is measured by using personal sampling, the uncertainty is mostly determined by the analytical method used and any non-compliance effect introduced by the individual that has to wear the personal sampler, such as incorrect fixing of the sampler or not wearing the sampler at all for some time. If exposure is modelled, uncertainty stems mainly from the variation of concentration levels within the various microenvironments and the variation in the time spent therein.

PROBABILISTIC EXPOSURE ASSESSMENT

In the past, if exposure has been modelled, this has generally been done using the "deterministic" approach. In this approach, "point estimates" are used for the various parameters to generate a single estimate of exposure, that are based on specific assumptions. For example, in order to "be on the safe side", the precautionary principle is often applied and "worst case" situations are assumed. However, it has become obvious that there were fundamental difficulties associated with the concept of the "most exposed individual" developed by Kimbrough et al. (1984). In fact, it is practically impossible to determine the maximum thinkable concentration level of a pollutant an individual could be exposed to.

But even when more reasonable data were used to characterise the "most exposed", such as the 95th percentile of the frequency distribution of air concentrations, the fact of using several parameters in the exposure model and assuming the 95-percentile for each parameter, generally leads to a result which is totally unrealistic. However, even if more realistic assumptions are made, the result of such deterministic procedure will always remain a point estimate of exposure.

A more advanced procedure is what has become known as "probabilistic" exposure assessment. In probabilistic exposure assessment, use is made of the frequency distribution of the parameters involved in the exposure model, i.e. the range of possible values that an input variable can take is being considered. This leads to a more realistic exposure assessment. The condition for carrying out a probabilistic exposure assessment is the availability of distributions of the model parameters.

The information contained in these frequency distributions is then combined.
If the very simple model given in Equation 1 is considered, two frequency distributions are needed: one for the concentration of air pollutant X determined at a specific site, the other for the time that people may spend at this site. Assuming that the pollutant concentration varies between 10 and 100 $\mu g/m^3$ and the time T spent at the site varies between 6 minutes and 6 hours, the extremes of the possible exposure would be 1 $\mu g/m^3 \cdot h$ and 600 $\mu g/m^3 \cdot h$. The most likely exposure would depend on the shape of the two frequency distributions and can be calculated by a Monte Carlo method. In this powerful statistical tool, a computer randomly selects one concentration value for pollutant X from the respective frequency distribution and multiplies it by an equally random-selected value from the frequency distribution of T. This procedure is repeated thousands of times using computer programmes such as "Crystal Ball" (Decisioneering Inc., Aurora, Colo., USA) or "@RISK" (Palisade Corp., Newfield, NY, USA).
In a recent evaluation of earlier studies on the comparison of modelled and measured exposure data, Hänninen et al. (2003) state that "all reviewed simulation model validations predicted the mean or median values with fair to good accuracy, but all underestimated the exposure variability". In the analysis of their own data, the authors compared modelled $PM_{2.5}$ exposures with personal exposure data measured on some 200 adults living in Helsinki. It is concluded that using Equation 2 and information on two and three microenvironments (home indoors/other, and home indoors/work indoors/other for the non-working and the working population, respectively) the probabilistic model predicts $PM_{2.5}$ exposure fairly well: the mean is underestimated by < 20 %. This finding applies to non-ETS exposed study participants. If the whole study population is considered (i.e. including ETS-exposed subjects), the agreement was less good because the models did not sufficiently take into account specific microenvironments that are important for ETS exposure, e.g. special smoking rooms in the working environment.

POLICY IMPLICATIONS

In the past, ambient air quality standards were generally set without taking into account to what extent people were really exposed to the air that was regulated. In fact, data from different sites in an ambient air pollution monitoring network were given equal weight without taking into account existing differences with regard to the number of people likely to stay in the vicinity of a specific site or the time spent next to it.
In the European Union, a first change was introduced with the publication of the Council Directive on air quality standards for nitrogen dioxide (European Communities, 1985). In Annex III of this directive it is fixed that in establishing monitoring stations Member States should select - to the extent possible - sites with the presumably highest risk of exposure.

In 1999, Council Directive 85/203/EEC was replaced by the "First Daughter Directive" (European Union, 1999). Annex VI prescribes how the sampling points for the measurement of air pollutants mentioned in the title of the daughter directive have to be located. The text states very clearly that for the protection of human health "Sampling points … should be sited:

(i) to provide data on the areas within zones and agglomerations where the highest concentrations occur to which the population is likely to be directly or indirectly exposed for a period which is significant in relation to the averaging period of the limit value(s);

(ii) to provide data on levels in other areas within the zones and agglomerations which are representative of the exposure of the general population."

This means that exposure is given much higher priority than in the past. What has not yet been achieved is to provide a legal background for the contribution of indoor air to total air exposure. In view of the difficulties to regulate indoor air (Seifert, 1993) it is very unlikely that this gap will be and can be closed in the next future. However, in performing a valid risk assessment the indoor air needs to be taken into account. It is only in doing so that the financial resources available to reduce population exposure to air pollutants can be used in a meaningful and successful way.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

CONSUMER PRODUCTS AND INDOOR AIR QUALITY: AN EMERGING ISSUE AND OPPORTUNITY

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ABSTRACT

While there is an extensive literature on emissions and exposures to pollutants from outdoor sources, and to some well-defined indoor sources of combustion, biological agents, and interior fixtures, much less is known about the contribution of consumer products to indoor air pollution. Additional information is needed on consumer attitudes and the responses to product information, e.g., perceptions of risk and optimisation of risk and safety communication to consumers. Further, more information is needed about quantifying some types of emissions, the impact of the ageing of products on emissions, and the availability and applicability of testing methods and scenarios for assessing the exposures of building inhabitants. The European Commission's EIS-CHEMRISKS is being designed as a European-wide expert network to systematically exchange and assess information on risks from chemicals released from consumer products/articles. The EIS-CHEMRISKS project is a collaboration led by the Institute for Health and Consumer Protection, in collaboration with the European Commission Health and Consumer Protection Directorate-General, with involvement by Member State experts within the European Union and EU enlargement countries, by academia, NGOs, trade associations, and industry within and outside the EU.

INDEX TERMS

Consumer products, emissions, human exposure, scenarios, EIS-CHEMRISKS

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INTRODUCTION

Many agencies, industry and academia have studied IAQ issues and identified the presence of indoor air pollutants. These pollutants include radon, asbestos, environmental tobacco smoke, and some chemical emissions from consumer products. Impacting the types and potential levels of human exposures to pollutants are "human factors" and "residential factors." Human factors include the choice of the consumer products to buy and use, the usage patterns of products within the residence, cooking methods, and a decision to smoke or not. Residential factors that help determine the types and levels of exposures include microclimate, building and room ventilation rates, and running heating and cooling systems. Indoor sources of emissions of air pollutants include both primary emitters and secondary source/sink re-emitters. Sources in addition to the ones noted above include construction materials, interior fixtures and furnishings, outdoor sources, and sources of biological agents.

This paper discusses the above topics and introduces a new European Union-wide effort from the European Commission's Institute for Health and Consumer Protection. This is the European Information System on Chemical Risks (EIS-CHEMRISKS), which will provide publicly available Web pages on exposures and risks from chemicals released from consumer products/articles.

HUMAN EXPOSURE

Assessing human exposure to an environmental agent involves the qualitative description and the quantitative estimation of the agent's contact with (exposure) and entry into (dose) the body. Exposure assessments have several common elements (WHO, 2000): the number of people exposed at specific concentrations for the time period of interest; the resulting dose; the contribution of important sources, pathways and behavioural factors to exposure and dose. Quantitative estimation of exposure is the central feature of assessment activities. The quantitative estimation of exposure can be approached in two general ways: direct assessment, including point-of-contact measurements and biological indicators of exposure; and indirect assessment, including indoor monitoring, modelling, questionnaires, and the use of results from producer testing methods. Both approaches are complementary, rely each on different kinds of data, and have different strengths and weaknesses.

An important aspect of consumer protection is to prevent or reduce exposures to environmental agents. It is usually not possible, however, to measure the necessity or effectiveness of mitigation strategies directly in terms of prevented disease, reduced premature death, or avoided dysfunction. The method of choice to be used for consumer protection, often conducted initially during the early phases of the research and development of a product is instead is to measure or estimate the actual or expected human exposure. The exposures are used along with the product's toxicology profile, to assess whether a product is expected to be safe, i.e., to cause

adverse health effects during its use. As has been stressed by the World Health Organization, it is important to recognize that terminology and definitions of exposure vary among organizations and nations corresponding to the different aspects of the contact between people and environmental agents (WHO, 2000).

EMISSIONS FROM CONSUMER PRODUCTS

Within the European Commission's Directive on general product safety (EC, 2001), a "product" shall mean any product - including in the context of providing a service - which is intended for consumers or likely, under reasonably foreseeable conditions, to be used by consumers even if not intended for them, and is supplied or made available, whether for consideration or not, in the course of a commercial activity, and whether new, used or reconditioned. Consumer products of relevance in the present context include textile-containing products; toys; furniture; wall coverings; office machines; household products; cosmetics, toiletries and other personal care products; automotive aftermarket products; adhesives and sealants; pesticides; hobby materials; plastic and rubber materials; coatings and coating-related products.

Recent publications reviewing important aspects of the assessment of indoor exposures to consumer products are available (e.g., Whitmyre et al., 2001; Wallace et al., 2001). Developing data about the relative indoor emissions from various types of consumer products remains an important area for research, especially when considering the variations in consumer products, consumer attitudes and housing conditions encountered across the world. It is therefore important to be able to estimate primary emissions of chemicals from consumer products using monitoring or testing methods, and/or via modelling. Volatile organic compounds (VOCs) may well survive topical finishing processes and be emitted over a certain period of time. The emissions of VOCs can lead to short-term or long-term health impacts. Emission rates of most chemicals in products are greatest when product are new; emissions are likely to continue at for longer periods at low levels for products such as carpets and pressed-wood products. Noted to be of particular concern are long-term exposures to VOC emissions from room air fresheners and bathroom deodorants, which are intended to maintain an elevated concentration of deodorant in the room (Wallace et al., 2001).

SCENARIOS AND EXPOSURE FACTORS

Estimating the exposures to a physical, chemical or biological agent in the residential environment requires an understanding of the known or reasonably expected sources of the exposures. This understanding can be used in a stepwise approach progressing from less refined, more conservative assessments, to more refined, data-rich assessments, as judged to be needed for risk assessments. A key advantage of using the scenario(s) approach is that the initial estimates of

exposure can be developed with very little data; key disadvantages include that the initial assessments may have a high level of uncertainty.
The key scenarios associated with the source(s) of interest need to be identified; for example, what consumer products might be involved and how are they used? Important information includes human and residential exposure factors such as the frequencies, durations, and amounts used per each likely task, the location in the residence, and whether exhaust fans might be used or windows opened by the consumer? Several compilations of exposure factors have been published (US EPA, 1997; ECETOC, 2001, HC 1995; AGLML, 2000). Expert judgment and review of the original data is needed when deciding whether to use an exposure factor value, e.g., US EPA-published exposure factors outside the United States. Scenarios can also include data or assumptions about physical/chemical properties of the chemical of interest. It is also necessary to identify and characterize secondary source/sink emission properties of consumer products such as upholstered furniture, which could absorb and reemit chemicals emitted from other sources, thus increasing cumulative exposure. Further, topical finishes could change the properties of textile containing products, thus modifying the source/sink behaviour of these materials (Smith and Bristow, 1994).

While gathering analysing, and utilizing this information, it is important to recognize:

- The potential for meaningful intra- and inter-individual variations in the usage of consumer products (Weegels and van Veen, 2001);
- The potential contribution of non-consumer product sources (e.g., outdoor; smoking) to the exposures to a chemical or biological agent in the residential environment;
- That an unexpected exposure factor, e.g., poor eyesight, in a scenario could have a key impact on the exposure from a consumer product (e.g., Curry et al., 1994).

CONSUMER ATTITUDES AND THE RESPONSES TO PRODUCT INFORMATION

Consumer attitudes towards products, including perceptions of possible health and environmental risks, can play a role in purchase decisions and in how products are used. Studies have assessed how labelling and other factors such as product odour affect consumer beliefs, behaviour, and exposures (e.g., Kovacs et al., 1997; Riley et al., 2001; 2000).

TESTING METHODS

Testing methods for consumer products are standardised methods for identification and assessment of hazards for such products. They can provide information needed for exposure assessment when a product is used according to its foreseen and intended use. Testing methods can refer to the life cycle of the consumer product.

This includes identification of any adverse effects that the product can cause and, when appropriate, estimation of the relationship between dose, or level of exposure to a substance emitted by the product, and the incidence and severity of an effect. Taking into account the intended uses of any particular consumer product, the foreseen exposure of human populations as well as the estimated incidence and severity of the predicted effects likely to occur to an exposed human population, a risk assessment of the consumer product can be performed. For textile containing products a well-known testing method is that for formaldehyde emissions standardized by the American Association of Textile Chemists and Colorists (AATCC, 1998). For these and other consumer products working groups of the European Committee for Standardization (CEN) are developing testing methods, which ensure the safety of consumer products (CEN, 2002).

MODELLING METHODS

Various models are available for use in estimating inhalation and other exposures to chemicals in consumer products (Whitmyre, et al., 2001). These models serve to predict expected exposures, and use various types of data as inputs. The data might include time-varying emission data and the associated residential air levels of the chemical from use of a consumer product in a defined exposure scenario. The emissions and air levels might be available from monitoring or test studies of the product, or from a surrogate product. Lacking these types of data, the emissions and air levels can be modelled.

HEALTH IMPACTS

Most important chemicals potentially emitted into the air by consumer products are volatile organic compounds (VOCs). Their health effects include: eye, nose, and throat irritation; headaches, loss of coordination, nausea; damage to liver, kidney, and central nervous system. Some VOCs can cause cancer in animals; some are suspected or known to cause cancer in humans (WHO/EURO 2000). The ability of organic chemicals to cause health effects varies greatly from those that are highly toxic, to those with no known health effect. As with other pollutants, the extent and nature of the health effect will depend on many factors including level of exposure and length of time exposed. Eye and respiratory tract irritation, headaches, dizziness, visual disorders, and memory impairment are among the immediate symptoms that some people have experienced soon after exposure to some organics. At present, not much is known about what health effects occur from the levels of organics usually found in homes.

EUROPEAN INFORMATION SYSTEM ON CHEMICAL RISKS

EIS-CHEMRISKS is being designed as a European-wide expert network to systematically exchange and assess information on risks from chemicals released

from consumer products/articles. The JRC efforts will focus on filling the exposure data gaps in a systematic and coherent manner. This work will support the rapid exchange (RAPEX) notifications system of the General Product Safety Directive (EC, 2001) and may provide technical support to the relevant aspects of REACH (Registration, Evaluation and Authorisation of CHemicals), i.e. regarding downstream users.

The task of developing and operating EIS -CHEMRISKS is a very complex and demanding one, as heterogeneous users, and a multitude of sources are being targeted. The JRC will establish a single web-based gateway to all major European initiatives in the field of Human Exposure to Chemicals contained and released from products/articles. EIS-CHEMRISKS will act as an interactive EU wide information source and a common communication tool for the user society to develop and continuously update the themes mentioned below.

- European inventory and harmonisation of exposure data sources and data sets
- European Exposure Factors Database
- Standards for the determination of chemicals emissions from products/ articles
- Harmonisation of modelling approaches of exposure to chemicals released from products/articles
- Sectoral product/article specific state-of-the-art reports (textiles, toys, cleaning products, etc.)
- State-of-the-art reviews on promising emerging approaches for improving exposure assessment such as toxicogenomics and low-dose/concentration biomarkers.
- European Annual Status Report "Risks from Human Exposure to Chemicals released from Consumer Products/Articles".

CONCLUSION AND IMPLICATIONS

While there is an extensive literature on emissions and exposures to pollutants from outdoor sources, and to some well-defined indoor sources of combustion, biological agents, and interior fixtures, much less is known about the overall nature of the contribution of consumer products to indoor air pollution. More information is needed about quantifying some types of consumer product emissions, the impact of the ageing of products on emissions, and the availability and applicability of testing methods and scenarios for assessing the exposures of building inhabitants.

Further, additional information is needed on consumer attitudes and the responses to product information, e.g., how are perceptions of risk and safety developed, and how can risk and safety communication to consumers be optimised?

In addition to other information sources (ISEA, 2003; USEPA, 2003), the European Commission's EIS-CHEMRISKS is being designed as a European-wide expert network to systematically exchange and assess information on risks from chemicals released from consumer products/articles.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

AIR POLLUTION AND HEALTH: A EUROPEAN INFORMATION SYSTEM TO ASSESS THE HEALTH IMPACT AIR POLLUTION (THE APHEIS PROJECT)

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ABSTRACT

The Apheis project aims to provide European, national, regional and local decision makers, environmental-health professionals and the general public with an up-to-date and easy-to-use information on air pollution (AP) and public health (PH). For this purpose, Apheis has delivered the first of a series of standardised periodic reports on health impact assessments (HIA) in 26 cities in 12 Western and Eastern European countries.
Apheis centres have been created in all participating cities. Apheis adopted WHO guidelines and developed own guidelines for gathering and analysing data on AP and its impact on PH. Apheis has analysed the acute and chronic effects of fine particles on premature mortality and hospital admissions using the estimates developed by Aphea2 study and two American cohort studies. The present HIA was performed for different scenarios on the health benefits of reducing PM_{10} and black smoke (BS) levels.
The total population covered in this HIA includes nearly 39 million inhabitants. PM_{10} concentrations were measured in 19 cities (range: 20-50 $\mu g/m^3$). BS concentrations were provided by 15 cities (range: 20-65 $\mu g/m^3$). The age-standardised mortality rates (per 100 000 people) range from 456 in Toulouse to 1 127 in Bucharest. Reducing long term exposure to PM_{10} levels by 5 $\mu g/m^3$ would have prevented 5 547 premature deaths annually, 800 of which attributable to short-term exposure. A reduction of 5 $\mu g/m^3$ in BS levels would have decreased short-term deaths by over 500 per year.

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Apheis has created an active public-health and environmental-information network on air-pollution-related diseases in Europe using a standardised methodology. Apheis will provide policy makers with the information they need to better understand the health impact and cost of air pollution, so they can set priorities in a better-informed manner.
With its monitoring system, Apheis will continue to keep the information we provide as up-to-date and accurate as possible.

INDEX TERMS

Health impact assessment, outdoor air pollution, PM_{10}, Black smoke, Europe

INTRODUCTION

The Apheis programme started in 1999 with the aim to provide European decision makers, environmental-health professionals, the general public and the media with an up-to-date, easy-to-use information resource to help them make better-informed decisions about the issues they face concerning air pollution and public health.

METHODS

To meet these goals, during its first and second year the Apheis programme assembled a network of environmental and health professionals in 26 European cities; created an epidemiological surveillance system that generates information on an ongoing basis; and conducted the present HIA of air pollution in these cities.

RESULTS

The second-year report released the findings of the health impact assessment of particulate air pollution it conducted in 26 cities in 12 European countries during 2001.
The report, a broad-based European HIA of air pollution, embraced data from 12 countries totaling 26 cities: Athens, Barcelona, Bilbao, Bordeaux, Bucharest, Budapest, Celje, Cracow, Dublin, Gothenburg, Le Havre, Lille, Ljubljana, London, Lyon, Madrid, Marseille, Paris, Rome, Rouen, Seville, Stockholm, Strasbourg, Tel Aviv, Toulouse and Valencia.
Most European cities daily measure particulate air pollution (or very small particles) using one of two techniques: PM_{10} (particles less than 10 micrometers in size); or black smoke (black particles less than roughly 4 micrometers in size). Levels of air pollution are reported in microgrammes per cubic meter ($\mu g/m^{3)}$.
Levels of particulate air pollution, including PM_{10} and black smoke, vary widely across Europe. The annual average levels in Apheis cities range from 14 to 73 $\mu g/m^3$ for PM_{10} and from 8 to 66 $\mu g/m^3$ for black smoke.

The EC/DGSANCO-funded Apheis (Air Pollution and Health: A European Information System) study (Medina et al., 2002) revealed in particular that air pollution continues to pose a significant threat to public health in urban environments in Europe despite tighter emission standards, closer monitoring of air pollution and decreasing levels of certain types of air pollutants.

In specific, the report observes that 2 653 premature deaths (or 9 premature deaths per 100 000 inhabitants) could have been prevented annually if long-term exposure to annual mean values of PM_{10} had been reduced to 40 $\mu g/m^3$ in the 19 cities that measured PM_{10} particles, whose populations total nearly 32 million inhabitants. This level of 40 $\mu g/m^3$ is the limit value set by the European Commission for all member states by 2005.

If the more ambitious limit value of 20 $\mu g/m^3$ set for 2010 had been achieved in the same cities, 11 855 premature deaths (or 43 premature deaths per 100 000 inhabitants) could have been prevented annually.

Even more significantly, the report shows that reducing long-term exposure to outdoor concentrations of PM_{10} by just 5 $\mu g/m^3$ would have prevented 5 547 premature deaths annually (or 19 premature deaths per 100 000 inhabitants) in all the cities, including those with the lowest pollution levels.

It should also be noted that at least 832 (or 15%) of the 5 547 deaths due to long-term exposure to PM_{10} could have been prevented by reducing short-term exposure to PM_{10} by 5 $\mu g/m^3$.

Concerning black smoke, according to a Dutch cohort study just published (Hoek et al. 2002), the effects of long-term exposure to this pollutant on mortality rates should be similar to the effects of PM_{10}. However, since no exposure-response functions were available for the chronic, long-term effects of exposure to black smoke when we conducted the Apheis study, this second part of our HIA was limited to acute, short-term effects, and thus addressed only a small fraction of the total, long-term impact of black smoke.

Conducted in the 15 cities that measured black-smoke particles and whose populations total almost 25 million inhabitants, this second part determined that nearly 577 premature deaths (or 3 premature deaths per 100 000 inhabitants) could have been prevented annually if short-term exposure to outdoor concentrations of black smoke had been reduced by 5 $\mu g/m^3$.

DISCUSSION

As part of Apheis' objective to bridge the gap between research findings and decision making, this report, which used the same standardized methodology in all its cities (Medina et al., 2001, WHO, 2000, WHO, 2001), constitutes the first HIA conducted simultaneously on both local and European levels.

The Apheis programme also uses ongoing cross-fertilization between multiple disciplines and regions to create skilled, local teams and to enrich methodology, know-how and quality of its findings.

This unique combination provides both local officials with standardized local data, analysis and knowledge for local decision making, and European officials with standardized local data analyzed to provide a global view for European decision making.
Numerous studies conducted in Europe and other parts of the world have shown that air pollution levels constitute a health risk (Katsouyanni, 2001, Atkinson, 2001, Le Tertre, 2002, Künsli, 2000, Pope, 2002, Hoek, 2002). The Apheis report demonstrates that reducing these levels, even by a small amount, could produce significant benefits to public health.
As another key point, the Apheis report stated that the major reason air-pollution exposure results in important health impacts is the ubiquity of the exposure, over which individuals have little control. This contrasts with other health-risk factors, such as cigarette smoking and diet, which individuals can better control.

CONCLUSIONS AND IMPLICATIONS

Even very small and achievable reductions in air-pollution levels, such as 5 $\mu g/m^3$, have a beneficial impact on public health, and thus justify taking preventive action in all cities, no matter how low their levels of air pollution.
Apheis's findings are consistent with those of other organisations, and add one more brick in the wall of evidence that air pollution continues to have an impact on public health.
This study constitutes the initial step in meeting the information and decision-making needs of the different audiences the programme serves.
As the next steps in fulfilling its mission, during its third year Apheis is researching key European policy makers and influencers concerned with the impact of air pollution on public health to understand how the programme can better meet their information needs. Apheis is also calculating years of life lost, or reduction in life expectancy, in order to estimate the health impacts of long-term exposure to air pollution.
In the future, if funded, Apheis will be responsible for the health impact (HIA) and comparative risk assessment (CRA) task of the ENHIS project being submitted by WHO-ECEH Bonn Office, Germany to the EC for approval in the framework of the 2003-2008 new public health programme of DG SANCO.

ACKNOWLEDGEMENTS

Apheis is supported by the European Commission DG SANCO programme of community action on pollution-related diseases (contracts N°SI2.131174[99CVF2-604]/SI2.297300[2000CVG2-607]/SI2.326507[2001CVG2-602]) and participating institutions.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

LINKAGES AND SYNERGIES OF GLOBAL, REGIONAL AND LOCAL EMISSION CONTROLS

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ABSTRACT

Many of the traditional air pollutants and greenhouse gases have common sources, their emissions interact in the atmosphere, and separately or jointly they cause a variety of environmental effects at the local, regional and global scales. Thus, emission control strategies that simultaneously address air pollutants and greenhouse gases could be beneficial at all scales. The paper reviews linkages between air pollutants and greenhouse gases in the atmosphere, the interactions of their impacts and identifies a number of potential strategic synergies and trade-offs between the mitigation of greenhouse gases and control of air pollutants.

INDEX TERMS

Linkages between climate change and air pollution, synergies in emission controls, regional and global emission controls

INTRODUCTION

Many of the traditional air pollutants and greenhouse gases have common sources, their emissions interact in the atmosphere, and separately or jointly they cause a variety of environmental effects at the local, regional and global scales. Thus, emission control strategies that simultaneously address air pollutants and greenhouse gases could be beneficial at all scales. A workshop, organized by the Task Force on Integrated Assessment Modelling of the Convention on Long-range Transboundary Air Pollution and hosted by the International Institute for Applied Systems Analysis (IIASA), reviewed the scientific knowledge on the linkages between air pollution and climate change and identified a range of

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potential synergies and trade-offs between greenhouse gas mitigation and air pollution control. This paper provides a brief summary of the workshop conclusions. The full conclusions and the presentations are available at http://www.iiasa.ac.at/rains/meetings/AP&GHG-Jan2003/announcement.html.

ATMOSPHERIC CHEMISTRY

Radiative forcings of the six long-lived trace gases covered by UNFCCC (CO_2, CH_4, N_2O, HFC, CFC, SF_6) have received much attention. However, there is increasing scientific understanding that also some short-lived air pollutants, notably ozone and fine particles, exert climate impacts.

Tropospheric ozone was identified to have the third largest global mean radiative forcing (IPCC, 2001) and therefore measures to reduce it will be beneficial in reducing climate change. The influence of tropospheric ozone on climate change is better understood than the role of aerosols.

Regional ozone levels build up on top of a considerable hemispheric background ozone baseline. Hemispheric ozone baseline concentrations have been increasing by about 0.5 ppb per year and are projected, in some scenarios, to increase in the future. With "safe" level of ozone being close to present background concentrations (WHO, 2003), the achievement of local air quality targets for ozone will increasingly need to address the sources of global ozone background. One of the important factors contributing to this increase is the rise in global methane emissions. Methane is important both in building up the hemispheric background of ozone and in enhancing intercontinental ozone transport. Methane also exerts direct radiative forcing and is a greenhouse gas with a relatively short atmospheric lifetime (~12 years). A methane emission reduction strategy will therefore be very effective in reducing both climate change and ozone concentrations. While natural methane emissions are important, the larger (and growing) share is anthropogenic. A multitude of studies show that there is significant potential for controlling anthropogenic methane emissions.

Climate research has found that aerosols have important radiative effects in the atmosphere (IPCC, 2001). Model simulations have shown that short-lived aerosols can lead to significant regional climate perturbations, especially affecting seasonal precipitation patterns, which may contribute regionally to floods and droughts (Menon *et al*., 2002). Sulphate, nitrate and organic carbon particles in the atmosphere affect the climate in the opposite direction than greenhouse gases, i.e., they tend to have a local cooling effect and can lead to reduced precipitation. Other carbonaceous particles (black carbon, soot) are thought to have a positive forcing on climate, though the magnitude of this effect is uncertain. Hence, while the reduction of black carbon will be beneficial in reducing climate change, this is not the case for the reduction of other aerosols.

At the same time, these fine aerosol particles cause serious health impacts. A wide body of scientific evidence demonstrates significant increases in mortality

from cardio-vascular and cardio-pulmonary diseases as well as cancer associated with exposure to aerosols measured as $PM_{2.5}$ (Pope *et al.*, 2002; Abbey *et al.*, 1999). While the specific agent within the aerosol mixture that causes these health impacts is yet unknown, significant efforts are now planned throughout the industrialized and developing world to control the various precursor emissions that form fine particulate matter (such as SO_2, NO_x, NH_3, VOC and primary particles). Present evidence suggests that small particles ($PM_{2.5}$) that have largest impacts on climate also cause the largest health effects.

Emission reductions necessary to reduce health effects of particulate matter (PM) will have to reduce not only black carbon but also other components of PM. The net effect of a PM reduction strategy to cut health-effects substantially may therefore be an increase in radiative forcing. To reach any given climate targets, such PM reductions will have to be compensated by further measures on other climate gases. Thus, strategies to reduce PM should be developed so that they place more emphasis on bringing down black carbon emissions than measures do at present. Such strategies will need to target diesel emissions, biomass burning as well as residential combustion of solid fuels and should place greater emphasis on non-road mobile sources. Preliminary estimates suggest that especially ships contribute increasingly to black carbon concentrations.

LINKAGES IN IMPACTS

There are a number of linkages between the effects of climate change and air pollution, but they can go into different directions and are not yet fully understood. Model results suggest, for example, that: (1) A temperature increase through climate change may reduce ecosystem sensitivity to acidification damage and tends to change deposition patterns so that there will generally be less critical load exceedance; (2) An increase in nitrogen deposition (through air pollution) may raise the ability of plants to store carbon counteracting CO_2 accumulation in the atmosphere; (3) Many air pollutants tend to weaken plant growth thereby reducing carbon storage capacity; (4) Both climate change and air pollution may adversely affect biodiversity.

SYNERGIES AND TRADE-OFFS OF MULTI-POLLUTANT STRATEGIES

Many of the driving forces underlying air pollution and climate change are identical: economic growth, consumption and production processes, and demography. A sustainable development strategy must address these issues in an integrated manner.

Many measures to cut air pollution also benefit the climate through reduction of GHG emissions and vice versa. Understanding these synergies in emission controls and addressing local, regional and global objectives simultaneously, rather than

separately, is needed to achieve overall cost-effectiveness. As marginal costs of further air pollution abatement measures tend to increase rapidly once a certain reduction level has been achieved, any potential for cost-savings for strategies to reach air quality objectives must be explored. Synergies may free resources that allow reaching more ambitious targets.

A study has calculated that the costs of reaching the emission ceilings of the Gothenburg Protocol could be reduced more than €5 billion per year by implementing the changes in the energy system necessary to achieve the reductions required by the Kyoto Protocol domestically (Syri *et al*., 2001). This indicates for industrial countries clear ancillary benefits of greenhouse gas mitigation measures on air pollution control costs. However, for developing countries ancillary benefits could work into the opposite direction: A continuation of the traditional high carbon energy development will result in unacceptable levels of air quality, or involve huge costs for applying emission control techniques to maintain air quality acceptable. An integrated approach could save money by investing more into a lower carbon strategy and less on air pollution control, rendering the low-carbon development as an ancillary benefit of air pollution control (Amann *et al.,* 1996). Such co-benefits would be even greater if impacts of pollution are included in the assessment: For China, it has been estimated that the cost of cutting CO_2 emissions by 5-10% would be offset by the benefits resulting from reduced health effects through air pollution. Including the effects on crop-yield increase (via reduced NO_x) increases the "no-regret" level of CO_2 emission cuts to 15-20% (Aunan *et al*., 2003).

Unfortunately, there are not only synergies, but also trade-offs, and it might be even more important for decision makers to be aware of potential trade-offs.

An increased use of biomass is seen as a very positive measure to reduce carbon emissions. However, if burned in small appliances in households without efficient emission controls, more biomass combustion would lead to a strong increase in PM emissions with serious health impacts, counteracting any PM control strategy.

The car industry has made major investments into the development of fuel-efficient diesel engines, with the aim to reduce CO_2 emissions. Unfortunately, diesel engines have much higher PM emissions (including black carbon) than gasoline engines, so that the increasing penetration of these new diesel engines causes serious concerns to air quality managers.

Synergies and trade-offs are also present in agriculture. For instance, certain ammonia abatement measures related to manure application can increase emissions of nitrous oxide (N_2O), which is an important greenhouse gas also covered by the Kyoto Protocol. There are, however, abatement techniques that can reduce this negative impact. Scenario analysis has shown that it is possible to cut ammonia emissions significantly and at the same time reduce nitrous oxide and methane emissions (Brink *et al*., 2001). An integrated approach tends to achieve such synergies at much lower cost.

There is the danger that sectoral CO_2 policies could push certain fuels from sectors with efficient cleaning devices (e.g., for the power sector) to other sectors, where

air pollution emissions can be controlled less efficiently (e.g., in small burners). Economic instruments can have significant effects on the distribution and levels of air pollution emissions. International emission trading, joint implementation and the clean development mechanism under the Kyoto Protocol have the potential to reduce the overall costs of greenhouse gas emission reductions for given targets. However, countries buying CO_2 permits from other parts in the world will reduce their domestic CO_2 emissions less than without trading, which will shift the significant co-benefits of CO_2 abatement measures to other regions. Thus, unconstrained trading of carbon permits may not be cost-effective, if air quality objectives were to be taken into account. In some countries, carbon trading may prevent the structural measures for CO_2 abatement required to achieve reductions of air pollutants (e.g., for NO_x) that are necessary to achieve the air quality objectives.

DISCUSSION

Further work on linkages and synergies between regional air pollution and climate change should provide policy makers with the information necessary to make the right choices: (1) To reduce pollutants maximising the positive linkages and minimising the negative ones; and (2) taking those measures that are most cost-effective in view of the objectives in both policy areas.

CONCLUSION AND IMPLICATIONS

Insight into potential synergies needs new analytical bridges between the temporal and spatial scales of air pollution (short- to medium-term, local to regional) and climate change (long-term, global). Targeted further research on these linkages might help policy in several ways: (1) Better insight into the potential synergies in emission control measures between air pollutants and greenhouse gases could free resources that allow reaching more ambitious targets. (2) The increased flexibility of multi-pollutant/multi-effect strategies would offer an increased potential for economic efficiency. (3) Measures that are necessary for an efficient global and long-term strategy could be connected with concrete local and near-term benefits (e.g., in terms of air pollution) both for industrialized and developing countries. 4) Including short-lived gases in a greenhouse gas control strategy could lead to a faster response of the climate system and thus bring climate change benefits closer to the world of today's actors.

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Round Table on Emission Trading in Greenhouse Gases and Air Quality in Europe

The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

EMISSION TRADING: GENERAL PRINCIPLES OF THE PROPOSAL FOR DIRECTIVE COM/2001/0581

P Dell'Anno*

INTRODUCTION

The proposal for the European Commission regulating the exchange of greenhouse-effect gas emission quotas[1] was presented after ample discussion between numerous organizations representing the economic, productive and environmental sectors, as well as Community institutions.
The proposal defines the new regulation as an instrument for environmental protection, having the purpose of reducing greenhouse-effect gas emission[2], yet producing less effect than others on competition conditions. The proposal is intended to achieve the environmental safeguard objectives indicated in art. 174 of the Treaty.
The new directive is to be approved following the procedure laid down in art. 175, para. 1, that is on the basis of the proposal presented by the Commission to Parliament and to the Council, which votes according to ***a qualified majority*** after receiving the opinion of the European Parliament (art. 251).
This initiative is among the Community acts aiming at putting the Kyoto Protocol of 11.12.1997 into effect at the U.N. ***framework*** Convention on climate change.
The general principle on which the system is based is the definition by each Member State of the emission quotas coming from certain ***combustion installations*** in accordance with the national share of the obligations contained in the European Agreement of 16.06.1998.
In all, the Community will emit the same number of tons of CO^2 as provided for in the Kyoto Protocol, proceeding meanwhile to adjust the individual Member

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[1] The proposal for the directive (COM/2001/0581) was published in the O.G.E.C. n° c 075E of 26.03.2002

[2] In the stage of first application, however, only carbon dioxide emission will be taken into consideration. This gas contributes 80% of the total emission of the Community, while emission control of other gases presents doubts so far unresolved.

States' quotas should they have acquired or sold quotas from installations situated in other Member States.

Structural profiles of the new regulations

The "***props***" supporting the proposal are the authorizations to be obtained by all the installations participating in the exchange system, and by the emission quotas measured in metric tons of ***carbon dioxide equivalent***. The undertaking named in this specific authorization will have the right to emit certain quantities of greenhouse-effect gas to an amount corresponding to the quantity of quotas assigned to it (in turn related to the installation's actual emission).
The authorization is issued to the installation or to a specific site, while the emission quotas may be transferred to other undertakings.
Each year the undertakings must present to the authority appointed by the Member State a number of quotas corresponding to the emission actually produced ***in that same year (v. *** sotto)***. Such quotas will be cancelled. Failure to present a sufficient number of quotas to represent the actual emission will entail fines being imposed.
Emission quotas are indicated in a special electronic register containing any variations in ownership (no transfer of ownership is valid unless registered), and the progressive cancellation of the quotas. During the initial stage of the system (from 2005 until the end of 2007), each Member State will assign emission quotas to the installations involved, free of charge and on the basis of transparent criteria and objectives, while a common European scale of fines connected to any violations is to be defined. In this first stage no binding objective will be in force that may limit the emission of greenhouse-effect gases on the part of Member States.

Functional profiles

The overall quantity of quotas to be assigned constitutes the total limit to the emission authorized by the system. The comprehensive number of quotas is left to the discretion of the Member States, who are to define it consistently with the European reduction objectives set down in the Kyoto Protocol, assessing the installations' technological potential for the reduction of direct greenhouse gas emission.
The exchange of emission quotas allows an undertaking to produce emission in excess of the quota assigned to it if it is able to find another undertaking willing to cede an unused part of its quota, in that it has produced less emission than the quantity to which it is entitled.
The principle of environmental invariability in emission quota exchange is based on the specific nature of the gases to control and reduce, and that is those greenhouse-effect gases producing consequences at planetary level, irrespective of the area where they are produced (interdependence and ***globality***).
Should the quota exchange occur within the State, the overall number of tons that may be emitted will undergo no variation, since the State is obliged to respect the overall emission limit to which it is committed.

On the other hand, the transfer of quotas between installations situated in different Member States will automatically entail the adjustment of the emission quotas authorized; this adjustment must be entered in the national registers to show a corresponding reduction in the national right in the case of alienation and the equivalent increase in the case of acquisition. Interconnection between national registers to avoid any evasion and non-compliance must be ensured, as well as supervision and adjustment of the effective national quotas.
The cornerstone of the system requires that sufficient quotas be made available to each installation to cover its actual emission.

The authorization system

The owners of installations carrying out the activities listed in Annex I must obtain the particular authorization for the emission of greenhouse-effect gases.
The authorization shall specify the obligations to be observed as regards supervision, notification and verification (i.e., in the alienation of quotas, in the emission levels effectively reached, in alterations made to the plants etc....). As already stated, every year the parties authorized shall return the number of emission quotas that corresponds to the emission produced ***the previous year (***)***.
The quantity of quotas is not harmonized on a European scale. The fraction of the emission generated by the sectors involved varies according to the fuel mix used for the production of electricity. Each State must approve a national assignment plan on emission quotas under its authority and must make prior communication to the Commission of the measures it attends to apply in assigning the quotas; the Commission (during the regulatory stage) may refuse the plan (within 3 months) should it contrast with the ***common(Community???)*** criteria used in order to create a European market of emission quotas featuring a uniform European price for each single emission quota.
Should an installation be in possession of sufficient quotas, whether assigned to it originally or acquired, no quantitative limit to emission exists[3] .
The directive also provides for the progressive reduction in the quotas to be assigned yearly in order to achieve the quantitative objectives of each State.
"Relative objectives" in the nature of loans may be taken on by the undertakings within one specific sector, on the basis of efficiency in relation to production.
One possibility under discussion is that the undertakings within one single sector should pool the quotas assigned to each one, thus enabling the relative trade association, acting on behalf of all the undertakings it represents, to engage in the purchase of further quotas or in the sale of quotas in excess of the contingent needs. At the end of the year, the necessary adjustments could be worked out among the undertakings involved.

[3] This means that the undertaking is obliged to respect only the emission limits fixed as CO_2 concentration but not limits regarding mass flow or emission factor (art. 4, sub-section 3, Ministerial Decree 12.07.1990). Hence the need to review law decree 372/1999 as regards the mass flow limit.

Relations with environmental norms

The quota exchange system could be integrated with the system defined in the ***IPPC*** directive, allowing States to use the single authorization procedure for installations producing greenhouse-effect gases as well, and introducing the obligation to request the presentation of more information than is ordinarily required.
This special authorization constitutes a necessary premise for the installation to continue to function; the plant must obtain a sufficient number of quotas to cover its own effective emission in for a certain period.
A plant taking part in the quota exchange system is not obliged to comply with the maximum greenhouse gas emission set by the IPPC authorization that it holds, "unless such emission risks causing significant local consequences" (page 9).
The IPPC authorization cannot, therefore, fix a limit value on direct greenhouse-effect gas emission, unless such emission has significant local repercussions.

Object profiles

The regulation of quota exchange will concern only those activities listed in Annex I ("core activities").
They include combustion systems with a thermal power superior to 20 MW, oil refineries, coke works, metal, cast iron and steel production, cement works, plants for the production of glass and ceramics, paper factories.
Chemical works and waste incinerators are exempt if they do not exceed the threshold of 20 MW in the production of electricity and heat.
The quotas assigned shall be fixed at a level not superior to that of the emission accumulated by participating plants had they been regulated (only) by the IPPC directive.
Emission quotas created by the exchange system will be recognized directly throughout the whole territory of the Union.
The quotas will hold good for a period of no more than 3 years (in the initial phase); they can be set aside and carried over without limitation from one year to the next within the period of validity.
The States are obliged to set aside (in reserve) the unused quotas and to carry them over to the new assignments, at the end of the period in question, increasing the quotas already fixed by a corresponding amount.

Party profiles

Authorizations can be issued exclusively to the plants emitting greenhouse gases and that are included in Annex I of the directive. However, access to the quota market will also be open to intermediaries, that is to parties (individuals or corporate bodies, public or private) ***under no obligation by virtue of special authorization***.
NGO are also allowed to acquire quotas in order to eliminate them from the market, increasing thereby the shortage of quotas and their contingent value, and reducing the overall quantity of emissions that may be produced by the system.

Every party intending to trade and to hold quotas must open an account with its own national register, in the form of an electronic tracking system, in which every transaction shall be transcribed.
Any irregularity in the handling of quotas or in the notification of the emissions produced by installations will entail the sanction of the non-tradabililty of the quotas until there is full compliance with the requirements of the directive.
The Commission, by means of a special regulation, will specify detailed norms regarding the functioning of the national registers.

Controls

The fundamental principles for effecting controls and notifications of emissions will be determined according to the procedure of the regulation committee (Ann. IV), while specific detailed criteria for the activities of a given plant will be laid down in the relative authorization.
Compulsory criteria have been established for the notifications (Ann. V) that Member States can attribute to their own bodies or to independent inspectors, laying down, moreover, who will bear the costs.

Sanctions regarding non-compliance with obligations

Violations of the obligation to return a sufficient number of quotas to cover the emissions effected and duly verified will entail the imposition of fines, quantified either in the lump-sum fine of 100 euro per ton of emission in excess, or double the average market price in a given period, whichever is greater.
The Member States shall also establish sanctions for violations of the directive that shall be "effective, proportional and dissuasive".
The imposition of a fine does not waive the obligation of the management of an installation that has released emissions in excess of the amount authorized, to return quotas corresponding to those excess emissions the following year.

Access and participation on the part of the public

The outcome of controls, notifications and verifications, information on the quotas assigned and established in national registers and on violations to the directive, are to be made accessible to the general public.
Assignment of quotas is to come about in conditions of the greatest transparency and must be based on objective criteria.
The national plan for the assignment of quotas shall be published by the Member State, which must organize a public consultation.
The plan is to be presented to the Commission prior to the final decision, "taking into due account the comments of the general public".
The States have the duty to present a report to the Commission on issues relative to the setting-up of the quota exchange system (assignment of rights, functioning of the national registers, controls, notifications, verifications) and on compliance with the norms.

General innovative principles inferable from the directive

(a) Globalization of environmental themes (reduction of greenhouse gases of anthropic origin) and burden sharing at national, European and Community levels.

(b) New concept of pollution (from absolute ***disvalue*** to relative ***disvalue***, being a negotiable right to pollute within authorized limits).

(c) Separation between the transferibility of the authorization (and the relative installation) and of the limits allowed. The authorization for the installation is distinct from the authorization for the emissions.

(d) Necessity of a single unitary policy on ET and exclusion of the possibility of restrictive policies at local level (except in the case of proven specific needs to face important acute or chronic events: reference to national environmental standards that shall not be exceeded).

(e) Primary role of technical environmental knowledge (monitoring, control, registration of data and of deeds).

(f) Reduction of the economic costs of alignment with Kyoto objectives together with a significant increase in feasibility and efficacy.

Emissions and Control

The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

TECHNO-ECONOMIC ANALYSIS OF AN INNOVATIVE PROJECT FOR THE PRODUCTION OF ENERGY FROM WASTE THERMO-DESTRUCTION

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ABSTRACT

This study has been carried out in order to assess the techno-economical feasibility of a pilot project regarding the disposal of special waste material through thermo-destruction and energy recycling. The project was conducted by G.E.S.P.I. ltd., Augusta, Syracuse, Italy. It mainly consists of making a special transformer, which can use a part of the heat generated from organic animal remains oxidation process and turn it into a solid product (calcium carbide); which in turn generates a combustible gas.
It has been proved that through a particular technique the combustion of this gas had a low environmental impact.
The analysis of the process economic advantages has been carried out by using the Actualised Economic Result Index, carefully considering the cost of gas production, as well as the cost of the plant building and maintenance. From the experimental results obtained, it is possible to state that, although such an innovative project has some limits, the replacement of the petrol by-products as fuel seems to be interesting; especially if we consider the present prices of diesel oil and green petrol.

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INDEX TERMS

Waste thermo-destruction, energy recycling, combustible gas, economic advantages, low environmental impact.

INTRODUCTION

Energy production and/or supplying is one of the most debated problems, in relation to both the optimisation of the available resources and the research of alternative sources. It can be seen as part of the wider problem of a possible alternative energy recycling, which could result from a more rational management of the waste. The relation between energy production and waste disposal is one the basic environmental problems today; indeed, there is a growing tendency of reducing the quantity of waste, which characterize our "consumer" society, and a tendency of searching for new alternative sources of energy. The latter, apart from being an exhaustible resource, causes a high degree of air pollution, due to its combustion. Such problems are often the basic topics of the debates atn international congresses and meetings regarding the environment and aiming at planning a worldwide environmental policy which deals with an integrated disposal of waste. In Italy the most important law on the disposal of waste dates back to Decree n° 22 of 5 February 1997 (the so-called Ronchi Decree) (1), which is based on the principles of the waste maximum use and of its recycling (including the controlled dump) (2-3), even for energy production purposes (4), suggesting incineration and thermo-destruction as the safest waste management systems. Obviously, Italy is not among the world best countries as to waste disposal, both because of the people's mentality and of the number of plants available at present. For such reasons, the quantity of incinerated waste in Italy is about 15 % of the total waste, while in other countries (such as Sweden and Denmark) is about 60 % (5).

Nowadays, however, there is a growing use of technologies for the energy recycling from waste, once considered totally useless. So we can hope to see the improvements in the future (6).

The present study should be regarded in the context of the increasing number of new techniques for energy production from the waste. The base of this study consists of a techno-economic analysis of the pivot project for implementation of an incineration plant for special and dangerous waste, which exists in the industrial area of Augusta, Syracuse, Italy. It uses the thermal energy as a result of waste thermo-destruction to produce acetylene as an alternative fuel that doesn't originate from oil. Acetylene can be produced in the plant without any great modification of the same and then can be used to produce electric energy, with emissions in the atmosphere which are qualitatively higher then those resulting from a traditional fossil combustible.

THE PIVOT PLANT

The pivot plant, which is the object of our study, is essentially made up of the integration of different technologies, such as:

1) a furnace for the waste thermo-destruction and heat production;
2) a plant for the baking of limestone and the production of CaC_2;
3) a plant for the production of acetylene from calcium carbide;
4) a plant for the electric energy production, by means of alternative and/or internal combustion engines.

Technology of the thermo-destruction furnaces and of the acetylene production plant, is modern and need little structural and process changes in order to be used in the pivot plant.
The process includes two operative stages. The first consists in the production of acetylene from calcium carbide, using energy products resulting from the controlled combustion of waste as a source of energy. In the second operative stage, the produced combustible can be used to feed the combustion plant for the production of electric energy or, otherwise it can be sold directly. The use of a hyper-detonating product, like acetylene, as fuel for an internal combustion engine is feasible if we apply the technique of water injection in the engine aspiration conduit.
In the following paragraphs we will briefly describe the thermo-destruction plant used in the research activity, the process of acetylene production from calcium carbide, and the technique of water injection to control combustion in an alternative engine.

THE THERMO-DESTRUCTION PLANT

The thermo-destruction disposal plant belongs to the category of controlled combustion semi-pyrolytic furnaces. It was created for general purposes, mainly related to the composition of the materials to be treated and, thanks to its versatility, can be used with a wide range of solid waste.
Because of the extreme heterogeneity of the waste typologies, as to their composition and aggregation stage, a correct mixing operation is necessary. In this specific case, the furnace has a feature which makes it basically different from traditional static furnaces, that is a rotating principal combustion firebox. This has many advantages:

1) it enables a rapid and complete charging operation and a rational arrangement of materials inside the furnace, as the liquid and semi-liquid materials amalgamate with the solid waste, which undergo a process of homogenisation avoiding the formation of preferential zones;
2) the process of thermo-destruction is significantly accelerated;

3) the produced pyrolysis gasses, expanding inside the waste mass, cause its uniform heating, thus regulating the process of decomposition;
4) the scum elimination is very rapid and rational, without any manual intervention and with little powders emission.

Therefore, the rotation allows you to solve the principle problems with static pyrolytic furnaces, where the combustion of little inflammable, high-humidity content material takes a long time and where the powders elimination requires the operator manual intervention.
The incinerator is constituted of a principal rotating firebox, followed by a fixed firebox. The disposal capacity for each of the three furnaces of the plant is about 4,000 Mg/year.

PRODUCTION OF THE COMBUSTIBLE

The original technique of acetylene production from calcium carbide hasn't been used for about twenty years, because of the simplicity and cheapness of the modern method of production based on the methane.
The planning and implementation of the pivot plant for acetylene production is inspired by the old methodology of CaC_2 in the new effort to be independent from traditional combustion resulting from oil.
The production of calcium carbide (CaC_2) from calcium carbonate ($CaCO_3$), raw material widespread on earth (there are still some active caves in Sicily), after the latter's turning into oxide, is obtained through the following reaction:

$$CaCO_3 \rightarrow CO_2 + CaO \quad (1)$$

$$CaO + 3C \rightarrow CO + CaC_2 \quad (2)$$

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2 \quad (3)$$

The preparation of calcium oxide trough heating (calcination) of the natural calcium carbonate or limestone, as shown in endothermic reaction (1), is dependant on temperature and pressure; in normal conditions, the carbonate's dissociation is complete at the temperature of 882° C and can be helped by the CO_2 elimination from the reaction box. In practice, in the industries limestone is heated in rotating furnace at a temperature comprised between 850-900 °C. In the above-mentioned pivot plant the heat produced by the waste combustion is used for calcination.
Reaction (2) can be industrially obtained insufflating calcium oxide (obtained through the described process) and coal in a reaction furnace. Such reaction is very endothermic and takes place at about 3000 K. The necessary heat to reach such temperature is obtained by reaction (3) which is very exothermic; in the attempt to optimise energy.

PRODUCTION OF ELECTRIC ENERGY

For an optimal exploitation of the combustible produced through the above-described methodology, it is necessary to set up a power plant made up of remotely controlled Internal Combustion Engine. This should adequately modified and paired with an electric generator (7-8).
In order to work properly and avoid detonating combustion, the thermal engine should be endowed with a water injection plant, which we have fully described and experimented (9-11).

EVALUATION OF THE PROJECT ECONOMIC FEASIBILITY

In order to evaluate the economic feasibility of this innovative project, we have analyse carefully the combustible production costs and plant building and maintaining costs. As to the plant building, we have to consider the fixed costs which are shown in table 1, where we can also see the necessary quantities of materials, and the unit and the total costs (rounded off by defect).
The core of the plant is made up of generator units, which employ the produced combustible.
After defining the fixed costs of the plant construction, we should carry out an analysis of variable costs, which include the costs of the alternative combustible (acetylene) production and the costs of the plants maintenance. Obviously, these costs vary in relation to the quantity of energy produced and the working time of the plants, prices, the year, and the present trade-union policies.

Table 1. Fixed costs of the plant (€)

Description	Quantity	Unit Cost	Total Cost
Reactors construction	2	129,114	258,228
Storage plant	1	51,645	51,645
Conveyer Belt (m)	15	5,164	77,468
Grinding Mill	1	36,151	36,151
Coal injection plant	1	10,329	10,329
Process automation	1	10,329	10,329
Gas analyser	1	51,645	51,645
Dregs evacuation plant (m)	7	10,329	72,303
Generator	2	10,329	206,582
Planning and Carrying out 5 %	-	33,569	33,569
TOTAL	-		**808,255**

We also show a list of variable costs, divided into categories, which were provided by the company, although they are not taken into consideration by the present economic analysis.

- Raw materials: Limestone; Coke; Water.

- Ordinary maintenance of the plants: oil, oil filters, and air filters change; month inspective and predictive intervention on the generator, whose cost varies according to providers; personnel (n. 2 workers).

Analysis of output

With this innovative process, 18 kg/h of combustible are produced; if we consider that in the plant there are two incinerators, each one connected to a generator, and that each generator unit uses about 9 kg/h of combustible, producing 210 kWh of electric energy, we obtain about 420 kWh of power.
The energy produced can be used as follows:

– 100 kWh can be used for the plant work;

– the remaining 320 kWh can be sold to ENEL, which doesn't produce enough energy and is therefore obliged to buy energy produced from alternative sources, paying a fixed additional contribution of 0.09606 Euros (Ł 186) per kW, for the first eight years of production, and 0.05835 Euros (Ł 113) per kW, for the following years, according to EC laws (Green Certificate).

Since the plant has a production potential of 8,000 hours a year (equal to 326 working days), if we consider the kilowatts produced, the working hours, and the CISA tax, which amounts to 3 % of the obtainable gross proceeds, we can find the possible income resulting from selling, per contract, the produced energy to ENEL, as shown in table 2. The net proceeds are calculated in relation to the withholding tax of 3 %.
Tables 1 and 2 show the costs and the incomes obtainable from the production of

Table 2. Incomes obtainable from selling the electric energy (€)

Income Years 1-8	**€/kW**	**Income/Hour**	**Hours**	**Income/Year**	**Net Income/Year**
320 kWh	0.09606	30.73	8000	245,916	238,538
Income Years 8-10					
320 kWh	0.05835	18.67	8000	149,400	144,918

electric energy, using the above described pivot plant; through these data we can calculate the Net Present Value, as the **Economical Result Updated** (**E.R.U.**), that is the updated value of costs and income discounted at a suitable rate, in order to verify the investment validity; it shows the present value of the income (meant as difference between receipts and expenses) resulting from the project. Table 3 shows the net cash-flows divided by year, during a period of 10 years: indeed, we can hypothesise that the wear and tear of the machines and the technological decay will cause the company to replace parts of the pivot plant, in particular the refractory material and the mill, while some metallic parts could be reused. In our calculations, we suppose that the plant is built in one year and that its fixed cost (tab. 1) is completely assigned to the year 0, that the funds are the company's own, and that the income is divided by year (tab. 2) and according

to the diversified prices included in the contract with ENEL and in EC laws.
The costs have been calculated according to the above-mentioned techno-economic data provided by the company, including the costs of the machines wear and tear, and the consequent maintenance costs. The table's last cell shows the E.R.U. calculated at the company opportunity cost of 6 % and equal to 91,535.84 Euros; supposing that the capital invested is totally the company's own. Since it is difficult to evaluate the real opportunity cost of the capital according to which we could update the above-mentioned cash-flows, a sensitivity analysis is to be

Table 3. Calculation of the updated total value (E.R.U.)

Year k	Costs/€	Income/€	Net Flow	Updated Value (i=0.06)
0	808,255		-808,255	-808255
1	80,825	238,538	157,713	148785.8
2	80,825	238,538	157,713	140364
3	80,422	238,538	158,116	132757.5
4	87,032	238,538	151,505	120006.7
5	93,230	238,538	145,308	108582,8
6	109,653	238,538	128,885	90858.7
7	117,329	238,538	121209	80611.03
8	125,542	238,538	112,996	70895.2
9	134,330	144,918	10,588	6267.164
10	143,733	144,918	1185	661.7868
			E.R.U.	**91535.84**

preferred; for this purpose, we progressively changed the interest rate from 0 to 12 % and calculated the corresponding values of the E.R.U. (tab 4.). As we can see in table 4, the rate after which the cash- flow becomes negative is 8.94 %, which can be immediately considered as the Internal Rate of Return (I.R.R.) of the project, that is the rate at which the income updated value is equal to the costs updated value.

Table 4. E.R.U. sensitivity analysis with respect to interest rate

rate	0	0.01	0.02	0.03	0.04	0.05	0.06
E.R.U. (€)	336,964.98	244,768.14	289,391.55	202,868.28	163,485.66	126,432.11	91,535.84
rate	0.07	0.08	0.09	0.1	0.11	0.12	
E.R.U. (€)	58,639.79	27,600.25	-1,714.46	-29,425.06	-55,642.42	-80,468.4	

DISCUSSIONS AND CONCLUSIONS

The company we are talking about, like others in this sector, is particularly concerned with the search of solutions to the problem of waste disposal through thermo-destruction which are economically advantageous and respectful of the environment.
The project we have examined exploits the heat resulting from the waste combustion to produce acetylene as an alternative combustible to those derived from oil; it then employs acetylene in an internal combustion engine with H_2O injection into the firebox. In this study, we also made an economic evaluation of

the project, in order to relate the technical aspects to the economic ones. Such evaluation shows interesting results, both technical and economic.
From the technical point of view we noticed that the use of the combustible so obtained has the advantages of gas feeding, which has been widely experimented in the last three years and is considered the most respectful of the emission limits fixed by the strict international laws. Moreover, it has other important advantages which can be summarised ad follows:

- optimal reuse of the energetic dregs resulting from the waste controlled thermo-destruction;
- diversification the primary energy sources;
- a greater respect of the environment in the combustible production process;
- further reduction of the pollutants which are emitted by the exhaust of the thermo-mechanic converter using this combustible.

From the economic point of view, the analysis has given interesting results too:

a) the Economical Result Updated (E.R.U.), which is the updated sum of the cash-flows predicted during the investment horizon time (that is, a period of ten years at the updating rate of 6 %), has been equal to 91,535.84 Euros;
b) the internal rate of return (I.R.R.), which is the interest rate at which the economic characteristics of the investment allow to extinguish the debt, giving back capitals and interest without income or loss, has made the updated net value equal to zero in a period 10 years with a rate of 8.94 %.

As we can notice, the E.R.U. is not particularly high. But we have to point out that we supposed that the whole necessary capital to build the plant is assigned to the year 0 (the year of investment evaluation) and entirely the company's own. Therefore we didn't hypothesize either an expenditure sinking plan or third party contributions or financing facilities. However, an European innovative law (the above-mentioned "Green Certificate") allows to get financing facilities at a rate ranging from 3.6 % to 4.1 %, and a capital account contribution of part of the necessary sum for the building of plants, producing electric energy from alternative sources. Therefore, using such facilities, the investment on this project becomes much more convenient than at present from a financial point of view. Moreover, if we suitably change the input data in table 3, we easily obtain the results concerning the investment return, when using the above-mentioned financing facilities.
In conclusion, we can state that the pivot project and the relative economic evaluation we have here discussed show interesting perspectives in both energy production from waste and diversification of the energy sources and the protection of the environment and the sustainable development.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

CATALYTIC CONTROL OF EMISSIONS FROM STATIONARY SOURCES

TJ Benstead[1, *] and RJD Evans[2]

ABSTRACT

The use of catalytic technology in stationary sources pre-dates the use of catalytic converters in automotive applications, albeit initially for process - rather than for air pollution control - purposes. The first legislation to regulate and enforce emission control standards was enacted in the United States (US) in 1970 and defined clear requirements for the control of pollutants from both mobile and stationary sources that lead to the formation of photochemical smog.

Whilst mobile sources were the main focus of initial development effort, these standards also provided impetus for the development and application of catalytic emissions control technology for stationary sources, identified as primary emitters of nitrogen oxides (NO_x), carbon monoxide (CO), volatile organic compounds (VOCs) and other air toxics which react in the presence of sunlight to form the photochemical smog known to be harmful to human health and vegetation.

During the 1980s, other industrialised nations such as Japan and Germany introduced similar measures aimed at curbing emissions from stationary sources; the German TA Luft standards and subsequent amendments becoming firmly established as engineering guidelines for the stationary emissions control industry across Europe. In the 1990s, the European Union (EU) published several directives on air quality and industrial air pollution and these standards form one of the key criteria against which European nations seeking to accede to full EU membership are to be measured.

A wide range of techniques are available to engineers when considering how to control NO_x, CO, VOCs and other air toxics present in industrial manufacturing process streams or the exhaust from stationary heat and power plants. This paper

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will describe the catalytic technologies used today and why catalysis has proved to be one of the most durable, reliable and cost-effective emission control technologies.

INDEX TERMS

Air Quality, Industrial Air Pollution, Stationary Source Emissions Control, VOCs, CO, NO_x

BACKGROUND

Catalytic control has been used successfully on a variety of industrial applications for over fifty years and pre-dates the use of catalysts from the mid-1970s to control air pollutants from automobiles, an application which in itself effected an unprecedented improvement in ambient air quality.
The first commercial application of catalytic oxidation on stationary sources dates back to the late 1940s when catalysts were applied for process - rather than for air pollution control - for site-specific energy recovery and odour control in the US [(1)] and by the mid-1950s, several systems had been installed in industrial plant applications in and around the Los Angeles area.

LEGISLATIVE CONTROLS

The US Clean Air Act of 1970 and subsequent energy crisis of 1973 provided further impetus to develop catalytic technology for emission control, establishing clearly defined control criteria for six principal air pollutants identified as:

- Ozone (atmospheric)
- Oxides of Nitrogen (NO_x)
- Carbon Monoxide (CO)
- Oxides of Sulphur (SO_x)
- PM_{10} (particulate matter less than 10 μm)
- Lead (Pb)

Whilst the initial political and developmental focus centred on automotive emissions, these standards applied equally to stationary emissions sources, identified as primary emitters of NO_x, CO, volatile organic compounds (VOCs) and other air toxics which are known to react in the presence of sunlight to form the low level ozone and photochemical smog which can be hazardous to human health, vegetation and accelerates the deterioration of various industrial products such as rubber.
During the 1980s, Canada, Korea, Japan, Taiwan and Germany introduced similar measures aimed at curbing emissions from stationary sources. In 1986, Germany introduced its TA Luft (Technische Anleiting zur Reinhaltung der Luft) guidelines on air quality that have become a firmly established engineering standard across the stationary emissions control industry outside North America with the latest so-called "½ TA Luft" standards, introduced in 2002, set to form the basis of

subsequent European Union (EU) legislation. In the 1990s, the EU published several directives on air quality and industrial air pollution and these standards (Chapter 22) form one of the key criteria against which European nations seeking to accede to full EU membership are to be measured.
On both sides of the Atlantic, the scope of regulatory focus is now broadening to encompass other air pollutants from stationary sources including particulate matter (PM) and specific VOC compounds such as formaldehyde which are known to present additional dangers to health and, in the US, are classified hazardous air pollutants, or HAPs.

VOC AND CO EMISSION SOURCES

Chemical and industrial processes involving combustion will form undesirable by-products requiring specialist emissions control. VOCs, air toxics and other malodorous substances can be vented or discharged from a wide range of processes but the type will vary depending on the process conditions and applications. Most VOCs are emitted from solvent-based processes but can also come from unreacted feedstock or decomposition products.
Typical examples of VOC emissions include ethanol and acetaldehyde from bread baking, caffeine and other VOCs from coffee roasting and formaldehyde, phenols and phthalates from resin manufacturing industry. Petrochemical plants will emit a variety of aromatic and aliphatic hydrocarbons whilst the printing industry generates alcohol and acetate-based VOC emissions. Other VOC sources include chlorinated hydrocarbons used in the manufacture of pharmaceuticals or as solvents in wooden furniture manufacture and ethylene oxide from hospital sterilisation ovens. Typical VOC & CO sources may be classified as follows:

- Surface Coating (can, coil, wire, film, sheet metal, textile, paper, wood, plastics).
- Printing & Converting (flexographic, lithographic, rotogravure, screen printing).
- Solvents in Manufacturing (adhesives, dry cleaning, pharmaceutical, electronics).
- Chemical & Petrochemical Industry (chemical, oils, resins, paint/inks, petroleum).
- Industrial & Commercial Processes (carbon fibre, food, beverage, hospital sterilisers).

The most practical and effective technique for destroying VOCs is incineration, a process in which VOCs captured from an industrial process are oxidised at elevated temperatures and converted to carbon dioxide (CO_2) and water (H_2O) as shown below.

$$C_xH_{2y} + (x + y/2)\ O_2 => xCO_2 + H_2O + \text{Heat}$$

Several other VOC capturing techniques also exist (e.g. biological fermentation, adsorption, condensation) but by far the most commonly specified methods for the control VOCs are thermal or catalytic oxidation.

CATALYTIC OXIDATION OF VOCS, HCS & CO

In a typical catalytic oxidiser, or incinerator, a blower drives the exhaust fumes into the catalytic incineration unit, where a burner preheats the gas to operating temperature (monitored and maintained by thermocouples and a temperature controller). Preheated gas is then passed across a VOC catalyst to combust the VOCs. Oxidation of the VOCs produces additional heat (exotherm) and this may be used to heat incoming fumes via a heat exchanger. Recuperative heat exchangers can recover between 50% and 75% of the heat released during oxidation. Regenerative oxidisers are even more efficient, employing multiple ceramic chambers (often bare substrates) to recover as much as 90% to 95% of the heat from oxidation. In both cases, the result is additional fuel savings.

A thermal oxidiser operates by passing the fumes over a hot surface (typically an array of ceramic blocks) in order to combust or oxidise the VOCs. In contrast to thermal oxidation techniques, which require high temperatures and hence large amounts of fuel to maintain the temperatures, a catalyst will react and oxidize VOCs at much lower temperatures, meaning less fuel and lower costs. Catalytic oxidation of benzene, for example, requires a temperature of 227°C (440 °F) and a residence time of 0.24s for 99% destruction in a catalytic oxidizer but 793°C (1460 °F) and a residence time of 1.0s for 99% destruction in a thermal oxidizer [4]. The lower temperature required for catalytic oxidation also extends mechanical durability of key components such as the heat exchanger resulting in lower maintenance costs.

A typical VOC catalyst comprises PGM (platinum group metals) mixed with a high surface area alumina-based washcoat and applied to the surface of a honeycomb support structure or substrate of fabricated stainless steel foils (metal monolith) or extruded cordierite (ceramic monolith) or ceramic pellets or beads. The precious metals are applied in such a manner to provide as many reaction sites as possible in a stable configuration to ensure high performance and long life.

Below is a list of engineering design factors that, when allied with the catalyst supplier's field experience, ensure a catalytic system will meet the required performance criteria.

- Application or Process
- Exhaust Gas Composition, Flowrate, Pressure, Temp
- Catalyst Contaminants
- Required Destruction Efficiency
- Pressure Drop Constraints
- Maintenance Interval
- Durability Requirements
- Packaging Constraints

Over the past thirty years, catalytic oxidisers have been installed and operated successfully in a wide variety of VOC destruction applications with a proven track record of high efficiencies and long life. With the threat of global warming and increased public and political awareness of environmental issues and sources of air pollution, catalytic oxidisers will continue to play a major role in reducing VOC, HAP, CO and air toxic emissions from stationary sources.

NO_X AND CO EMISSION SOURCES

Principally NO (nitric oxide) and NO_2 (nitrogen oxide), oxides of nitrogen (NO_x) are emitted by combustion sources such as internal combustion (IC) engines, gas turbines, utility and industrial boilers, chemical and process heaters, nitric acid manufacturing plants, some chemical manufacturing plants and incinerators. NO_x is formed by the high temperature oxidation of ambient nitrogen (N_2) or by the oxidation of nitrogen in the fuel supply or chemical process.
CO is often emitted by the same sources that emit NO_x and formed by the incomplete combustion of VOCs across a burner in a thermal incinerator, from the incomplete combustion fuel and HCs or from cold spots in the combustion zone of an IC engine. CO emissions also increase significantly in gas turbines equipped with water or steam injection to lower the NO_x emissions. Typical NO_x & CO sources may be classified as follows:

- Chemical & Petroleum Industry (refinery boilers, process heaters, nitric acid plants)
- Industrial & Commercial Processes (greenhouses, crematoria, cement kilns)
- Engine Applications (diesel engines, lean and rich burn IC engines)
- Heat & Power Generation (gensets, stationary gas turbines, utility/industrial boilers)

NO_x and CO have been identified as air pollutants requiring tight emission control as both have been shown to contribute either directly or indirectly to respiratory problems.

CATALYTIC CONTROL OF NOX AND CO

Catalytic oxidation is the by far most cost-effective and proven technique for controlling emissions of CO. CO oxidation catalysts are similar in composition and function to VOC catalysts, comprising PGMs applied to, or mixed with, an oxide support or washcoat applied to a honeycomb metallic or ceramic substrate. Oxidation catalyst technology is ideally suited to CO conversion as it is readily converted to CO_2 at temperatures in the range 260-540 °C found in many process exhaust gas streams.
There are a variety of non-catalytic methods for minimising NO_x (since it is virtually impossible for combustion sources to emit zero NO_x emissions). Although quite effective, these techniques, such as low NO_x burners, clean-burn engine modifications, water and steam injection for gas turbines, are limited in their ability to reduce the emissions of NO_x to very low levels. Thus, the method of choice for tight NO_x emission control is often catalytic.
The type of catalysts used to control NO_x will depend on the type of equipment that is emitting the NO_x. NO_x from nitric acid plants, for example, is controlled using a "NO_x abatement catalyst". NOx emissions from so-called 'rich burn'

exhaust containing less that 1% oxygen (O_2) is typically controlled using a non-selective catalytic reduction, or NSCR, catalyst - often referred to as a three-way catalyst (TWC). NOx emitted from 'ean burn' exhaust (i.e. over 1% O_2) such as gas turbines, thermal incinerators, chemical processes, boilers and IC engines, is more usually controlled with a selective catalytic reduction (SCR) catalyst.

NSCR DENOX

Three-way catalysts (TWC) used on stationary engines operate in the same manner as those that have been employed with such success over the past thirty years to control automotive emissions. A typical TWC will simultaneously convert over 98% of the NO_x and CO and most of the unburned HC emissions as indicated in the NSCR reactions below.

- $CO + \frac{1}{2} O_2 => CO_2$
- $H_2 + \frac{1}{2} O_2 => H_2O$
- $HC + O_2 => CO_2 + H_2O$
- $NOx + CO => CO_2 + N_2$
- $HC + H_2O => H_2 + CO_2$
- $NOx + H_2 => H_2O + N_2$

These reactions can only occur in this manner when the oxygen content of the exhaust is controlled to less than 1% (typically about 0.5%), accomplished by attaching an air/fuel controller (lambda sensor) to the engine to maintain the required stoichiometric mixture as practised routinely in the automotive industry today.
NSCR is proven emission control catalyst technology with over a billion catalyst units equipped to automobiles since the mid-1970s and well over 2,000 stationary engine installations in service today.

SCR DENOx

SCR catalysts are used to reduce NO_x from exhaust streams containing greater than one percent O_2. As the name implies, NOx is selectively reduced by reacting it with a reagent, - usually ammonia (NH_3) or an ammonia-based reductant such as urea - across an SCR catalyst which reduces the NO and NO_2 to nitrogen and water, as shown below.

- $4NO + 4NH_3 + O_3 => 4N_2 + 6H_2O$
- $2NO_2 + 4NH_3 + O_2 => 3N_2 + 6H_2O$

Most SCR catalysts use base metal chemistry, employing vanadium, tungsten, titania, silica and/or zeolite-based materials depending on the required temperature of operation. These can be extruded into a honeycomb structure or coated directly onto a metallic or ceramic honeycomb support.
The reduction of NO_x is dependent on the volume, reductant concentration, operating temperature and activity of the SCR catalyst. The major factors influencing catalyst selection include process gas temperature and a thorough

examination of potential contaminants such as particulate and catalyst poisons. The majority of the SCR catalysts in use today are designed to function in the 315-425 °C temperature range where conversions in excess of 95% are routinely achieved.

Low:	120-350 °C	Porous extrudates in bed reactor.
Medium:	265-425 °C	V/Ti/W on high-density honeycomb.
High:	345-590 °C	Zeolite on ceramic substrate.

The reagent injection system should be designed to ensure complete mixing of the reagent with the flue gas as an aid to the conversion process. Ammonia is typically used as the reductant at a 1:1 mole (or volume) ratio. Some unreacted ammonia will pass or "slip" through the process and this slip ammonia is usually limited by regulation to less than 20 ppm and, in some cases, less than 5 ppm. As a precaution, a slip catalyst may also be used to remove any residual ammonia from the stream prior to venting.
SCR/CO catalyst technology is a proven technology for a wide range of industrial heat and power generation applications, particularly in the US, which has over twenty years' experience and several thousand stationary field installations in service today.

CONCLUSIONS

- Catalytic control technology has been successfully applied to control process and exhaust emissions from stationary sources for over half a century.
- The advent of emissions control legislation since the 1970s and increasing environmental awareness worldwide has continued to provide impetus to the development of catalytic systems for stationary source emissions control.
- Precious and base metal catalytic technology is proven to be a durable, reliable and cost-effective emissions control option for a wide range of chemical, process and stationary heat and power generation applications.
    - Catalytic control technologies provide for:
    - High conversion efficiencies and long life.
    - Lower reaction temperatures
    - Significant fuel savings
    - Lower material installation costs
    - Reduced levels of pollutants
    - Smaller installation footprint
- Installation of catalytic control systems is often the most a cost-effective means of ensuring compliance with EU directives on air quality and industrial air pollution.

ACKNOWLEDGEMENTS

The author would like to thank Johnson Matthey Plc for allowing the use of internal documentation in the compilation of this paper.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

THE EMISSIONS MANAGEMENT SECTOR: RESPONDING TO THE NEEDS OF A NETWORK OF CITIES

RJD Evans[1, 2, *]

ABSTRACT

Transports' contribution to air quality problems is greatest in cities, where high traffic volumes generate both congestion and pollution. This localisation of pollution has in turn provided the impetus for policy measures that devolve air quality management from a national to a local level and specifically, for cities. As a result there has been an emergence of city-based initiatives seeking to tackle poor air quality based on technological approaches.

This paper will use a case study example to highlight the role that the emissions management sector can play in servicing the needs of an individual city or network of cities. The case study example of London, will illustrate the emissions reduction capabilities of diesel particulate filters as a clean diesel offering in competition with alternative fuels. Diesel Particulate Filters (DPFs) will be shown to cut particulate matter (PM_{10}) emissions by greater than 90 percent, as well as cutting hydrocarbon and carbon monoxide emissions. London Buses accounted for eight percent of central London PM_{10} emissions prior to the introduction of DPFs and just three percent after. The paper will further highlight the role of the emissions management sector as a common factor connecting a network of cities into a market and conclude by discussing the relevance of clean diesel technologies to cities in central and eastern Europe.

INDEX TERMS

Clean diesel technologies, Diesel particulate filters, Emissions control, Particulate matter, public transport

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INTRODUCTION

The problem of transport-related air pollution is increasingly being defined as a local problem, both in terms of its effects and because of the devolution of policy responsibility for issues, such as environmental protection, from a national to a local government level. This devolution of air quality management has promoted the development of new technology-based tools from the environmental industries sector that aid the policy maker. This paper will illustrate the benefits of clean diesel technologies and their relevance to cities across the world, including those in central and eastern Europe.

BACKGROUND

The majority of European cities already have well established public transport systems in which buses play a significant role. This has highlighted the issue of buses' contribution to local pollution inventories, particularly within a city centre environment. Of the air pollutants, particulate matter (PM) emissions of less than 10 microns in diameter (PM_{10}) is increasingly of concern because of its health effects and because of the growing number of cities where the PM_{10} air quality standard is exceeded. This focuses attention on the contribution of diesel engines to the overall pollutant inventories and to sectors such as buses within the public transport mix.

CASE STUDY: LONDON

Estimates of PM_{10} emissions for central London in 1995 identified buses as accounting for eight of PM emissions, with levels as high as 54 percent measured in areas where car use was restricted, as in the case of Oxford Street (Brown, 2000). These measurements led the Public Transit Authority (PTA) and London Transport Buses (LTB) to review technology options that could help cut PM emissions from buses. The alternatives to the conventional diesel engine are broadly split into three categories, as illustrated in Table 1.

Table 1. Technology Options to Reduce Bus Exhaust Emissions

Alternative Fuels	**Alternative Power-trains**	**Clean Diesel Technologies**
Gaseous fuels	*Electric power*	*Clean fuels*
Natural gas, liquid petroleum gas, hydrogen	Battery, fuel cell	ULSD, emulsion fuels
Biofuels	*Hybrid-electric*	*Exhaust after-treatment*
Bio-ethanol, bio-gas or bio-diesel	Engine, fuel cell or turbine with battery	Oxidation catalysts, DPFs, EGR or SCR

At the time of London's assessment, commencing in 1996, alternative powertrains were still in their early demonstration phases and therefore expensive, difficult to source and not always practical. With London's extensive use of double-decker buses and in-door garages, gaseous fuels were also unattractive (Evans, 2000). This led to the emphasis of technology investigation and demonstration being placed on clean diesel technologies.

In practical terms the challenge for clean diesel technologies is to cut the four main regulated pollutants; carbon monoxide (CO), hydrocarbons (HC), particulate matter (PM) and oxides of nitrogen (NO_x). The CO, HC and PM emissions in diesel exhaust are the result of incomplete combustion of fuel and can only be fully removed by further oxidation of pollutants to carbon dioxide and water. In contrast, NO_x must be reduced to nitrogen. Unlike the gaseous pollutants, PM is a complicated mix of solids and liquids. Essentially droplets of diesel fuel burn incompletely to form fine particles of carbon (soot) and these particles then absorb unburnt and partially burnt hydrocarbons and agglomerate to form larger particles. They will also absorb water and sulphur compounds present in the diesel exhaust. PM also includes a portion of solids derived from burnt engine oil (ash) and metals from engine wear. The relative composition of PM varies by engine type and application.

The UK environmental industries sector responded by offering LTB both lower sulphur content diesel fuel and exhaust after-treatment in the form of oxidation catalyst and diesel particulate filter (DPF) systems. Clean diesel fuel was offered both as a way of cutting pollutant emissions and as an enabler for the use of DPF systems. Lowering the sulphur content of diesel helps both to cut the sulphur-content of PM and to promote a cleaner burn in-cylinder, as well as enhancing the performance of exhaust after-treatment. Oxidation catalyst technology helps cut HC, CO and the HC-content of PM but catalysts cannot oxidise carbon to carbon dioxide because the flow-through monoliths used do not give the required residence times. Instead DPF systems are employed to trap the PM from the diesel exhaust, thereby preventing it from passing into the environment and retaining the carbon where it can be subsequently oxidised. This can be accomplished by either using a fuel borne catalyst, a catalyst applied to the filter (catalysed soot filter or CSF) or by an active oxidant like nitrogen dioxide (NO_2), generated by an oxidation catalyst upstream of the filter, as in the case of the Continuously Regenerating Trap or CRT.

Table 2 illustrates the results of LTB laboratory-based testing on the Millbrook London Bus Cycle. The cycle has been derived from real-world measurements of vehicle speeds seen on a typical London bus route, operating from Brixton to Oxford Street. In a series of tests on this cycle, using a bus equipped with a Euro 2 engine, the effects of lowering fuel sulphur were tested along with the use of oxidation catalyst and DPF systems. The initial results seen on the Euro 2 bus running on the then pump diesel (<0.2% S) diesel are set at an index of 100 (Brown, 1997, Evans, 2000) and compared with low sulphur diesel (< 0.05%) and Ultra Low Sulphur Diesel (ULSD) with a sulphur content < 0.005%.

Table 2. Summary of Diesel and After-treatment Effects from LTB testing

Clean fuel	Retrofit	CO	NMHC	NO_x	So_x	PM_{10}
Pump Diesel	None	100%	100%	100%	100%	100%
Low S Diesel	None	100%	100%	100%	42%	87%
Low S Diesel	Oxicat	59%	54%	98%	42%	44%
ULSD	None	83%	91%	91%	1%	54%
ULSD	Oxicat	16%	25%	88%	1%	30%
ULSD	DPF	16%	22%	84%	1%	11%

The results illustrate the reductions in PM emissions achieved by the lowering of fuel sulphur and the reductions in all of the main pollutant emissions as a result of a switch from low S Diesel (<0.05% S max) to ULSD (<0.005% S max). They also illustrate that the greatest reductions in PM, HC and CO results from DPF use, which in this example was the CRT. The results of the LTB study led to the subsequent switch to ULSD and the implementation of a bus retrofit programme that has helped cut buses contribution to central London's PM_{10} emissions from 8% to 3% (Greater London Authority, 2001).

OTHER STUDIES

As with London, other cities across Europe, North America and Asia have opted to switch bus fleets to ULSD and DPF systems. Notable examples include Berlin, Hong Kong (Tsang & Ha, 2001), New York (Lowell, 2003), Paris, Tokyo and Stockholm.

SUMMARY OF TECHNOLOGY STATUS

DPF systems are now established, with over 50,000 units in the field since 1995. The strengths and weaknesses of DPF systems are summarised in Table 3.

Table 3. Strengths and Weaknesses of DPF Systems

Strengths	Weaknesses
Performance for PM, CO and HC	Offer only small overall NOx reductions, some NO_2 increases possible
Proven durable and reliable	Have duty cycle and servicing requirements
Allow for the continued use of diesel (benefits of fuel economy, durability and known maintenance costs)	Need ULSD to function reliably and effectively
Easy to police (self enforcing and easily monitored by smoke meter readings	
Low entry cost option compared with gaseous fuels	
Certified by a wide range of Government agencies as proven technology	
Experience to date provides a wide range of designs for different vehicle types	
Compatible with deNOx technologies like emulsion fuels, EGR and SCR	

DPF systems have been tested in combination with NO_x reduction technologies, including diesel-water emulsion fuel, Exhaust Gas Recirculation (EGR) and Selective Catalytic Reduction (SCR). These offer around 10 percent (Schmelzle, Bernard & Schulz, 2000), 40 to 60 percent (Chatterjee, Conway, Viswanathan *et al*, 2003) and 60 to 80 percent NO_x reduction (Allansson, Blakeman, Chandler *et al*, 2000) respectively. Emulsions and EGR systems are commercially available but SCR systems are still under development.

DISCUSSION

DPF systems are sold in the form of packaged stainless steel exhaust systems, as an aftermarket replacement for a conventional mild-steel silencer. The number of suppliers is limited as much of the technology in this area is patent protected. The suppliers, who fall within the environmental industries sector, market these systems direct to the end user (bus operator) but with a strong involvement of the PTA in decision-making. In line with after-market products, bespoke designs, high levels of service and small volumes contribute to the cost of systems. Nevertheless, unit costs commence from 5000 euros – a low entry cost resulting in a high benefit-to-cost ratio for emissions reduction. In Swedish studies, this positive benefit to society has been demonstrated (Ahlvik, 2001).

The environmental industries sector is actively targeting the promotion of the benefits of DPF system to city authorities across Europe. This has proven including those in Belgium, Germany, the Netherlands, Hong Kong, Tokyo, the UK and USA, who have acted to support their uptake through incentive programmes. Within these countries, each city tends to respond to the uptake of environmental technology based on its own unique circumstances, albeit with reference to national environmental policy concerns and the activities of other cities in the same country. On a regional level, government initiatives that have sought to link cities in different countries have played a more limited role in progressing clean diesel policy initiatives. Instead it is arguably the marketing activities of the environmental industries sector that have allowed cities to share experience and thereby created a common market centred on a network of cities.

Through accession to the European Union, cities in the central and eastern Europe will become subject to the same trend to devolve air quality management to a city level. Their cities share the same problems and opportunities as their western counterparts. In addition to its health impacts, PM_{10} pollution is a general blight on air quality affecting both the local population and the many tourists who visit cities in the region. Both categories have expectations about acceptable levels of air quality and are aware of the damage caused by pollution to the general city centre environment, as well as to specific historical landmarks. The opportunity to directly address this PM_{10} pollution is therefore attractive, particularly given that bus-based public transport takes a far greater modal share of passenger travel in the region at 39 percent, compared with just eight percent in western Europe.

For the latter, car travel dominates, at 83 percent compared with 45 percent in central and eastern Europe (Dora & Phillips, 2000). Therefore, both from a local government and an environmental industries perspective, the cities in the region should represent a significant market opportunity for clean diesel technologies. The main barriers to the uptake of DPF systems in the region are awareness and fuel (ULSD) availability. This paper aims, in a small part to address for former barrier and encourage policy makers to consider the latter.

CONCLUSIONS & RECOMMENDATIONS

For the emissions management/environmental industries sector, the primary market for clean diesel technologies is for city centre buses and public service vehicles. The best performing product is the diesel particulate filter (DPF), capable of cutting PM_{10} pollution from buses and trucks by greater than 90 percent. This results in a market comprised of a developing network of cities across Europe and more recently in North America and Asia. The cities themselves share the common problem of PM_{10} pollution but policy mechanisms that promote communication between cities are arguably under developed. In the absence of a mechanism to promote this dialogue to create a common network, it is the commercial activities of the environmental industries sector that effectively coordinates cities into a common market. For cities in central and eastern Europe, the opportunity exists to opt for these clean diesel policies to take advantage of this developing market. The main barriers to this are awareness and ongoing dialogue with the environmental industries sector and the availability of the enabling ULSD fuel. These barriers can and are being addressed.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

SIZE-FRACTIONED PARTICULATE MATTER EMISSIONS IN FINLAND IN 1990-2020

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ABSTRACT

Particulate matter (PM) air concentrations have been shown to have harmful effects on human health, possibly with no threshold. Recent evidence suggests that smaller size fractions of PM, such as fine particles ($PM_{2.5}$), represent an important element in impacts. Integrated assessment models (IAMs) provide support to emission reduction policies to reduce environmental and human health effects of air pollution. The Finnish Regional Emission Scenario (FRES) model has been developed as a part of the Finnish IAM on air pollutants focusing on acidification and PM. This study reports the FRES model results of primary PM of different sizes (total suspended particles, PM_{10}, $PM_{2.5}$ and PM_1) and the main precursor gases for secondary PM (SO_2 and NO_x). The emissions are calculated for several activity sectors, and the time period covers past (1990), present (2000) and future (2010 and 2020) with official national energy and activity scenarios. The emissions of primary $PM_{2.5}$, SO_2 and NO_x have decreased substantially during the 1990s (34%, 70% and 26%, respectively) due to the introduction of emission control measures in power plants, industry and traffic sectors. In the future the emissions from power plants and industry will remain approximately at the present level. The traffic emissions of PM and NO_x continue to decrease along the renewal of vehicle fleet. The emissions from small residential heating devices have become relatively more important due to deficiency of emission controls. The FRES model results are used to depict alternatives for national control options and abatement strategies to reduce harmful effects.

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INDEX TERMS

Air pollution, aerosol, particulate matter, emissions, scenarios

INTRODUCTION

The abatement of harmful effects from air pollution is an important issue in national and international policy making. In the end of 1900s the focus was on acidification. Successful reductions of acidifying emissions, *i.e.* sulphur dioxide (SO_2), nitrogen oxides (NO_x) and ammonia (NH_3) in Finland, were governed by a series of Committees with representation of relevant Ministries, industries and NGOs (*e.g.* Acidification Committee, 1998). The Committees' concrete reduction proposals have been supported by additional calculations on environmental side effects of integrated assessment models (IAMs), which describe emissions, their abatement options and costs, atmospheric transport and impacts in a consistent and quantitative manner. Currently the main attention is on the health effects of ground-level ozone and particulate matter (PM). The development of the national IAM system for PM is currently in progress (Johansson et al., 2003).

Particulate matter in the atmosphere is a complex mixture of different sizes, chemical species and origins. Primary PM is emitted directly to the atmosphere by anthropogenic activities and natural processes. Secondary PM mostly originate from anthropogenic sources. They are formed from precursor gases of sulphur dioxide (SO_2), nitrogen oxides (NO_x), ammonia (NH_3) and volatile organic compounds (VOCs).

Reports on annual emissions (*e.g.* Statistics Finland, 2002) are usually based on detailed data collection and calculation systems, typically including several thousand point sources. As data intensive systems they are heavy to use, and not applicable for future emission projections. The Finnish Regional Emission Scenario (FRES) model was developed to calculate past, current and future emission estimates at a sectoral, spatial and temporal aggregation level practical for IAM use, including source specific emission height in four classes. This paper presents the FRES model results for primary PM and main precursor gases of secondary PM. The analysis covers the years 1990, 2000, 2010 and 2020 with three different official national energy and activity scenarios.

METHODOLOGY

The Finnish Regional Emission Scenario (FRES) model has been developed to work as a part of the integrated assessment model system of air pollution. Currently FRES calculates the annual emissions of primary total suspended particles (TSP) and finer size fractions (PM_{10}, $PM_{2.5}$ and PM_1), and SO_2 and NO_x of the precursor gases of secondary PM. The emissions of NH_3 and VOCs are being added to the model, and the national total emissions for these are presented

in Johansson *et al.* (2003). The emissions are calculated at point source and municipality level from all the anthropogenic emission sources, *i.e.*, fuel combustion activities and industrial processes. In addition, the model includes primary PM emissions from several fugitive dust and other non-combustion PM sources. The main features of the model are described in this paper. The model structure and the data sources for PM, SO_2 and NO_x are reported in more detail in Karvosenoja and Johansson (in press).

The basic structure of the FRES model is a combined top-down approach of aggregated emission source sector description with more detailed bottom-up calculation of large point sources. The top-down feature makes a relatively light model structure possible, while the annual activity rate inputs of the source sectors are described in a relatively aggregated level. Large point sources and their emission control facilities are described in more technical detail, which enables the estimation of emissions more accurately both spatially and in the terms of emission quantities.

The main sector division of the FRES model is as follows:

- Fuel combustion sectors (11 fuels)
  - o Power plants and combustion in industry (plants utilizing boilers with thermal capacity exceeding 50 MW_{th} as point sources)
  - o Domestic combustion
  - o Traffic, off-road and machinery
- Industrial processes (plants with emissions >20 Mg(PM, SO_2 or NO_x) a^{-1} as point sources)
- Other non-combustion sources for PM (fugitive dust, meat frying, tobacco smoking *etc.*)

The emissions are calculated from annual activity rates, unabated emission factors (*i.e.*, emission factors before emission control devices) and utilisation and emission removal efficiency information of emission control technologies. Spatially the emissions are at point source and municipality level. In this paper the emissions are presented only at country level.

The activity data for 1990 and 2000 were determined using national statistics (Statistics Finland, 2002). The source sector specific unabated emission factors of area sources and control technology removal efficiencies were estimated based on national and other literature (*e.g.* McDonald *et al.*, 2000; Ylätalo and Hautanen, 1998; Venkatram *et al.*, 1999; Kleeman *et al.*, 1999; Chow *et al.*, 1994). The plant-specific emission factors of the point sources and the utilization rates of emission control technologies of the existing energy system were determined based on the data of the register on air pollution permits of the Finnish environment administration VAHTI (Korkia-Aho *et al.*, 1995) containing technical, fuel use and emission information on the Finnish industrial and energy producing plants.

The activity data in 2010 and 2020 were based on three national energy and activity scenarios of the Finnish climate strategy by the Ministry of Trade and Industry

(2001). All the scenarios assume an average annual economic growth of 2.4%, with higher growth (5.1%) in electronics industry and slightly lower growth rates in energy demanding heavy industries, *e.g.* forest industry (1.8%), chemical industry (1.4%) and metal industry (2.0%). The first scenario "Baseline" does not include any additional restrictions on energy production system, leading to a 16% and 22% increase in the total primary energy consumption in 2010 and 2020, respectively, compared to 2000, met by a more extensive use of hard coal. The EU burden sharing agreement for Finland is the stabilization of emissions at the 1990 level. In the other two scenarios, "Kyoto-gas" and "Kyoto-nuclear", this agreement would be met. Both Kyoto-scenarios include greenhouse gas emission reduction measures, *e.g.*, more emphasis on energy saving and fuel switching to low carbon content fuels in centralized heat and power production. "Kyoto-gas" includes a strong shift from coal to natural gas and biomass. In "Kyoto-nuclear", one new 1400 MW_e nuclear reactor would be introduced to the Finnish energy system, with a moderate shift from coal to biomass and gas. The utilization of emission controls in new capacities was estimated based on legislative requirements, *e.g.*, the Large Combustion Plants Directive of the European Union (EC, 2001).

RESULTS

All emissions have clearly decreased during the 1990s (34%, 70% and 26% for $PM_{2.5}$, SO_2 and NO_x, respectively) (Figure 1). It has been mainly due to introduction of emission control measures in power plants, industry and traffic sectors.

Small-scale wood combustion and traffic sources are the major sectors in primary PM emissions, especially in the smallest size fractions. These sectors contributed to 48% and 26%, respectively, of PM_1 emissions in 2000. The primary PM from non-combustion, non-industrial sources, consisting mainly of fugitive dust emissions, account for a considerable share of the coarse particle sizes, *i.e.* TSP and PM10, but only a minor part in PM2.5 and PM1. However, the uncertainties are largest in fugitive dust and domestic wood combustion, and the emissions of these sources should be considered as order of magnitude estimates (Karvosenoja and Johansson, 2003; Karvosenoja *et al.*, 2002). Stationary industrial activities, *i.e.* power plants, and combustion and processes in industry, caused 90% of the total SO_2 emissions in Finland in 2000. Traffic contributed to more than half of the total NO_x emissions.

The major part of the Finnish industrial and power plants are already equipped with efficient emission reduction measures of SO_2 and NO_x, and substantial further reductions in future emissions are not anticipated. Strong increase in the use of hard coal in the "Baseline" scenario would result in increase in SO_2 and NO_x emissions. PM emissions in large industrial and power plants are efficiently controlled, and emissions from these sources are relatively low. Therefore, primary energy choices of electricity production do not affect PM emissions significantly.

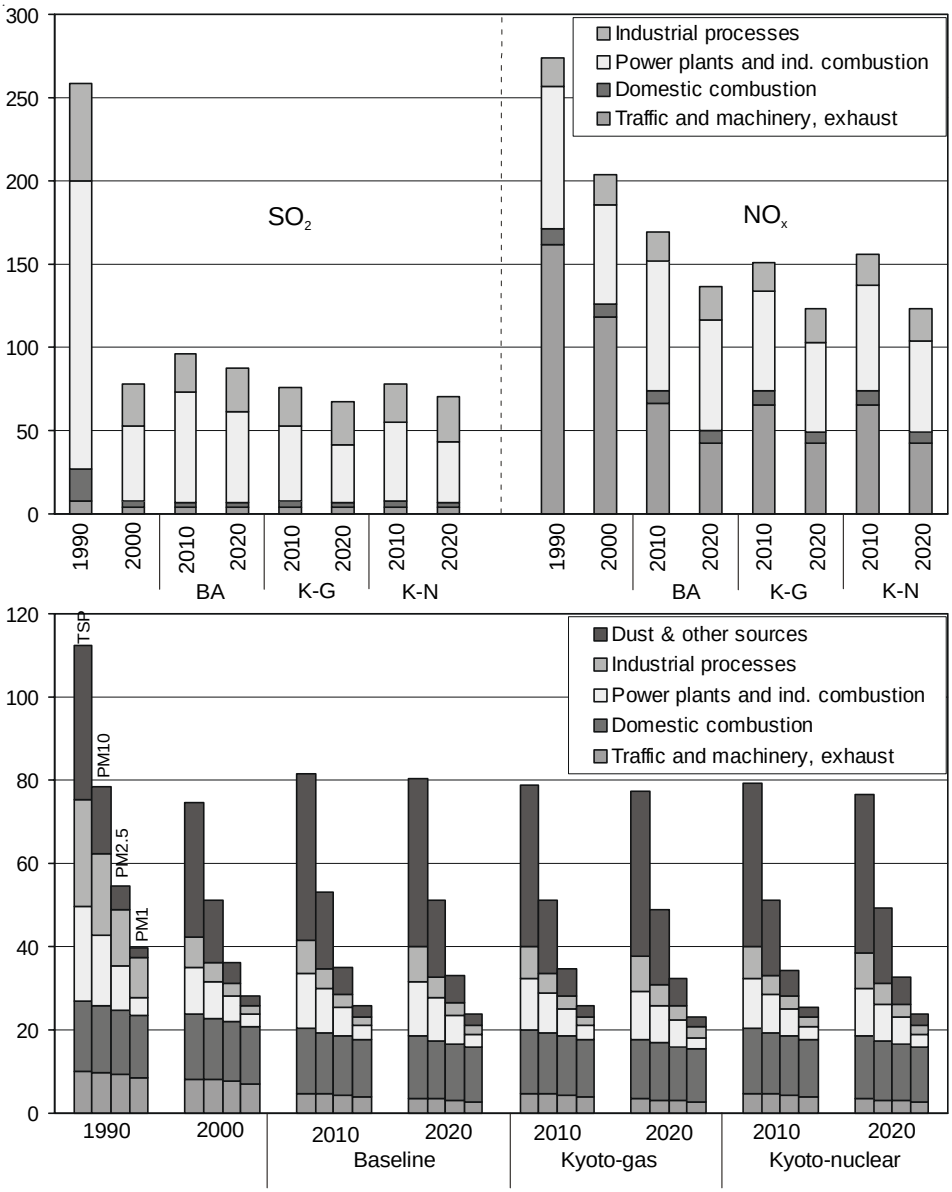

Figure 1. Finnish emissions of SO_2, NO_x and primary PM (TSP, PM_{10}, $PM_{2.5}$, PM_1) in 1990, 2000, and 2010 and 2020 in three national scenarios (BA=Baseline, K-G=Kyoto-gas, K-N=Kyoto-Nuclear)

Slight increase in wood use in the domestic sector in all scenarios do not increase PM emissions because of assumed renewal of combustion equipment, and thus decrease in average emission factors. Traffic emissions of NO_x and PM will continue to decline substantially along the renewal of vehicle fleet in all scenarios.

DISCUSSION AND CONCLUSIONS

The Finnish Regional Emission Scenario (FRES) model was used to calculate primary PM, SO_2 and NO_x emissions in 1990, 2000, 2010 and 2020 with three national scenarios. The major contributing sectors were power plants and industry for SO_2 and NO_x, traffic for primary PM and NO_x and domestic combustion for primary PM. The results for 1990 and 2000 are well convergent with the values in national statistics for all pollutants (Karvosenoja and Johansson, in press; 2003). Finnish industrial and power plants already utilize efficient emissions reduction measures for SO_2 and NO_x. Therefore, relatively little cost-efficient emission reduction potential was found in the present energy production system (Karvosenoja *et al.*, 2001). Furthermore, the emission levels in new large combustion plants are regulated by legislation, mainly the Large Combustion Plant Directive of the European Union (EC, 2001), and thus the standards of emission reduction technologies are high. The future development in emissions is thus merely dependent on the changes in the energy production structure, *i.e.* the amount of primary energy use and the choices of primary energy carriers in new plants rather than additional efforts in technical emission control measures. The analysis indicated that the measures and fuel choices to prevent climate change induce also leads to reductions in SO_2 and NO_x emissions. As a side effect the implementation of the "Kyoto" scenario would lead to a notable reduction in Finnish ecosystem area threatened by acidification compared to the "Baseline" (Syri *et al.*, 2002). In addition, lower Finnish emissions of SO_2 and NO_x would consequently result in lesser formation of secondary PM and decreased human exposure.

Primary PM emissions are efficiently controlled by technical measures in large combustion plants. In 1995 the average removal efficiency in Finnish power plants and industry was higher than 99% for TSP and higher than 98% for PM2.5 (Karvosenoja and Johansson 2003). Domestic wood combustion and traffic are currently the biggest contributors to primary PM. In addition, these activities occur partly in densely populated urban areas, and the emission heights area close to the human respiration level. Road traffic exhaust emissions of new vehicles are regulated by European legislation. For domestic combustion equipment there are no Finnish emissions standards at present. Contribution of wood combustion on PM population exposure have to be investigated in the future.

The FRES model, which is comprehensive at source, fuel specific, sectoral and spatial levels to describe the total PM and precursor gas emissions, is the first completed module in the Finnish IAM for PM. It enables operative scenario analysis and detection of source contribution to total emissions, and provides the necessary spatially resolved input for atmospheric dispersion modelling.

ACKNOWLEDGEMENTS

The development of the Finnish Regional Emission Scenario (FRES) model has mainly been carried out in two projects aiming at national integrated assessment

modelling of PM in Finland. The authors gratefully acknowledge the financial support from the Ministry of the Environment and the KOPRA project in the technological programme "FINE Particles - Technology, Environment and Health 2002-2005" of the National Technology Agency of Finland (Tekes).

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

MANAGING THE IMPACT OF VEHICLE EMISSIONS IN URBAN AREAS FOR THE PURPOSE OF LOCAL AIR QUALITY MANAGEMENT

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ABSTRACT

Road transport is a major source of local air pollution particularly in towns and cities. Road traffic accounts for over half of the emissions of nitrogen oxides (NO_x) and over 75% of the areas identified as at risk of failing to meet air quality targets. Local authorities in Great Britain (England, Scotland and Wales) have completed statutory review and assessments of air quality. Some 129 local authorities have identified a risk of one or more air quality objectives being exceeded by a relevant date specified in the Air Quality Regulations, 2000. In such locations, air quality management areas (AQMAs) have been designated. In most cases, AQMAs are designated because of the impact of vehicle emissions of nitrogen dioxide (NO_2) and particulate matter (PM_{10}). Having designated an AQMA a local authority is under a duty to prepare an Action Plan to address the air quality problems found. National policy responses include regulatory measures to reduce vehicle emissions and improve fuels, tax based measures to encourage the supply and use of cleaner fuels and vehicles and the development of an integrated transport strategy that supports sustainable development. However, national measures alone have been insufficient to reduce air quality impacts. Additional local measures are required if air quality objectives are to be met.

This paper will critically review national and local measures being introduced in the UK and the outcomes of the national review and assessment process to assess the likelihood of air quality objectives being secured in areas where road transport is the major contributor to air quality exceedences.

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INDEX TERMS

Air quality management areas, transport, vehicle emissions, action plans, policy

INTRODUCTION

Prior to the 1990s, air pollution was regulated on a *reactive* basis (Beattie *et al*., 2000). In 1990 the UK Government issued a White Paper žThis Common Inheritance' (Department of Environment, 1990), introducing a new strategic framework for controlling emissions and improving local air quality in Great Britain (Elsom *et al.,* 2000). This approach introduces the concept of an AQMA as a designated zone for air quality improvements.

The designation of air quality management areas (AQMAs) is a statutory requirement of air quality legislation in Great Britain, where specific air quality objectives are predicted to be exceeded by certain target dates (Beattie *et al*., 2001). The spatial location of AQMAs reflects the distribution of population within the GB space, with the less densely populated (and thereby less trafficked) administrative areas of Scotland and Wales having proportionately fewer AQMAs. This is also due to lower background concentrations of air pollutants experienced within the northern and western regions of GB, with the exception of urban centres where background concentrations of NO_2 and PM_{10} from vehicle traffic is elevated (Woodfield *et al.,* 2003a).

NO_2 is the pollutant for which most AQMAs are designated in GB (see table 1, Woodfield *et al.,* 2003b), with predicted exceedences of the NO_2 annual mean objective requiring more than 75% of declaring authorities to do so for traffic emissions. A further 20% of AQMAs will see traffic emissions contribute to predicted exceedences (Woodfield *et al.,* 2001a).

Local authorities across GB are therefore paying particular attention to the transport solutions to resolve the air quality challenges faced. To date, local authorities have been advised on air quality management, transport planning and land-use planning

Table 1. Emission source responsible for air quality objective predicted exceedences

Emission source(s)	% of local authorities
Traffic only [a, b]	74
Traffic mainly (minor contribution from industry) [a, b]	12
Traffic [a, b] and industry [b, c]	5
Industry only [b, c]	4
Traffic [a, b] and construction emission source [b]	1
Traffic [a, b] and domestic source [c]	1

[a] NO_2 objective(s) [b] PM10 objective(s) [c] SO_2 objective(s)

through national strategies and guidance (DETR *et al.,* 2000; DEFRA and Welsh Assembly Government, 2002). However, national policy measures have struggled to address the air quality consequences of the growth in vehicle numbers and mileage travelled. The policy challenge is illustrated by the scale of growth in the number of cars registered in the UK, which increased from 17.4m to 26.7m between 1986 and 2000. Today some 82% of journeys by mileage are made by car, demonstrating a clear need for national and local policy to address this increasing reliance on the car. The difficulty for governments, central and local, is to balance public expectations of personal mobility and accessibility with a clean atmosphere that poses no significant risk to public health (Longhurst, 1996).

METHODS

The method used in this paper is one of critical evaluation of primary and secondary sources. Refereed and grey literature is considered. In addition primary data from questionnaire surveys, telephone interviews and case studies are used. Data are presented from a number of research projects undertaken by the Air Quality Research Group, UWE (see www.uwe.ac.uk/aqm/research), and also from local authority scientific assessment reports and the AQMA Archive and database maintained by the Air Quality Research Group, on behalf of Defra and the devolved administrations.

RESULTS

Early transport policy in GB was more concerned with how to simply accommodate traffic in towns, with a report on Traffic in Towns published in 1963 (HM Government, 1963). Sustainable principles of managing and reducing traffic impacts were not then fully appreciated. Indication of an emerging sustainable transport policy came in 1997, with a Royal Commission on Environmental Pollution Report (Royal Commission on Environmental Pollution, 1997) focusing on a need to address congestion and travel behaviour (Bamford, 1998). The main points of the Report were:

- that fuel consumption of cars must be reduced;
- permitting of heavy lorries on motorways to be introduced;
- tighter EU limits for new vehicle emissions;
- fuel prices to be raised by more than 6% per year;
- local councils should be able to charge for road use;
- improved provision of access into towns and cities for cyclists and buses, and
- greater integration of transport and land-use planning.

Following the publication of the Report, the UK government published various White Papers and introduced legislation to address key transport issues, including A New

Deal for Transport: Better for everyone (DETR, 1998a), the Road Traffic Reduction Act 1997 (HM Government, 1997). The Auto-Oil programme has, over the last decade, worked to reduce emissions from vehicles, having a demonstrable impact on reducing emissions over the last decade (Longhurst *et al.*, 2002).

More recently, within urban and congested areas the attention has focused on how to reduce the number of vehicles on the roads and reducing the demand for specific road space. Proposals for local authorities to charge vehicle users for using certain roads have emerged, and central government has provided local authorities with powers to emission test vehicles on a proactive basis (Longhurst *et al.*, 2002).

Reducing emissions from road vehicles involves either specific emission control measures or traffic management measures, or indeed a combination of the two. In terms emission control measures, examples are 'end of pipe' technology (e.g. fitting particulate traps to vehicles), the use of alternative fuels (such as LPG, methane or hydrogen) or the enforcement of emissions standards (e.g. through the use of Low Emission Zones). Transport Management measures involve a whole range of public transport improvement measures, parking permitting and measures to reduce overall travel time (Mediavilla-Sahagun *et al*., 2003). At a national and international level, telematic technology is linking urban traffic control systems with air quality management systems (Elsom, 2002), to look at electronic charging, driver communication and other such strategies.

Local action to reduce traffic congestion and impact from traffic emissions in areas of impoverished air quality requires collaboration between Local Transport Planning departments, Environmental Health departments and external agencies. Beattie *et al.* (2002), reports on the lack of involvement of the Highways Agency (the agency and operator of the major trunk road network, including all motorways, in England) with respect to pollution hot spots identified by local authorities. 56% of local authorities envisaged requiring assistance from the Highways Agency to deliver their Action Plan. Action on the part of local transport planners was much more advanced however, with transport planners taking a lead in implementing action plans in some local authorities.

With many local authorities having submitted Action Plans, and many more in the process of being developed, local authorities are investigating the potential effectiveness of transport measures in delivering air quality improvements. Measures being considered are road pricing initiatives and Low Emission Zones (Carslaw and Beevers, 2002), particularly within London, and management techniques such as High Occupancy Vehicle (HOV) lanes and vehicle prioritisation schemes (Beattie *et al*, 2002).

Source apportionment is a requirement of an Action Plan, so as to ensure actions and measures are targeted at the most significant emission sources (Defra *et al*., 2002). Local authorities are also required to consider the effectiveness of potential actions and measures in terms of the air quality improvement afforded, cost-effectiveness, practicality and perceptions and wider (non-air quality) impacts such as impacts on noise, visual amenity, social equity and sustainability (Defra

and Welsh Assembly Government, 2002; NSCA, 2001). Where traffic management options, in addition to those proposed in Local Transport Plans, are proposed to improve local air quality, other local policies must be considered such that wider and unintended socio-economic and environmental impacts are minimal.
Local Transport Plans, for many local authorities, are the most effective mechanism for implementing actions to reduce air quality problems. Traffic management schemes, where priority is increased for buses, cyclists and non-car modes are local policy measures anticipated to assist with many of the pollutant hot spots. Where emissions from the motorway or trunk road network have led to localised pollution hot spots, regional and national policy, rather than local policy, is more likely to impact upon air quality. Speed controls, demand management and junction configurations all play a role in affecting the speed, composition and flow of the traffic, none of which can be influence through local government policy alone.
Traffic congestion was identified as exerting the greatest influence on the AQMA decision-making process within local authorities (Woodfield *et al.,* 2001b), and air quality improvement was considered to be a key additional benefit from finding solutions to local transport problems.

DISCUSSION

Historically, transport policy was less concerned about the potential for traffic-related emissions to impact on health and well-being and more concerned with the physical constraints imposed in towns and cities as the popularity of the motor car increased. In more recent years, the urgency to manage increasing levels of car usage, dependency and miles travelled have led to numerous policy developments, nationally and locally. Transport is widely recognised as a significant and increasing source of air pollution and impact on human health (Colville *et al.,* 2001), with the link between air quality and health underpinning the National Air Quality Strategy (DETR *et al*., 2000) and the specific pollutants for which air quality standards and objectives are set.
The success and effectiveness of Action Plans will require integration of various policy packages (Beattie *et al.,* 2002). Funding schemes for Action Planning measures to be executed are important for effective implementation and a reduction in pollutant concentrations. Much of the financial assistance is likely to be provided through a local transport bidding process the Local Transport Plan in the short-term. These work on a five-year cycle, with local authorities bidding for funding, although the longevity of the systems is in doubt. More recently, Government has speculated that action plans for air quality may not be required by all local authorities with AQMAs, with those local authorities with issues relating to local traffic being incorporated into Local Transport Plans[1].

[1] In a letter dated 22 July 2003 to all Chief Executives of local government from the Office of the Deputy Prime Minister and Local Government Association regarding 'Reducing Local Authority Plan Requirements'

Local government needs to develop air quality strategies, to ensure that all aspects of local government planning policy considers the potential impact on local air quality (Beattie *et al*., 2001).

CONCLUSION AND IMPLICATIONS

If reducing emissions from road vehicles involves either specific emission control measures or traffic management measures (as mentioned), or more likely a combination of the two, then this requires policy integration at the national and local level. In the short to medium-term, advancements and developments in vehicle and fuel technology are assisting with an overall reduction in total emissions. Future developments, by way of hydrogen fuel-cell engines and other such technical fixes, for example, will provide solutions to some of our problems. However, local policy implementation will have to be more effective to deliver solutions to address the specific pollution hot spots in the short to medium-term for delivering the air quality objectives across Great Britain. Cleaner, quieter vehicles may be in use, but until congestion is reduced and travel behaviour changes more radically, towns and cities will remain choked, noisy and potentially unhealthy environments for future generations to experience.

ACKNOWLEDGEMENTS

The authors would like to thank the UK Government and devolved administrations of the Department for Environment, Food and Rural Affairs, the Scottish Executive, National Assembly for Wales, Greater London Authority and Department of Environment Northern Ireland for use of the national air quality review and assessment archive.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

ESTIMATION OF NO_x EMISSIONS RELEASED FROM THE COGENERATION SYSTEMS IN URBAN AREA

A Sato[1, *], Y Ichikawa[1]

ABSTRACT

A Gaussian plume model was applied to compute spatial distributions of concentrations of nitrogen oxides released from cogeneration systems in urban areas of Tokyo. Calculated annual mean ground-level concentrations were 1.6 ppb, which are equivalent to approximately 3.1% of ambient air concentrations.

INDEX TERMS

Cogeneration system, Nitrogen oxides, Gaussian plume model, building effect.

INTRODUCTION

More than 3,850 cogeneration systems have been introduced as energy-saving equipment for both commercial and industrial uses since the 1980s in Japan. Cogeneration systems produce not only electric power but also heat. The heat produced when energy is generated can be used for hot water supply and air conditioning, so cogeneration systems are located near sites where the heat is required. Almost all of the cogeneration systems operate by internal combustion, such as gas turbines, gas engines and diesel engines that burn fossil fuel, thus exhaust gases from cogeneration systems contain NO_x emissions. The impacts of these emissions on air quality, by taking into account building downwash, must therefore be considered because many cogeneration systems have stacks that are lower than the height of a nearby building in urban areas. In this study, a Gaussian plume model, which includes building downwash algorithms, was used to estimate the effect of emission of pollutants from cogeneration systems on ambient air concentrations of pollutants in the metropolis of Tokyo.

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SIMULATION DETAILS

The Gaussian plume model called METI-LIS (Ministry of Economy, Trade and Industry - low rise industrial source dispersion model) was applied to calculate ground-level concentrations of nitrogen oxides released from individual cogeneration systems introduced at the center of the Tokyo metropolis. METI-LIS is a steady-state Gaussian plume model, which was developed by improving the ISC (Industrial Source Complex) model developed by U.S. EPA (1992) to predict the dispersion of hazardous air pollutants emitted from industrial establishments. In METI-LIS, dispersion parameters on the lee side of buildings were modified to predict not only maximum concentration but also annual average concentration accurately and these parameters were treated as functions of source height, aspect ratio of building and so on. Modifications of these dispersion parameters were mainly based on wind tunnel experiments of dispersion from a point source through regularly arranged identical obstacles, and the performance of the model was compared with wind tunnel measurements of actual industrial sites and several field experiments (Kouchi and Okabayashi, 2001).

Calculation domain was 22,600 m x 18,500 m on one area of the Tokyo metropolis and cell size was 500 m x 500 m^2. The number of establishments installing cogeneration systems within this calculation domain was 143, and the total electric power generation capacities were 102 MW. Source input data (e.g., location, stack parameters, and emissions factors) for emission inventories were obtained from investigations, carried out by Japan Cogeneration Center, on cogeneration systems introduced in Japan and catalogs of individual cogeneration systems. A map of the cogeneration systems introduced within the calculation domain and emission characteristics are shown in Figure 1 and Table 1, respectively.

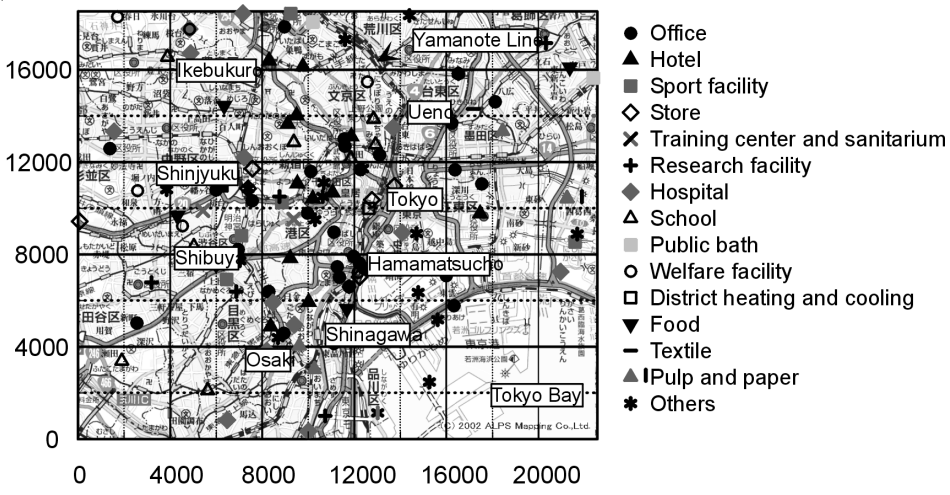

Figure 1. Map of cogeneration systems for commercial and industrial uses introduced within the calculation domain.

Table 1. Emission characteristics of cogeneration systems.

Total electric capacity (MW)	102
NO_x emissioin (Nm^3/H)	68.4
Stack height (m)	50 (office, hotel) 10 (others)
Stack inside diameter (m)	0.5
Stack gas exit temperature (K)	423

We calculated hourly concentrations of nitrogen oxides based on hourly meteorological data, which were obtained from surface meteorological observations made at both manned stations and a mesoscale observation network called AMeDAS (Automated Meteorological Data Acquisition System) operated by the Japan Meteorological Agency, and averaged the hourly concentrations over a year. We estimated only increments of nitrogen oxides emitted from cogeneration systems introduced within the calculation domain, and the background concentrations of pollutants generated by other sources including industry and traffic were not considered.

In this study, we simulated three scenarios (Table 2). S1 was the scenario in which the emission inventories, by taking account all installed cogeneration systems, were used and building downwash effects were not considered. S2 was the scenario in which the same emission inventories as those in S1 were used but building downwash effects were considered. The buildings being considered were only those for establishments installing cogeneration systems within the calculation domain and for hotels and offices with dimensions of 50 m height and 30 m width, and for other establishments with dimensions of 10 m height and 20 m width. It was assumed that all cogeneration systems were set at the center of the

Table 2. Simulation case study statistics

Scenario	S1	S2	S3
Building downwash	no	yes	
Building height (m)	-	50 (hotel, office) 10 (others)	
Building width (m)	-	30 (hotel, office) 20 (others)	
Number of cogeneration sites	143		204
Total electric capacities (MW)	102		152

roofs of the buildings. S3 was the scenario that supposed cogeneration systems spread through 10 percent of the total number of hotels, stores and hospitals within the calculation domain and source conditions of each cogeneration system and building dimensions were the same as those in S2. Total electric power generation capacities of all cogeneration systems assumed in S3 were 152 MW.

RESULTS AND DISCUSSIONS

Calculated concentrations of nitrogen oxides of the center of Tokyo (the area inside of the Yamanote Line), where many cogeneration systems are introduced, were higher than those of surrounding areas and the annual mean concentration within that area was 0.5 ppb in S1 (Figure 2(a)). In S2, which incorporated building downwash effects into S1, the concentrations were 0.6 to 2.5 ppb in most calculation points and the annual mean concentration of the center of Tokyo was 1.6 ppb (Figure 2(b)). Moreover, at the areas along the Yamanote Line, such as Shinjuku, Osaki, Hamamatsucho, and Tokyo, the concentrations of 3 to 7 ppb were obtained, and there were also areas within the calculation domain that showed concentrations higher than 10 ppb. When the concentrations of nitrogen oxides obtained from S1 and S2 were compared, those obtained from S2 that took building downwash effects into consideration were approximately 1.5 to 3.5 times those obtained from S1 in 90 percent or more of the calculation points

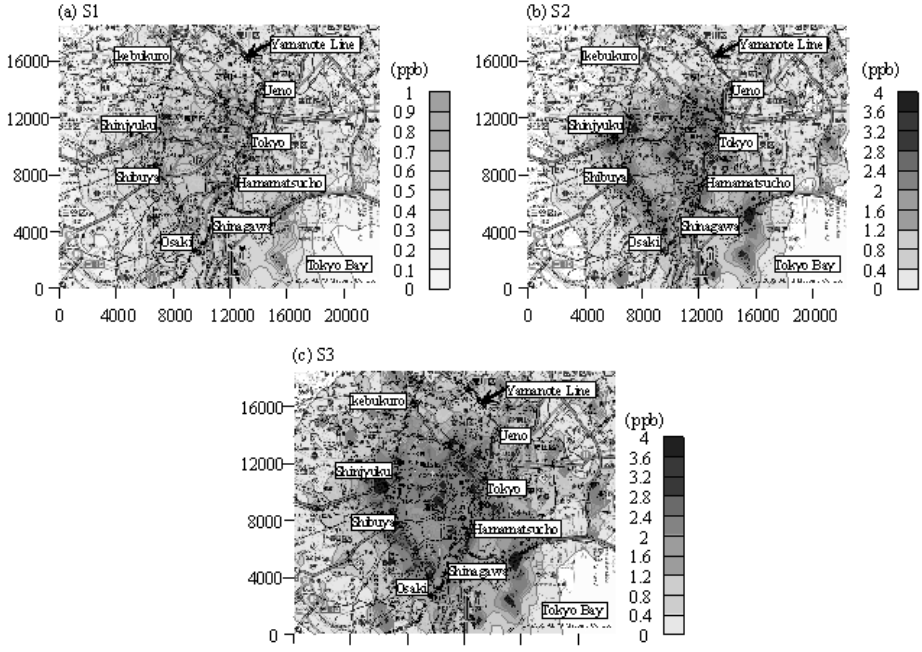

Figure 2. Contour plots of ground-level annual average concentrations of nitrogen oxides.

within the calculation domain. Because METI-LIS is based on the Gaussian plume model and does not produce estimates for a cavity recirculation region directly downwind of a building, there is a possibility that a higher concentration may be observed near the building. The annual average concentrations of nitrogen oxides measured in general environmental atmospheric measuring stations within 23 wards of Tokyo in 2000 were 51.4 ppb and the annual mean concentration calculated in S2 corresponded to 3.1% of ambient air concentrations.
In S3 that supposed cogeneration systems spread through 10 percent of the total numbers of three types of commercial establishments (hotels, stores, and hospitals) within the calculation domain, the area where calculated concentrations of nitrogen oxides showed over 2.0 ppb spread to the surroundings of the Yamanote Line. The average concentrations on the Yamanote Line inner side was 2.0 ppb, which was about 1.3 times that obtained from S2. The total power generation capacities (152 MW) of cogeneration systems assumed by S3 were about 1.5 times those of S2 (102 MW), and it turned out that the annual average concentrations also increased proportionally. Moreover, in the area distant from the center of Tokyo, there were also several places where concentrations of nitrogen oxides were higher than those of circumference areas.

CONCLUSIONS

The spatial distribution of concentrations of nitrogen oxides released from cogeneration systems actually installed in urban areas of Tokyo was calculated using a Gaussian plume model. Emission inventories were obtained from catalogs of individual cogeneration systems and annual mean ground-level concentrations were estimated. Calculated annual mean concentrations of nitrogen oxides of the center of Tokyo were 1.6 ppb, which were equivalent to approximately 3.1% of ambient air concentrations. Although it was assumed that the cogeneration systems were installed on the roof of all buildings in this study, cogeneration systems can be installed in the underground of a building and can exhaust through a lower chimney near the ground. Source conditions including stack heights and operating hours will be refined to improve prediction accuracy by taking actual conditions into consideration in a future work.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
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RECOVERY OF NOT DANGEROUS SPECIAL WASTES FOR THE PROTECTION OF THE ATMOSPHERE AND ENERGETIC SAVING

S Sciacca*, R Fallico, M Ferrante, M Campo, P Pesce and P Cutello

ABSTRACT

The recovery of not dangerous special wastes is a particular problem today, especially as regards recycling. From this viewpoint a system that uses biological sludge containing elevated concentrations of Calcium Hydroxide in order to cut down acid gases coming from the combustions of furnaces has been developed. The sludge, classified as not dangerous special waste, comes from the treatment systems of industrial waste-sewages of a petrochemical plant of Siracusa, Sicily, Italy. The technology developed for the system includes an inertization process to elevated temperatures, allows the elimination of the polluting agents contained in the sludge and subsequently the recovery of the same in the productive cycle of the existing furnace. The first phase of process consists of the dehydration treatment of sludge to 200°C, the produced material therefore comes subsequently inertized to 950°C with the reaction of calcination and transformation of the Calcium Hydroxide to quicklime, the destruction of the organic fraction and the oxidation of metallic salts. The obtained quicklime after carbonation reacts with the CO_2 and the contained SO_2 in the combustion smoke. Therefore the inert material is reusable in the productive cycle of the same furnace or as an inert substance for other products. In the cycle the recovery of the thermal energy of the smoke occurs, this allows the heating of the air flow used in the furnace section for tile drying. The smoke is washed with plain water and consequent precipitation of sulphates and salts of the metals present are also recovered. The technology used gives a valid alternative to the problems deriving from special waste disposal underground in terms of energy and production of inert material with a reduction of polluting gases with particular reference to CO_2 and SO_2. The

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reduction of CO_2 emission, in particular, places this technique in a prime position to achieve the objects of the Kyoto agreement.

INDEX TERMS

Recycling politics, biological sludge, petrochemical refuse, plant recovery, emission control.

INTRODUCTION

In South-eastern Sicily, (Priolo Sr) there exists a large petrochemical plant that, for the typology of its products, has an elevated environmental impact. The quality of the emissions and the refuse produced from such plants underlines the problem of the co-existence of such industries with the criteria of environmental safeguard and the health of the community. In particular, the petrochemical industry deals with industrial waste-waters by means of an active mud purifier. From such a process remarkable amounts of mud are obtained, classified according to the catalogue CER 19,08,12 "Mud produced from the biological treatment of industrial waste-waters varies from that at 19.08.11" and therefore is not dangerous special refuse. The chemical-physical characteristics of this mud, than permits its re-use in the furnace, is elevated containing Calcium Hydroxide -$Ca(OH)_2$) - that allows the reduction of acid gases that are formed during the combustion processes in the furnaces, as well as the chemical composition and, above all, the elevated concentration of organic substances that makes their recovery possible to be used as an alternative fuel. The reduced dimensions and residual abilities of the existing sites, the possibility to reclaim the areas currently used for the storage and the current tendencies for the recovery of otherwise wasted energies, have suggested the continuation of experimentation to reuse the refuse produced in the petrochemical industry to produce energy.

METHODS

The current technology uses a process of inertization to elevated temperatures, to remove the polluting agents contained in mud and subsequently to recover them for insertion in the productive cycle of the furnace. The peculiarity of the technology used gives a valid alternative to ones deriving from the disposal in landfills of special refuse with the recovery of energy and, thanks to the backwashing of the emissions, there is the recovery of important raw materials with the consequent reduction of emissions, especially CO_2. The reduction of the emission of CO_2 is a crucial point for the realization of a model of sustainable development and is one of the main agents responsible of the greenhouse effect. The treatment of mud includes a first phase of dehydration to 200°C in a rotating dryer maintained at a lower than atmospheric pressure. The dried material is then inertized in a fluid bed furnace

where, at 950°C, the reaction of calcination takes place with the transformation of calcium hydroxide to lime, the destruction of the organic fraction and the oxidation of metallic salts. The obtained lime is then moved to a section of carbonation for the successive reaction with the contained CO_2 in the smoke of combustion of the fluid bed such as that coming from the furnace of the baking of bricks. Such a reaction produces an inert material made up of carbonate reusable in the productive cycle of the same furnace or that can be sold. In carbonation, the thermal recovery of the smoke energy also takes place by means of an exchanger heating the used air flow in the section of lateritious drying of the furnace. The system also has one section of smoke treatment made up of: a post-combustion zone, immediately leading to the fluid bed, that guarantees turbulence of the same smoke with a speed greater than 10 m/sec and time of permanence greater than 2 sec at a max temperature of 1200°C; a Quencer where the smoke undergoes washing with plain water with the consequent precipitation of sulphates and salts of the metals that can therefore be recovered for the successive disposal as refuse. The purified smoke then passes to the carbonator, already described in the thermal section, for the reduction of carbon dioxide and subsequently to a sleeve filter for the elimination of eventual powders. The input into the atmosphere takes place by means of a stack. The emissions are within the fixed and authorized limits of the law DPR 203/88. The described technological cycle provides a good answer to the disposal in authorized landfill with the recovery of:

– used thermal energy for the drying of tiles; ~
– inert materials made up of calcium carbonate usable as additives for the clay employed in the tile and terracotta production in the precasts in cementitious conglomerates and in crock plasters; usable inert materials as street foundations and environmental recovery.

RESULTS

The furnaces of the cement works are particularly adapted to eliminate the organic compounds that are contained in the refuse, are completely degraded to the normal conditions of combustion thanks to the high temperatures reached (1200-1500 °C) for a sufficient time (more than 2 sec.) and for the presence of oxygen. Of the considered micro pollutants, there is no increase in the concentrations of NO_x, due to the optimal conditions of combustion, neither those of SO_x due to the low tenor of sulphur in the used refusal and due to the entrapment action of the fused alkaline mass, while efficiency of the powder removing system using sleeve filters in the plant does not involve a significant increase of the powder concentration. The on site storage is only temporary destination until definitive disposal ca be arranged. The recovery of the refuse, in this way, represents, for the petrochemical industry a valid solution to decrease costs. By means of the analysis that we carried out on our results in would seem that this industry would benefit from this form of refuse recycling. The process of experimented recovery

constitutes an alternative way of disposal that is more cost effective and environmentally safer with regard to traditional methods.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

ODOURS MANAGEMENT AT WASTE TREATMENT FACILITIES: ODOUR SOURCES, ODOUROUS COMPOUNDS AND CONTROL MEASURES

E Senante*, L Galtier, C Békaert, L Lambolez-Michel, V Decottignies and A Budka

ABSTRACT

This article deals with odours management at waste treatment facilities. In addition to a bibliography study, this paper is a synthesis of information collected from waste operational sites. Some typical odorous compounds from waste treatment facilities have very low detection thresholds value and can be detected by human nose at very low concentrations. Thus, management of odours is an important stake and appropriate methods have to be implemented to reach acceptable levels for surrounding people. All the methods used to reduce odours must be integrated in a global odours management plan, to encourage the reduction at the source in accordance with a continuous improvement approach of facilities management.

INDEX TERMS

Odorous compounds, detection threshold, odour sources, odour control.

INTRODUCTION

As a phenomenon directly perceptible by residents living around waste management facilities, odours represent the following major stakes: reduction of nuisance (to improve the acceptability of waste treatment facilities) and respect to regulatory odours thresholds (progressive introduction of this parameter in international regulations). Odour control must be included in a continuous improvement approach for waste management. In order to decrease this nuisance

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for the surrounding area, it is important to have a good knowledge of the sources of odours, their composition, and the critical conditions in which these odours are spread in the atmosphere. Identify, classify and characterise odours are necessary steps to implement appropriate methods to reduce odours.
Information presented in this paper deals with odour sources, odorous compounds and their characteristics (typical odours, detection threshold, etc…), and a resume of control measures.

DENTIFICATION AND CHARACTERISTICS OF ODOROUS COMPOUNDS

Odorous compounds in atmospheric emissions of waste facilities have been listed and their properties have been studied and referenced in several studies. This chapter is a synthesis of information collected in the bibliography and from internal data regarding odour composition and odorous compounds characteristics. Table 1 summarises this information in order to present a list of odorous compounds that can be found in waste atmospheric emissions, as well as their principal properties: specific odour, source or activity at the origin of odorous compounds and detection threshold values.

Detection threshold value

Table 1. Odorous compounds in waste activities emissions

Chemical	Formula	Family	Odour description	Sources	Odour detection threshold (ppm)
Hydrogen sulphide	H_2S	Sulphurous	Rotten egg	Anaerobic degradation	0.00047 - 0.0081
Methylmercaptan	CH_3SH		Rotten cabbage		0.0016
Ethylmercaptan	C_2H_5SH		Rotten cabbage		0.00076
Dimethyl sulphide	$2(CH_3)$-S		Deteriorated vegetables		0.001
Diethylsulphide	$2(C_2H_5)$-S		Etherated		0.0045 - 0.31
Dimethyldisulphide	$2(CH_3)$-2S		Putride		0.03 - 0.14
Carbon Oxysulphide	COS		Pungeant, sharp		
Carbon Disulphide	CS_2		Sweet		
Ammonia	NH_3	Nitrogenous	Pungeant, sharp	Sludge, manure, landfill gas, leachate	0.5
Methylamine	CH_3-NH_2		Fish in decomposition		3.2
Ethylamine	C_2H_5-NH_3		Pungeant		0.95
Dimethylamine	$2(CH_3)$-NH		Fish		0.34
Trimethylamine	$3(CH_3)$-N		Fish		0.00044
Methylindole (Skatole),	C_9H_8-NH		Feces		0.0008 à 0.1
Cadaverine	NH_2-$(CH_2)_5$-NH_2		Rotting meat		_
Indole	C_8H_6-NH		Faecal, nauseating		0.0006
Formaldehyde	H-CHO	Aldehyde	Acre	Landfill gas, fresh MSW	0.1-1
Acetaldehyde	CH_3-CHO		Fruit		0.05
Butyraldehyde	C_3H_7-CHO		Rancid		0.013
Propionalehyde			Rancid		0.072

Acetic acid	CH_3-COOH	Acid	Vinegar	Aerobic degradation	0.48-1
Butyric acid	C_3H_7-COOH		Butter		0.001
Valeric acid	C_4H_9-COOH		Transpiration		0.0008
Formic acid	HCOOH		Pungeant		20-49
Propionic acid	CH_3-CH_2-COOH		Pungeant		0.16
Isovaleric acid	CH_3-CH_2-$CH(CH_3)$COOH		Cheesy		
Chemical	Formula	Family	Odour description	Sources	Odour detection threshold (ppm)
Ketone	CH_3-CO-CH_3	Ketone	Sweet fruit	Landfill gas, MSW waste	0.42 - 100
Methyl ethyl ketone	CH_3-CO-C_2H_5		-		5.4
Methyl isobutyl ketone	CH_3-CO-CH_2-$CH(CH_3)_2$		-		0.68
Ethanol	CH_3-CH_2-OH	Alcohol	Sweet	Landfill gas, MSW waste	84
Buthanol	C_3H_7-CH_2-OH		-		2.6
Phenol	C_6H_5-OH		Medicinal		0.04
Cresol	C_6H_4-CH_3-OH		-		0.00028
Benzene	C_6H_6	Aromatics	Gum-like	Landfill gas (and also present in ambiance due to traffic), polluted soils	2.3 - 43
Toluene	$C_6H_5CH_3$		Naphtalenes		0.082 - 42
Xylene	$C_6H_4(CH_3)_2$		Sour		0.0051 - 5
1,3,5 Trimethylbenzene	$C_6H_3(CH_3)_3$				0.04
Ethylbenzene	$C_6H_5CH_2CH_3$		Sour		2.3
Trichlorethylen	CH-Cl-C-Cl_2	Chlorinated	Solvent	Landfill gas	28
Propyl acetate	CH_3-COO-CH_2-CH_2-CH_3	Esters	Fruit	Landfill gas, MSW waste	0.67
Butyl acetate	CH_3-COO-$(CH_2)_3$-CH_3		Rubber		0.39
Ethyl acetate	CH_3-COO-CH_2-CH_3		Grass		3.9
Limonene	$C_{10}H_{16}$	Terpenes	Lemon	Organic matter degradation	0.5
Pinene	$C_{10}H_{16}$		Forest		10

According to the European Committee for Standardisation, draft standardised method prEN 13725, the detection threshold is the concentration at which 50% of people perceive the odour (CEN, 2000).

The French National Institute for Research and Safety (INRS) has published the olfactory detection threshold values for more than 250 chemical substances (Rousselin *et al*, 1994). These threshold has been also published by Leonardos *et al* (1969) and Termonia (1999).

As it is shown in Table 1 for some families of odorous compounds, and particularly for sulphurous compounds, detection thresholds are very low. The human nose is able to detect very low concentrations, sometimes below the detection limit of measurement equipments, and high dilutions of odorous emissions are necessary to avoid nuisance generated by these compounds (e.g. depending on the site, dilution factors over 1 000 could be necessary to avoid annoyance for surrounding residents).

IDENTIFICATION OF ODOUR SOURCES AT WASTE FACILITIES

Odours sources at waste treatment facilities can be classify in two "categories"

- All the stages "around" the waste treatment process.All the operations of discharge from trucks, waste discharging handling, stocking, mixing in open air may produce odour emissions with a diffusive character.
- Treatment process itself: all the odours produced as a result of the biological degradation that may occur during the process: landfill gas, leachate etc.. These sources can be diffusive or canalised.

Then, each waste activity has its own particular odours sources in relation with their specific operations.

SYNTHESIS AND DISCUSSION ABOUT ODOUR CONTROL MEASURES

In the last years, odour control has become an important stake for waste activity sites, from a regulatory point of view, for the surrounding people and for worker comfort. In order to minimise odours nuisance and to respect odours regulatory threshold values, there are mainly two types of means to control odours :

- Reduction at the source: it concerns all the operational modifications and techniques able to avoid or reduce odour release.
- Techniques to reduce odours once they have been spread in the atmosphere.

Actions should be taken to encourage the reduction at the source as the best method to reduce odours from a technical and economical point of view. It should be noticed that all the techniques, means, and methods to reduce odours must be integrated in a global odours management plan which includes worker training and communication with neighbourhood and administration.

Control at the source

The efficiency of the "reduction at the source" techniques is difficult to assess as it is linked to site specific characteristics. However, the following techniques can be implemented to control odours at waste treatment facilities.

Collection and treatment of odorous emissions

- Aspiration and treatment of odorous canalised emissions.
- Control of the outflow of odorous air.
- Optimisation of landfill gas collection .

Reduction of the operation area and temporary capping

Reduction of the operation area reduces the exchange surface between waste and air and is the first means for reducing odours production, when surfaces are exposed to the ambient air.

Management of highly odorous wastes

The implementation of a plan to control the reception of highly odorous wastes such as sewage sludge can be very efficient. Planning deliveries according to the meteorological conditions, non reception of these especially odorous wastes on Saturday, the immediate capping after disposal are some actions that can reduce considerably odour nuisance.

Techniques to reduce odours once they have been spread in the atmosphere
Neutralising products

The term "neutralising" products includes a large variety of products that, depending on the supplier, can have different names: odours destructor, odour masking, etc… Most of these products have a similar chemical composition based on essential oils. It seems that their mechanism may vary from masking with a more pleasant odour to a real chemical neutralisation of odorous compounds. Efficiency in terms of odour reduction or chemical compounds reduction have not yet been demonstrated.

The main systems for neutralising/masking products application are on site application and air diffusion.

On site application: On site application systems are based on direct contact between the odorous source and the product. It can be spread using a "backpack" system (little volume) or with a tractor unit (large volume). This kind of application is efficient for punctual sources as the surface of application can be chosen by the operator. However, it is a non-automatic system, as such it requires worker operation to drive the truck and to diffuse the product.

Air diffusion*:* The principle of this technique is the dispersion of small droplets of product in the air. This dispersion can be done by a canon or by ramps (generally around the site). The use of a canon enables to move the system according to the evolution of the operation activities but its efficiency depends strongly on the wind velocity. Ramps include nozzles in order to disperse product in small droplets. Nozzles are generally made of stainless steel, copper or polyvinyl chloride. This system is usually coupled with an automatic switching apparatus controlled by weather conditions (wind direction and wind velocity) that enables to diffuse the product only when odour dispersion is unfavourable for surrounding residents.

Forced ventilation

The principle of this system is to dilute odorous emissions in ambient air to low concentrations using fans by accelerating natural dispersion of odours in the air. Five fans have been implemented on the same landfill site. They switch on depending on the wind velocity.The first assessment of the olfactory nuisance for surrounding people shows a significant reduction of this nuisance but several change in operation have been set up at the same time to reduce odour diffusion (landfill gas collection, covering…), thus, the real efficiency of fans is quite difficult to assess separately. Moreover, fans represent an expensive investment and operational costs in term of energy consumption.

CONCLUSION

Odorous compounds present in waste activity sites have been identified and their detection threshold value have been listed. For some typical odorous compounds, and particularly for sulphurous compounds, the detection threshold value is very low and the human nose is able to detect very low concentrations. Comparison between typical concentrations in odorous emissions and detection thresholds shows that high dilutions of these compounds are necessary to avoid neighbourhood annoyance.

There are mainly two types of means to control odours at waste treatment facilities: odours reduction at the source and reduction once the odour has spread in the atmosphere. Before using "neutralizing/masking" products, it is recommended to identify odour sources and its characteristics in order to encourage simple solutions at the source as listed in this article. Therefore, the best technical and economic solution is to encourage reduction at the source in accordance with a global plan of continuous improvement in waste management facilities.

ACKNOWLEDGEMENTS

The Authors wish to thank SITA operators and managers and for all the written or oral contribution to this document.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

HEXANE CONTAINING WASTE GASES: EXPERIMENTAL DATA AND MODELLIZATION OF A FUNGI BIOREACTOR

G Spigno*, C Pagella, MD Fumi, DM De Faveri

ABSTRACT

In some preliminary works, a biofilter reactor inoculated with *Aspergillus niger*, a filamentous fungi, was successfully applied to remove hexane from contaminated air streams. The lab-scale plant consisted in a jacketed glass column ($177x10^{-6}$ m^3) packed with expanded clay. The aim of the present work was to carry out biofiltration runs to verify the stability of the system in the long run, and select the optimal operation conditions to reach an high hexane abatement. Connecting in series two identical bioreactors, allowed for a removal efficiency of almost 90%. With an inlet flow rate of $4x10^{-3}m^3/h$, the average elimination capacity was
150 g/m^3 reactor/h and started to decrease when the pollutant load was over 300 g/m^3 reactor/h. The system was more efficient for hexane concentration of 7-8 g/m^3. Residential time distribution analysis revealed the presence of a certain degree of axial dispersion inside the reactor. Kinetic experiments carried out on the bioreactors partially filled with the packing material up to about 14 mm of height, gave a maximum specific growth rate of 0.001 h^{-1}, while other kinetic parameters were derived from full-scale runs (saturation constant K_j, maximum degradation rate EC_{max}, yield coefficient, Y_j). A steady-state mathematical model with axial dispersion was tested to describe the biofiltration process. Simulation of the set of equation showed a very good correspondence between experimental and predicted data.

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INDEX TERMS

Biofiltration, environment, mathematical modelling, packed bed, pollution, VOCs.

INTRODUCTION

Volatile organic compounds (VOCs) are common pollutants produced from a variety of industries and their emissions are facing increasingly stringent environmental regulations (Mohseni and Grant Allen, 2000). Biological techniques have attracted considerable interest in the recent years because they offer a number of advantages when compared to other traditional air pollution technologies, such as combustion, oxidation, etc. (Ottengraf, 1986; Zarook *et al.,* 1993). Biotechniques are relatively cheap because of the low investment and operational costs and can show a good operational stability; are environmental friendly (they lead to the formation of not dangerous final products) and require ambient conditions for destruction of pollutants.

Biological systems for elimination of VOCs have been explored both on the experimental and mathematical modeling levels primarily in the Netherlands by Ottengraf *et al*. (Zarook and Baltzis, 1994; Ottengraf and Diks, 1992, Van Lith, David and Marsh, 1990) followed by many researches even though still now land area requirements and lack of process control restrict the industrial use of these systems.

Since hexane, a common pollutant from many food and chemical industries is highly hydrophobic, the presence of a liquid phase, which is typical of traditional biofilters, should prevent the pollutant mass transfer from the gas phase to the biological phase. That's why a vapor phase biological reactor (VPBR) was adopted. A VPBR consists in packed bed containing a biologically active support with microorganisms immobilized on it. Waste gases are conveyed through the packed bed and then through the biofilms formed on the surfaces of the porous solid where the pollutants undergo biological degradation. Generally, biofiltration prefers naturally present microflora, but for specific compounds, specialized pure or mixed cultures can reduce the lag-phase of adaptation to the pollutant compounds. Hexane is also a linear alkane with less that 10 carbon atoms, so that it is difficult to degrade for most of the bacteria, while filamentous fungi have a well documented history of fuel tank contamination and hydrocarbons degradation. Recently, biofilters with fungi on inert packing material have been developed (Cox *et al*., 1993; Christen *et al.,* 2002; Pagella *et al.*, 2000, 2001; van Groenestijn *et al.*, 2001). These microorganisms develop aerial structures (hyphae) which provide a large surface area for a direct mass-transfer from gas to biofilm. Pagella *et al.* (2001) had isolated a strain of *Aspergillus niger* from hydrocarbon contaminated soils (near gasoline station) which was able to growth on hexane as the sole carbon source. A lab-scale bioreactor had been set up and some first

trials could assess the feasibility of the process. In the present research further experiments were carried out to verify the stability in the long run of the system, to optimize the process and to find out a mathematical model able to correctly describe the process and predict the reactor performance.

METHODS

The lab-scale plant consisted in a glass jacketed column (or two connected in series), height 40 mm, internal ∅ 25 mm; packed with granular expanded clay from 4 mm from the bottom upwards. The gas stream was artificially created by mixing two flows, regulated by flowmeters: the first flow passing through an humidifier and the second made bubbling into liquid hexane at 30°C. All the plant worked at a constant temperature of 30°C. Hexane concentration in the inlet and outlet gas was monitored by a gaschromatograph (Perkin-Elmer 8500) (Pagella *et al.,* 2001). After inoculation with a spore suspension (0.17 g and 0.47 g for the 1st and 2nd column respectively) in malt extract broth, containing an additional carbon source, MEB was periodically fed to the biomass. The system worked for two months, with an inlet flow rate of $4x10^{-3}$ m^3/h, hexane concentration varying between 2 and 20 g/m^3.
For kinetic experiments the reactor was packed up to 14 mm of height so that uniform conditions could be assumed for almost all the biomass, flow rate $4x10^{-3}$ m^3/h, inlet concentration 6-7 g/m^3 (the optimal condition from the above described experiment). Biomass development was measured by dry weight of all the reactor support, after 20, 35 and 50 days. For RTD analysis the same bioreactor was employed with clay damped only with sterilized water. 1 ml of hexane (selected as the tracer) was injected since it corresponded to a maximum pollutant concentreation in the column of 7 g/m^3.

RESULTS

In the full scale biofiltration run, the 2nd column was connected after 12 days, and at 1 month the air and nutrient supply was interrupted for 2 weeks to simulate any drastic possible interruption. After this period the fungi kept on degrading hexane without any efficiency decrease. The great number of spores always observed under scanning electron microscope (not reported data) could explain this great capacity of biomass to stay latent even for long periods The removal efficiency (RE) increased along the time to demonstrate a progressive biomass adaptation to the new and adverse environment, while, globally, it tended to decrease when the hexane load (g/m^3 reactor/h) was increased (Figure 1).
RE in the plant considered as the sum of two reactors could reach the 90%, while considering the elimination capacity (EC), g-hexane/m^3 reactor/h, it appeared to be higher for the 1st column than the global system, obviously due to the higher hexane inlet concentration ($C_{jG(0)}$).

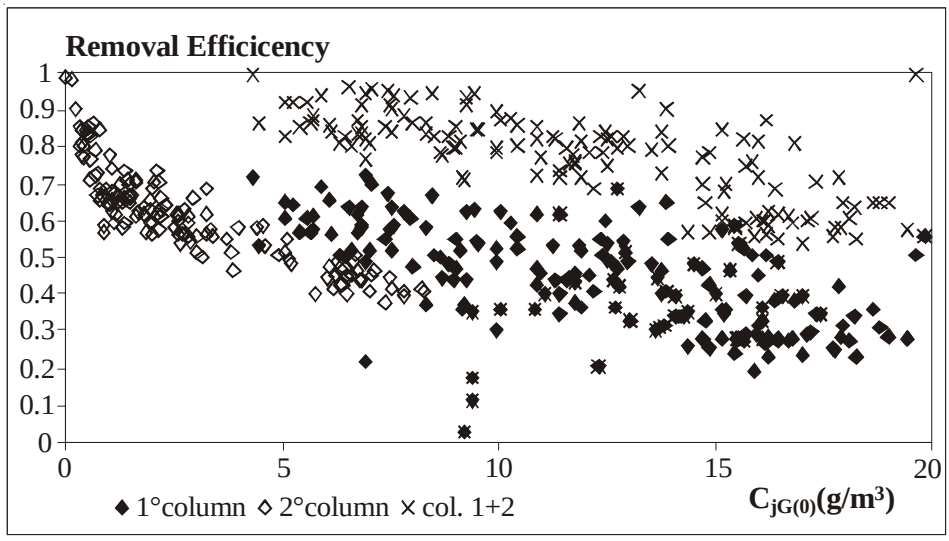

Figure 1. Removal efficiency as a function of inlet hexane concentration for the single columns and the sum of them.

The concentration/time of hexane leaving the reactor after injection of 1 μl of hexane gave a not-symmetrical curve which means the presence of a certain degree of axial dispersion. According to the dispersion model (Levenspiel, 1999), the exit age distribution function E_θ (in which time is measured in terms of mean residence time *t*/*mean time of passage*, was constructed and the dispersion coefficient *D* was evaluated from the variance of this curve (σ_θ^2) as $0.655 \cdot 10^{-4}$ m^2/s.

$$\sigma_\theta^2 = \frac{\sigma^2}{t_m^2} = 2\left(\frac{D}{U_g H}\right) - 2\left(\frac{D}{U_g H}\right)^2 \left[1 - e^{-U_g H / D}\right] \tag{1}$$

with U_g superficial gas velocity (m/h) and *H* reactor height (m).

Biomass development was evaluated in reduced height reactor, since the smaller length of the biofilters allows for a low contaminant removal efficiency that will keep the VOC concentrations at the inlet and at the outlet of the biofilter similar in magnitude, thus ensuring a somewhat uniform biomass growth along the bed (Alonso *et al.,* 2000).

Data of biomass increase vs time were interpolated by the Gompertz equation modified by Zwietering (1990) which is generally used to describe microbial growth:

$$y = B \exp\left\{-\exp\left[\frac{\mu^* e}{B}(\lambda - t) + 1\right]\right\} \tag{2}$$

with B asymptote value, μ^* maximum specific growth rate (h^{-1}), λ lag time (h). It was obtained $B = 0.51$, $\mu^* = 0.001\ h^{-1}$, $\lambda = 116$ h, parameters that confirm the slow fungal growth in the bioreactor.

To interpret experimental results, a mathematical model assuming a steady-state process and axial dispersion of the pollutant was developed, taking many simplifying assumptions (Zarook, Shaikh and Azam, 1998), obtaining the following equations for mass balance in the gas-phase (eq. 3), in the biofilm (eq. 5) and their relative boundary conditions (eq. 4, 6).

$$D\nu \frac{\partial^2 C_{jG}}{\partial h^2} - U_g \frac{\partial C_{jG}}{\partial h} + D_{ej}\alpha A \frac{\partial C_{jf}}{\partial \theta}_{|\theta=0} = 0 \tag{3}$$

$$at \quad h=0 \quad \frac{D\nu}{U_g}\frac{\partial C_{jG}}{\partial h} = C_{jG} - C_{jG(0)}; \quad at \quad h=1 \quad \frac{\partial C_{jG}}{\partial h} = 0 \tag{4}$$

$$D_{ej}\frac{\partial^2 C_{jf}}{\partial \theta^2} - \frac{X_f}{Y_j}\left(\frac{\mu^* C_{jf}}{K_j + C_{jf}}\right) - X_f m_S = 0 \tag{5}$$

$$for\ 0 \le h \le H\ and\ \theta = 0\ C_{jf} = \frac{C_{jG}}{m_j}; \quad for\ 0 \le h \le H\ and\ \theta = \delta\ \frac{\partial C_{jf}}{\partial \theta}_{|\theta=\delta} = 0 \tag{6}$$

with υ the bed porosity; K_j the saturation constant (g/m^3); D_{ej} the effective diffusion coefficient of pollutant j in the biolayer (m^2/h); α the fraction of support surface A per unit of volume (m^{-1}) covered by the biofilm; δ the effective biolayer thickness (m); C_{jf} the concentration of pollutant at a position θ in the biolayer, X_f the biofilm density (g-dry cells/m^3 biofilm); Y_j the yield coefficient (g-biomass/g-pollutant); m_S the maintenance coefficient (g-pollutant/g-biomass/h).

The above set of equation was expressed in dimensionless terms and solved using the simulation software gProms (v. 2.1.1).

The kinetic parameters were partly derived from full-scale biofiltration runs. Experimental data of EC as a function of inlet hexane concentration, were interpreted according to the general and commonly employed Monod kinetic model obtaining for the plant consisting of two reactors:

$K_j = 16\ g/m^3$ and $EC_{max} = 290$ *g-hexane/m^{3}reactor/h.*

Considering the total biomass present in the columns at the end of the experiment (biomass density 14.6 kg/m^3 reactor), from the EC_{max} it resulted a Y_j of 0.05 g-biomass/g-hexane.

Taking into account the void volume of the packed bed and the numerous SEM observations taken of the support particles inoculated by the biomass (not reported data) the following values for the model parameters were used to solve the equations:

$\alpha = 0.55$; $V_{biomass} = 1 \cdot 10^{-5}$ m^3; active biomass in degrading hexane (mycelium) = 3 g; $\delta = 5\ \mu$m.

The term $X_f \mu^* / Y_j$ in eq. 5 was substituted with $EC_{max} V_{reactor} / V_{biomass}$ and $\alpha \cdot A$ with $\alpha \cdot V_{biomass}$.

The maintenance coefficient was set very low at 0.0001 h^{-1}, D_{ej} was calculated from theoretical relationships as $2.17 \cdot 10^{-9}$ m^2/s (Spigno *et al.,* 2003), while a partition coefficient m_j of 0.2 was derived during the model simulation through a trial and error approach.

The correspondence between experimental concentration profiles of hexane along the reactor height was very good (Figure 2).

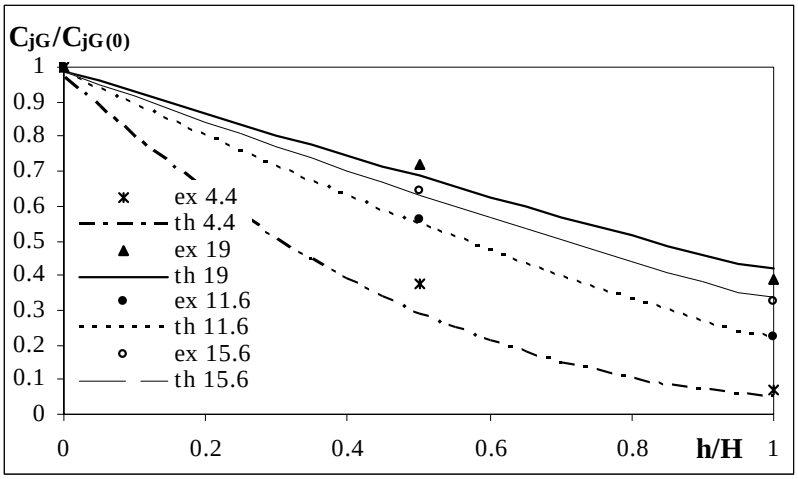

Figure 2. Hexane concentration profiles along the biofilter for different pollutant load (ex 4.4-19 g/m^3) and their comparison with model predicted profiles (th 4.4-19 g/m^3)

CONCLUSIONS

The present research revealed a good stability over a period of two months of a biofilter packed with expanded clay and inoculated with *Aspergillus niger.* Hexane could be removed from waste gas with an efficieny higher than 90% when two identical reactors were connected in series. The system resulted more efficient for concentration between 6 and 8 g hexane/m^3 air. It was demonstrated how it is quite easy derive kinetic and fluid dynamic parameters from experimental results, even with a reactor containing fungi which are, generally, more difficult to manage

than bacteria. It was also ahown that biofiltration, even though a very complex process, can be described with good accuracy using quite simplified mathematical models. The major limit of these models is that many parameters are difficult to be accurately determined and, because of the great intrinsic variability in microrganisms performances, some of them should be calculated case by case.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

INTEGRATED ENVIRONMENTAL MANAGEMENT SYSTEMS BASED ON MEASUREMENT TECHNIQUES

F Sporenberg[1, *], S Suder[1]

ABSTRACT

The production of materials for the textile building industry leads to gaseous emissions originating from coating products. For the exhaust air cleaning a combustion system with integrated heat recovery (thermo reactor) can be recommended. By the additional introduction of an operational energy- and exhaust air- management system based on specific measurement techniques an obvious positive contribution to environmental protection and energy saving can be made.

INDEX TERMS

Environmental management, Textile industry, Thermo reactor, Energy saving.

COATING PROCESSES IN THE TEXTILE INDUSTRY

At the production of fluorpolymer glass textures with textile coating units the texture construction, the coating arrangement and the fluorpolymerdispersion plays an important role. For the coating process on the basis of fluorpolymers as ground texture no synthetic fibers, but glass textures are applied with a necessary sintering temperature of 350 °C.
The specific coating is put on by means of a dispersion. The fluorpolymer part is 50 - 60%, the wetting agent part is 3 - 10%. The wetting agent part is necessary, on the one hand to prevent the water from a settling of the fluorpolymer particles, on the other hand to make a repeated putting on of fluorpolymer coats possible.

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GAS PURIFYING SYSTEM

At the drying of fluorpolymer glass textures the exhaust air is led by specific suction devices to a regenerative thermal afterburning unit (Thermo Reactor). An operational energy- and exhaust air-management system was introduced, so it was possible to reduce the operational costs caused by the energetic use remarkably.

In Figure 1 and 2 the concept of an energy- and exhaust air-management system are shown.

For the combustion of the organic hydrocarbon compounds from the production process a regenerative afterburning unit by means of a thermo reactor (Figure 3 and 4) was installed.

Characteristic for this type of reactor is beneath the optimal processing technology an integrated heat recovery, so the operational costs (natural gas) can be remarkably reduced compared to conventional combustion units.

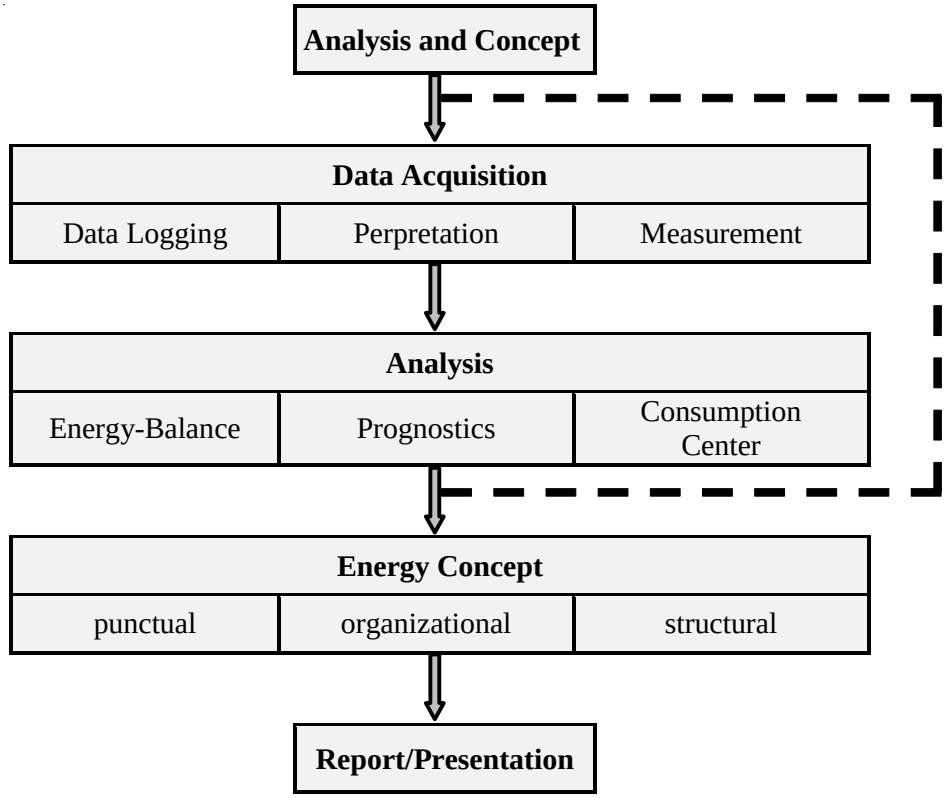


Figure 1. Energy-Management-System

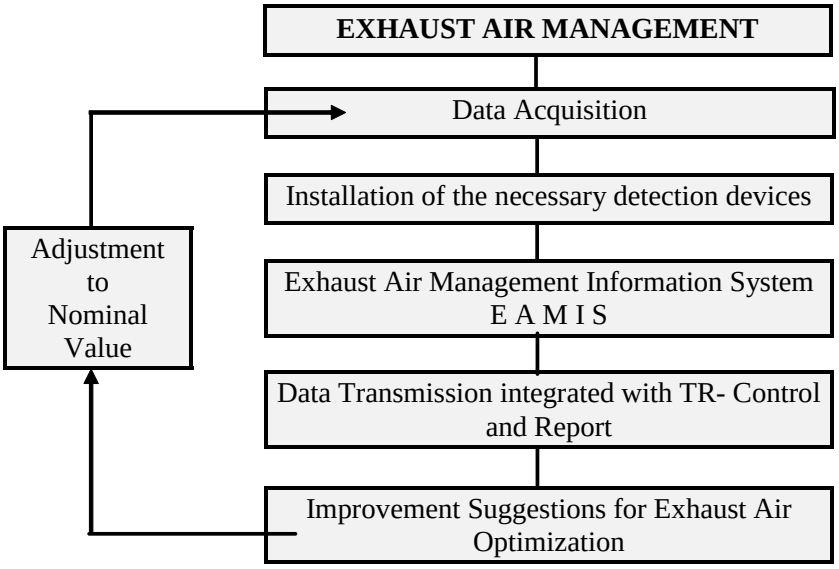


Figure 2. Exhaust Air Management

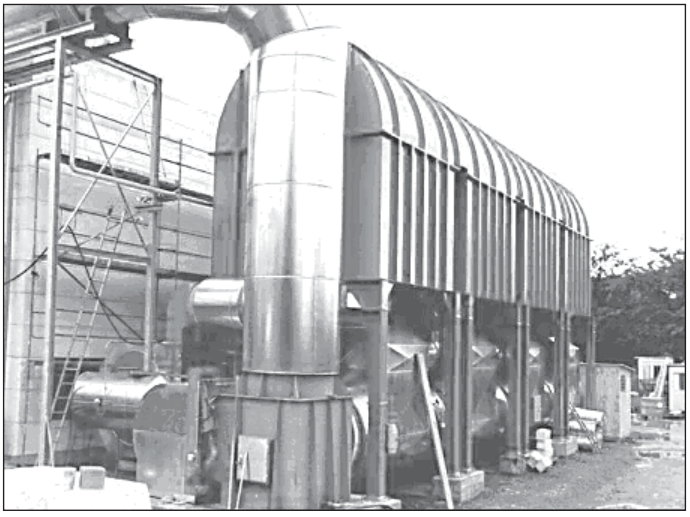
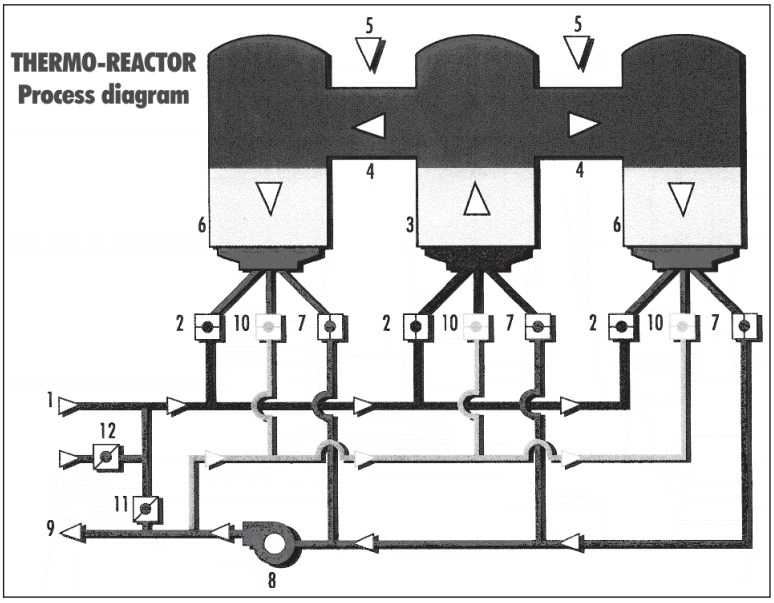


Figure 3. Construction of the Thermo-Reactor



1. Exhaust air inlet
2. Exhaust air inlet valves
3. Heat exchanger mass (oxidation phase)
4. Oxidation chambers
5. Additional burner
6. Heat exchanger mass (energy storage)
7. Pure gas outlet valves
8. Pure gas fan
9. Pure gas to stack
10. Flush air valves
11. Recirculation valve
12. Start-up valve

Figure 4. Thermo-Reactor - The Regenerative Exhaust Air Purification

ENERGY – AND EXHAUST AIR-MANAGEMENT SYSTEM

Within the scope of the technical measures at the production devices it was necessary to fit out all machines with continuous volume flow- and temperature-observation, current meter, as well as a lower explosion limit-device based on infrared measurement.

With corresponding electrical outputs on the basis of mA/mV the specific data is determined, digitalized and given onto a Bus-system.

Through the installation of a visualisation program the operational costs of the different operation units (electricity, natural gas etc.), as well as the specific exhaust air cleaning costs per time period can be seen.

The advantage is that a direct access onto each production machine unit with regard to productivity is possible.

Generally the maximum capacity leading to hightened operation costs can be avoided by means of special product plans.

As example in Figure 5 and 6 the electricity-, resp. natural gas-costs for different operation units like TNV, thermo reactor or two textile coating units are shown.

The total costs for natural gas and electrical energy are shown in Figure 7.

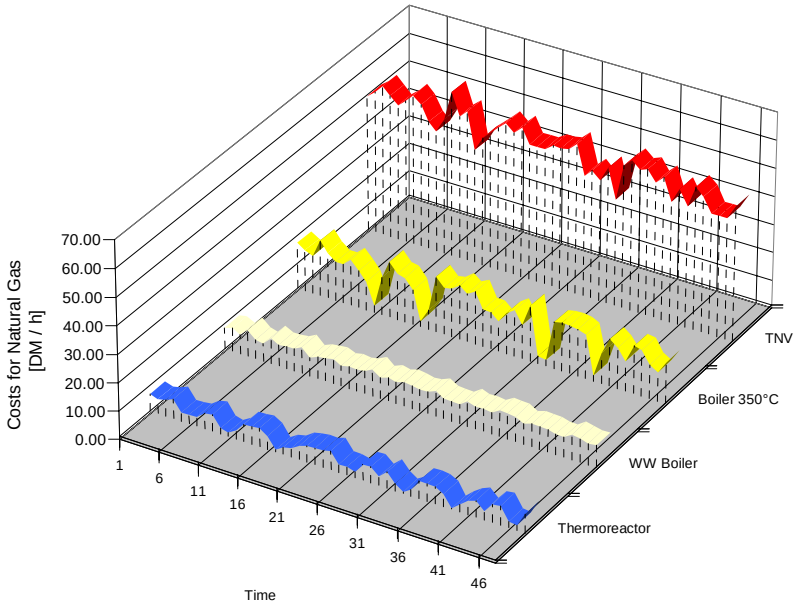


Figure 5. Natural Gas Costs for the Single Operation Units

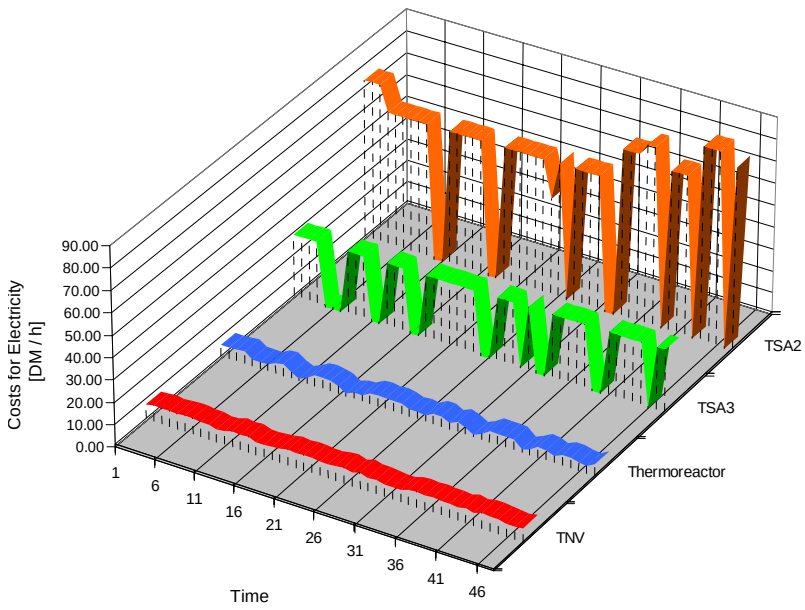


Figure 6. Electricity Costs for the Single Operation Units

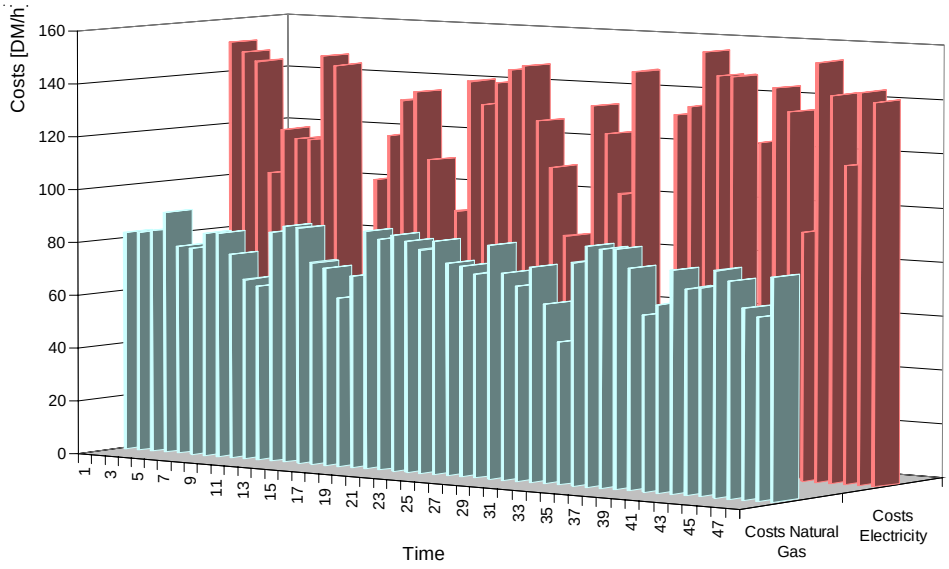


Figure 7. Total Costs for Natural Gas and Electricity

The systematical registration of the demand of the single operation units led to resulting exhaust air cleaning costs and can be directly related to the production. The specific exhaust air removal per product (PVC, PTFE) can be integrated into the actual manufacturing operational costs.

SUMMARY

The positive environmental measurement system is summarized in Tabele 1:

ENVIRONMENTAL MEASURE	*INVESTMENT*	*ENVIRONMENTAL EFFECT*
Air Cleaning	Thermo Reactor with Warm Water Heat Exchanger	According to 'TA-Luft' CO 100 mg/m^3 NO_x 190 mg/m^3 C_{org} 20 mg/m^3
Saving of Primary Energy with Heat Utilization Demand (4.BimSchV)		Saving of Natural Gas: 450.000 m^3 Natural Gas/Heat Period CO_2-Reduction 1200 t/Heat Period
Energy Management System	- Exhaust Air Control at Textile Coating Units combined with Frequency Transformer - Continuous Volume low Control at Machines according to Production	30 - 40% Saving of Electrical Energy

It can be recognized that by the introduction of an energy-/exhaust air-management system an obvious improvement of the environmental effects in regard to today's permitted values ("TA-Luft"), as well as a considerable saving of primary energy (natural gas) could be reached.

The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

GREENHOUSE GASES EMISSION FROM FERTILIZER PRODUCTION

G Avirović*, A Vešligaj and M Maren

ABSTRACT

"The fertilizer industry produces annually about 100 kg of fertilizer products for each man, woman and child living on our planet and is indirectly feeding nearly half of them – indeed a large and important activity."(Lie, 1997). At the same time the pollution and other environmental impacts arising from the fertilizer operations can also cause substantial local damage and contribute to global environmental impacts (e.g. greenhouse effect). Petrokemija,d.d. is the only fertilizer, carbon black and bentonite clay manufacturer in Croatia. The processes used in fertilizer production are multi-point sources of gaseous and solid air pollutants. The main pollutants in the air emission are ammonia (NH_3), nitric oxide (NO_x), sulfuric dioxide (SO_2), fluorides (F), particles of raw materials and finished products as well as greenhouse gases (GHGs). The most important GHGs are carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O). Carbon dioxide is emitted mainly from ammonia production and N_2O from nitric acid production. Nitric acid and ammonia are used as a raw materials in the manufacture of fertilizers. Although e.g. CO_2 emission from fertilizer is only about 2% of the emitted quantity resulting from human activities (IFA, 1998), the fertilizer industry will be put under strong pressure, and possible regulations will be passed to decrease its emission of GHGs. In this paper the inventory of direct greenhouse gases of Petrokemija fertilizer production is presented as well as the program containing measures to reduce its amounts.

INDEX TERMS

Fertilizer production, emission, greenhouse gases, inventory

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INTRODUCTION

Greenhouse gases (GHGs) are atmospheric compounds that store energy, thus influencing the climate. The most important GHGs are carbon dioxide (CO_2), nitrous oxide (N_2O) and methane (CH_4). The world community, concerned about the harmful effects of global climate change reached a landmark agreement at the United Nations Conference on Environmental and Development (UNCED) held in Rio De Janeiro in 1992 (The UN Framework Convention Climate Change). At the Kyoto Conference held in 1997 many nations of the world agreed to reduce greenhouse gas emissions. According to the Convention and the ensuing Kyoto Protocol Croatia is committed to reduce GHGs emission by at least five per cent below the base year level by the period 2008-2012 (Prvo nacionalno izvješće Republike Hrvatske prema Okvirnoj konferenciji Ujedinjenih naroda o promjeni klime, 2001).

The processes involved in the production of mineral fertilizers give off emissions containing pollutants that may contribute to environmental problems, both globally (e.g. greenhouse effect) and locally (e.g. acid rain, acidification, eutrophication, chemical mist, etc.). Generally, fertilizer production is responsible for approximately 1.2% of the total emission of the greenhouse gases in the world (Kongshaung, 1998). In West Europe fertilizer industry emits 1.8% of the CO_2/N_2O emissions (Kongshaung, 1998). The contribution of the different sectors and of the different gases to total GHGs emissions in Croatia are presented in Figures 1 and 2 (Prvo nacionalno izvješće Republike Hrvatske prema Okvirnoj konferenciji Ujedinjenih naroda o promjeni klime, 2001).

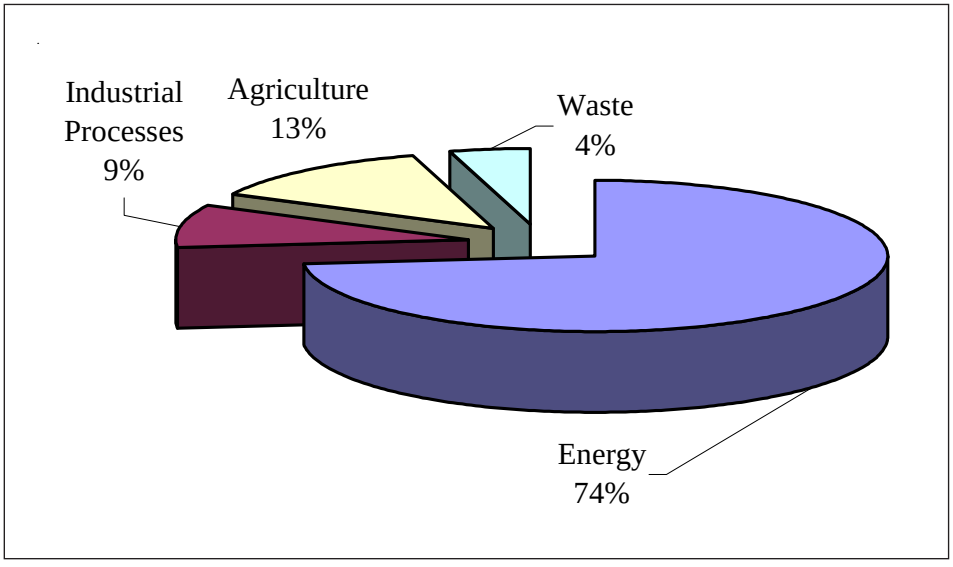

Figure 1. Emissions of GHG in 1995 by sectors in Croatia

Regarding the contribution of the different source categories (sectors) it can be seen that the energy is by far the largest source of emissions followed by agriculture and industrial processes. Petrokemija d.d. is the only fertilizer, carbon black and bentonite clay manufacturer in Croatia. The contribution of the GHGs emitters of Petrokemija's fertilizer processes (e.g. nitric acid and ammonia production) to total GHGs emissions in Croatia in 1995 was approx. 5%. Although the reduction of GHGs emissions from fertilizer production is not required by law, a possible future tax in addition to everything else motivated Petrokemija d.d. to study new methods and technologies to decrease its emissions of GHGs.

GREENHOUSE GASES EMISSION OF PETROKEMIJA'S FERTILIZER PRODUCTION

Petrokemija d.d. fertilizer production with 1.2 million tons per year capacity consists of several intermediate production plants (e.g. ammonia, nitric acid, sulfuric acid and phosphoric acid), finished products and two energy production plants. The main sources of GHGs emission in fertilizer production in addition to energy production plants are ammonia and nitric acid production.

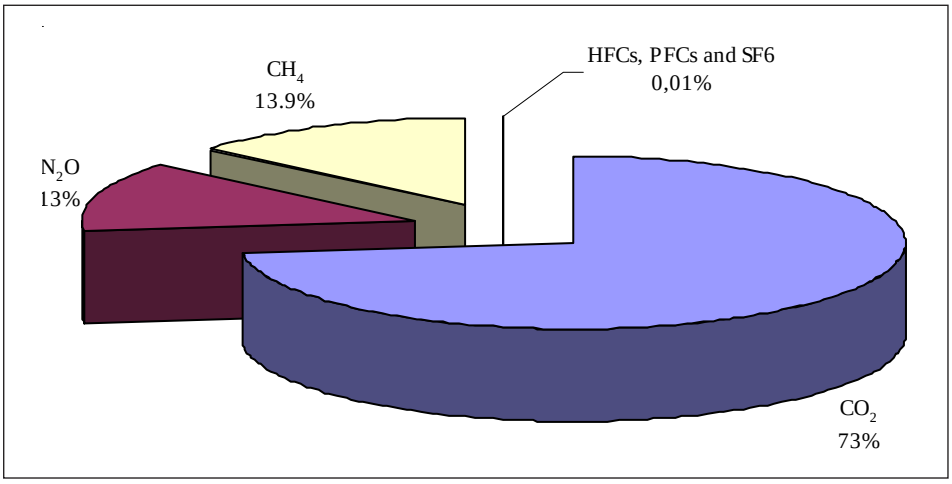

Figure 2. Emissions of GHGs in 1995 by gases in Croatia

Carbon dioxide emissions from ammonia production

In Petrokemija d.d. company ammonia is produced by a catalytic assisted reaction of natural gas (e.g. steam reforming process). Methane in natural gas feed is converted to hydrogen by way of reforming according to reaction:

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

$$CH_4 + air \rightarrow CO + 2H_2 + N_2$$

$$CO + H_2O \rightarrow CO_2 + H_2$$

Carbon dioxide is removed from the product hydrogen through caustic and amine absorption with final polishing by a methanation reaction. The purified hydrogen/ nitrogen streams converted to ammonia:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

Some of ammonia product is further converted to urea by reaction with carbon dioxide:

$$CO_2 + 2NH_3 \rightarrow NH_4CO_2NH_2 \rightarrow NH_2CONH_2 + H_2O$$

Production of urea is always linked to an ammonia plant due to the consumption of CO_2 (0,733 t CO_2 / t urea or 1,6 t CO2 / t N). In a Life Cycle Analysis for fertilizer it is not correct to include this reduced emission, as the CO_2 will be released during usage of the fertilizer (Kongshaug, 1998).

We estimated an emission factor of emitted CO_2 of 1,3 t CO_2 / t NH_3 in 2002 (1,5 t CO_2/ t NH_3, IPPC,1997). The total CO_2 formation in Petrokemija's ammonia plant in 2002 compared with data published by other authors are shown in Table 1 (Kongshaug, 1998).

Table 1. Emission of CO_2 from ammonia plants

	Total CO_2 formation in ammonia plant t CO_2/ t N	*Energy GJ / t N*
Modern Ammonia Plant	2,1	37,3
European Ammonia Plants	2,2	39
Ammonia plant 30 years ago	2,7(net)	47
Petrokemija's Ammonia Plant	2,4	42 (project value for natural gas)

Nitrous oxide emissions from nitric acid production

During the manufacturing of nitric acid, a non-negligible quantity of nitrous oxide is produced. The main reactions leading to the industrial production of nitric acid are:

1-catalytic combustion of ammonia with air:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

2-Oxidation and absorption of nitrous gases:

$$2NO + O_2 \rightarrow 2NO_2$$

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

Simultaneously nitrous oxide, nitrogen and water are formed during stage 1. in accordance with the following equations:

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$$

$$4NH_3 + 4O_2 \rightarrow 2N_2O + 6H_2O$$

The main parameters influencing the formation of N_2O are pressure and temperature of reactions, type and age of the catalyst, distribution and homogeneity of the air-ammonia mix, and configuration of the burner (Pottier, 2001).

Although nitrous oxide is not toxic, it has significant greenhouse qualities. In effect the life span of N_2O is long (more than 100 years) and its global warming capacity is 310 times higher than that of CO_2 for an equivalent weight (Pottier, 2001).

Emissions of N_2O from European nitric acid plants (Pottier, 2001) and Petrokemija's plants (I and II) are shown in Table 2.

Table 2. Emission of N_2O from nitric acid plants

	kg N_2O / t HNO_3 100%	*t $CO_{2\,(eq)}$ / t HNO_3 100%*
European nitric acid plants (average of various type of plant)	7	2,2
Medium pressure plants	5-9	1,5-2,8
Petrokemija's nitric acid plants I) II)	 7,5* 7,8*	 2,3 2,4

* measurement results in 1999

We adopted emissions factor estimated in 1999 for inventory.

Methane emissions from fertilizer production

The major sources of CH_4 are fugitive emissions from natural gas containing equipment and unburned methane from flare and it is minor.

Trend of GHGs emissions of Petrokemija's fertilizer production in 1998-2002

Petrokemija's fertilizer production has been engaged for a long time in monitoring and reporting its own emissions of GHGs. We provided a data of our GHGs emission in 1990-1995 for First National Communication in response to its Commitments to UNFCCC. Trend of emissions of total $CO_{2(eq)}$ emissions from Petrokemija's fertilizer production including emissions from energy plant in 1998-2002 is shown in Figure 3. It may be noted that yearly emission of total CO_2(eq) did not change significantly during the period 1998-2002.

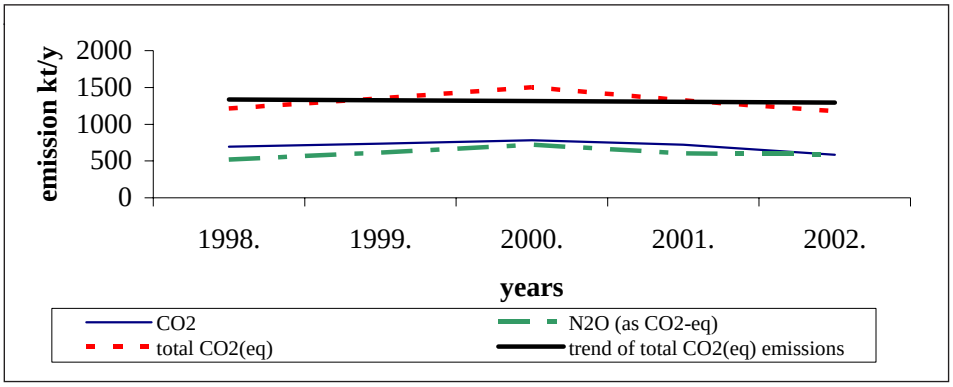

Figure 3. Trend of GHGs emissions from Petrokemija's fertilizer production in 1998-2002

Petrokemija's program of technological improvements to decrease GHGs emissions

Fertilizer industry must solve a number of operational problems and develop new technology on its way towards sustainability. Petrokemija d.d. analyzed its situation and focus on work towards energy savings and reduction of GHGs emissions from ammonia and nitric acid plants.

As shown in the Table 1 significant improvement in ammonia process design reduced the total CO_2 emission. By renewing the plants with modern technology it should theoretically be possible to reduce total energy content by 37% (Kongshaug, 1998).

Petrokemija plans to make a minor revamps of ammonia plant together with improvement of the energy efficiency. A reduction of energy consumption will also reduce the CO_2 emission.

A variety of methods for reducing nitrous oxide from nitric acid plants have been proposed. They may be classified as (Maurer and Groves, 2001):

a) Primary measures (The formation of N_2O is suppressed during the oxidation of ammonia.)
b) Secondary measures (N_2O is removed by decomposition or reduction from the gas stream between the catalyst gauzes and the inlet of the absorption column.)
c) Tertiary measures (N_2O can be removed from tail gas either by direct catalytic decomposition or reduction, generally using a hydrocarbon or ammonia.)

There are many advantages and disadvantages for the different N_2O mitigation options. Currently no reasonably-priced, proven technology exists for reducing N_2O emissions from nitric acid plants. The most promising techniques seem to be catalytic destruction in the ammonia combustion reactor and medium temperature tail gas catalytic destruction. But performances and cost must be confirmed (Pottier, 2001).

DISCUSSION

The emission of GHGs is truly becoming "a hot" issue. The fertilizer industry will be put under strong pressure and possible future regulations to decrease its emissions of GHGs.

The major sources of CO_2 are combustion of natural gas and fuel oil for steam and electricity and by-product CO_2 from ammonia production. Carbon dioxide emissions are decreased by the amount of CO_2 used in urea production. Besides that fertilizers play a positive role in CO_2 assimilation by improving the fixation of CO_2 by crops hence contributing to carbon sequestration. Nitrogen helps to stabilize carbon in soil organic matter: a kilogram of nitrogen is required for every 10 to 12 kg of carbon sequestered.

We try to be involved in further research, extension activities and programs for reducing emission of nitrous oxide.

We think all these facts have to be taken into consideration when we talk about fertilizer production and GHGs emission.

CONCLUSION AND IMPLICATIONS

Fertilizers have been important inputs to food production for a long time and will be even more so in the future.

Production of fertilizers can have an impact on the environment through emissions of CO_2, N_2O and other gases. Carbon dioxide, nitrous oxide and some other gases (e.g. NH_3, NO_x, SO_2, F) contribute to the greenhouse effect. On the other hand fertilizer industry has opportunities to help mitigate CO_2 emissions.

"The industry thus has a number of options to choose from, some of which have been demonstrated at full scale, others which at least appear promising. To what extent the industry adopts them in advance of the Kyoto greenhouse gas commitment depends not only on the rate of technical development but also on the commercial prospects for the ammonium fertilizer industry." (Nitrogen & Methanol No. 259, 2002).

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EMISSION MEASUREMENTS FROM CREMATION FURNACE

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ABSTRACT

The paper deals with a rather unusual topic but we believe that it is justified from the point of view of environment protection and ethical conduct.
Cremation furnaces are stationary facilities that emit harmful substances into the atmosphere. This has been confirmed by the recent legal act passed in Croatia, containing amendments to the Act on limit values of harmful substance emission from stationary sources, N.N. 105/02. Cremation facilities belong to this category of harmful substance emitters.
Measurements are used to determine the type and amount of pollutants in the flue gas, along with their GVE (emission limit value). The legal acts list the primary and secondary steps to be taken to decrease the emission as well as the times and methods used for individual chemical compounds.
In 2002, a new 720 kW furnace, type G-VL-A manufactured by TABO from Stockholm, Sweden, was installed at Zagreb Crematory.
The paper presents the situation in the cremation system up to now, the problems and proposed answers to these problems concerning the type and processing of measured harmful ingredients in the flue gas, and criteria for the assessment of these releases.
Furthermore, the paper describes the system and the prescribed operating technology of the newly installed furnace, the improvements in relation to the existing furnaces and the results of harmful substance emission measurements as well as their evaluation in keeping with the prescribed limit values of emissions.

INDEX TERMS

Cremation furnace, emission measurement

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INTRODUCTION

Zagreb City Cemeteries have had a crematory at the "Mirogoj" cemetery since 1986. Until recently there were two furnaces. Late last year a new furnace was installed and one of the old ones has become dysfunctional due to a fault. The crematory is operational for an annual average of about 5000 hours.

Croatia has a legal act prescribing a systematic measuring of emissions of harmful substances into the air from stationary sources as well as an obligatory reporting of the type and amount of pollution in the so-called emission register (House of Representatives of the Parliament of the Republic of Croatia, 1995). Clearly, furnaces belong to the group of stationary sources and so their proprietor is under obligation to respect the legal acts on measuring of emissions and to report them in the emissions register. With the initial measurements of harmful substance emissions it became apparent that the choice of the GVE criterion was quite inadequate for this type of stationary source. The crematory proprietor requested an opinion from the competent Ministry. The Ministry recognized the incongruity and recommended the acceptable GVE based on experience and values adopted by other countries. Finally, late last year Croatia passed a Regulation (The Government of the Republic of Croatia, 2002) covering, among other things, crematory facilities, types of pollutants in the flue gases that are to be determined by measurement, their GVE, the primary and secondary measures for reducing emissions and the frequency and measurement methods for individual compounds. This paper compares the measurement results for the emission of harmful substances from furnace with the values guaranteed by the manufacturer, as well as the criteria required by the regulations. The paper presents the results of continuous monitoring of the emissions of CO, NO_2 and O_2 in the course of one working day with four cremations taking place.

STATIONARY SOURCE- CREMATION FURNACE

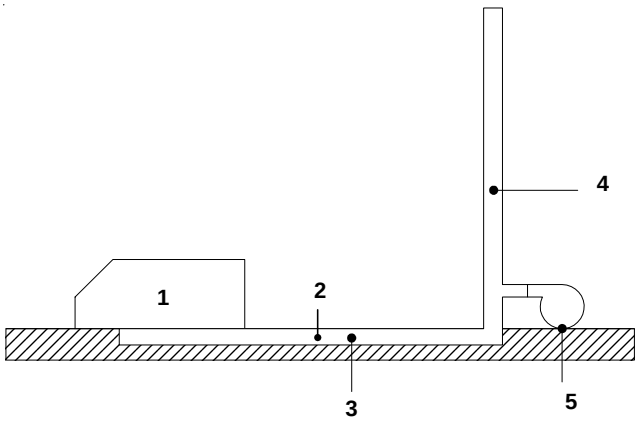
Since the beginning of its operation the crematory had two furnaces. From the very beginning care was taken to protect the environment, i.e. the air, by way of equipment installed for continuous monitoring of emissions (CO, NO_X, SO_2, CH_4) into the air. However, the system has been out of operation for more than six years. Only taking periodical measurements have monitored the emissions of harmful substances in the past five years.

Last year the reconstruction of the crematory was begun. A new furnace purchased from the same manufacturer was installed. Among the required features was the most highly placed request for a furnace that would save energy and be environment friendly. To be more precise, the investor was intent on purchasing a furnace that would emit harmful substances below the limit values prescribed by local regulations. The manufacturer's guaranteed values regarding the flue gas emission are presented in Table 1. The new furnace has a chamber for secondary incineration intended to perform additional burning of the released

gases, particles and hydrocarbon. The chamber is constructed in the shape of a labyrinth which retains the gases long enough to complete the burning process. An oxygen probe built into the outlet duct controls the quality of the outlet air. The cremation process is fully automatic. The parameters (air inflow, pressure and temperature in the incineration chamber, air inflow and temperature in the secondary chamber) are constantly checked so as to facilitate the optimal process. All this has made the flue gas content and the obnoxious odor in the flue gas as low as possible and satisfactory for release through the stack and into the environment.

About the same time the furnace was delivered, the aforementioned Regulation, listing cremators as a separate item, came into effect. The GVEs of the pollutants in the flue gas from furnaces are listed in Table 1.

Following the installation of the new furnace, emissions were tested with the aim to determine the actual amount of emissions in the flue gas, i.e. to verify the guarantees and make sure they were in keeping with the Croatian regulations governing the GVE. The types of harmful substances emitted from the furnace are, by and large, products of organic matter incineration. Organic compounds in the human body begin to disintegrate at high temperatures into various gas products (CO_2, NO_2, some SO_2) and water vapor. Chemically bound carbon is released in its elementary form, thus generating soot. Its incineration generates flue gas, which is then released into the atmosphere. Inorganic matter that constitutes the bones and blood remains in the ashes, which are transferred into the urn. The incineration of cotton and caskets made entirely of wood yields CO_2, NO_2, soot and water vapor. If the casket has parts made of galvanized or brass material, the residual ZnO will be released into the atmosphere. Synthetics and wool also generate smoke during incineration. Hydrochloride and hydro fluoride may be expected in the incineration of plywood, various polymers, surgical waste, etc.



1. Cremation furnaces;
2. O_2 probe;
3. Measuring point: CO, NO_2, O_2 and temperature;
4. Measuring point: solid particles (soot), HCl, HF, CH_4, Bacharach, O_2 and temperature;
5. Ventilator for additional air blown into the flue gases

Figure 1. Diagram showing the cremation furnace with the points for sampling of gases and solid particles.

METHODS

The measurements were taken in keeping with the commonly accepted sampling methods (HRN ISO 9096, 1992), (HRN ISO 10396, 1997) in order to ensure representative results. Concentration measurements for CO and NO_2 were carried out with the MSI COMPACT measuring apparatus, manufactured by Dräger, which has type approval of the State Institute for Standardization and Measurements. The method is of the electrochemical type. The concentration of solid particles is determined by the gravimetric method. The sampling of solid particles in the flue gas was carried out with an STL DUST SAMPLER. The ion selective electrodes were used to determine the concentrations of hydrochlorides and hydro fluorides. The IR sensor apparatus was used to indicate the presence of CH_4. The smoke number was determined by comparing the intensity of black on the filter paper caused by the flue gases with the Bacharach scale (graded 0-9). Measurements were taken during standard cremation time (60-80 min) and involving a standard casket. It is to be mentioned that the cremation furnace manufacturer guarantees the stated emission values for a wooden casket without any metal parts or nitro coating and with as little as possible synthetic material.
The measurements were taken in the gas-carrying duct, before and after the ventilator. Figure 1. shows the diagram of the cremation furnace with the points selected for sampling of gases and solid particles.

RESULTS AND DISCUSSION

Table 1. shows the comparison between the measured values and the values guaranteed by the manufacturer and the GVE in the Regulation. The characteristic process of cremation generates within one 60-80 minute cycle different amounts of emitted substances. It was possible to monitor in real time the emission of CO, NO_2, the amount of O_2 and the temperature. The results for one working day (I-IV cremation cycles) are shown in Figure 2.
At the onset of each cremation cycle there is a short period of an increased concentration of CO, which on the graph reads as a peak. The cause of this is that the beginning of the incineration involves rapid burning of wood and cloth with incomplete oxidation and generation of larger amount of CO, which cannot be completely oxidized in the secondary chamber. In the remaining part of the cycle the value of CO is significantly below the limit. The same trend was perceived in the emission of NO_2 but the values above GVE last longer within the cremation cycle and they are, on average, closer to the limit values. NO_2 is primarily the result of burning the nitrogen in the air at high temperatures. The total concentration of solid particles (soot) is measured for each individual cycle. The values vary depending on the amount and type of material used. So the largest amount of soot in one cremation cycle was 85 mg/m_n^3, which is 1.7 times more than the permitted value. The average daily value for four cremations during measuring time was below the limit value. The presence of HF, HCl and CH_4 was not detected.

The amount of O_2 during the cycle is, on average, about 15% without significant aberrations. Average temperature of the gases in the gas-carrying duct is 599°C. The gases are additionally cooled in the stack by blowing in 1700 m^3/h of air. The end temperature of the flue gas released into the atmosphere is 320°C.

Table 1. Comparison of the measured values, those guaranteed by the manufacturer and the GVE in the Regulation.

PARAMETER	Measured values – Mean value	Values guaranteed by Manufacturer	GVE in Croatian Regulations
Sampling point:	Gas-carrying duct		
Relation value:			
Amount of flue gas: m^3 (dry gas):	2963	1150	
Flue gas temperature: ^{0}C - before ventilator - after ventilator	 599 320	 500	
Oxygen volume ratio: % - before ventilator - after ventilator	 15,5 18,5		17
Harmful substances:			
CO mg/m^3_N	14,4	< 62,5	100
NO_2 mg/m^3_N	210,4	< 390	350
Solid particles mg/m^3_N	45,5	< 50	50
Organic substances in the form of vapor or gas CH_4 mg/m^3_N	ND	NG	15
HCl+HF mg/m^3_N	ND	NG	30
Bacharach	1	NG	1

ND- not detected; NG- not guaranteed

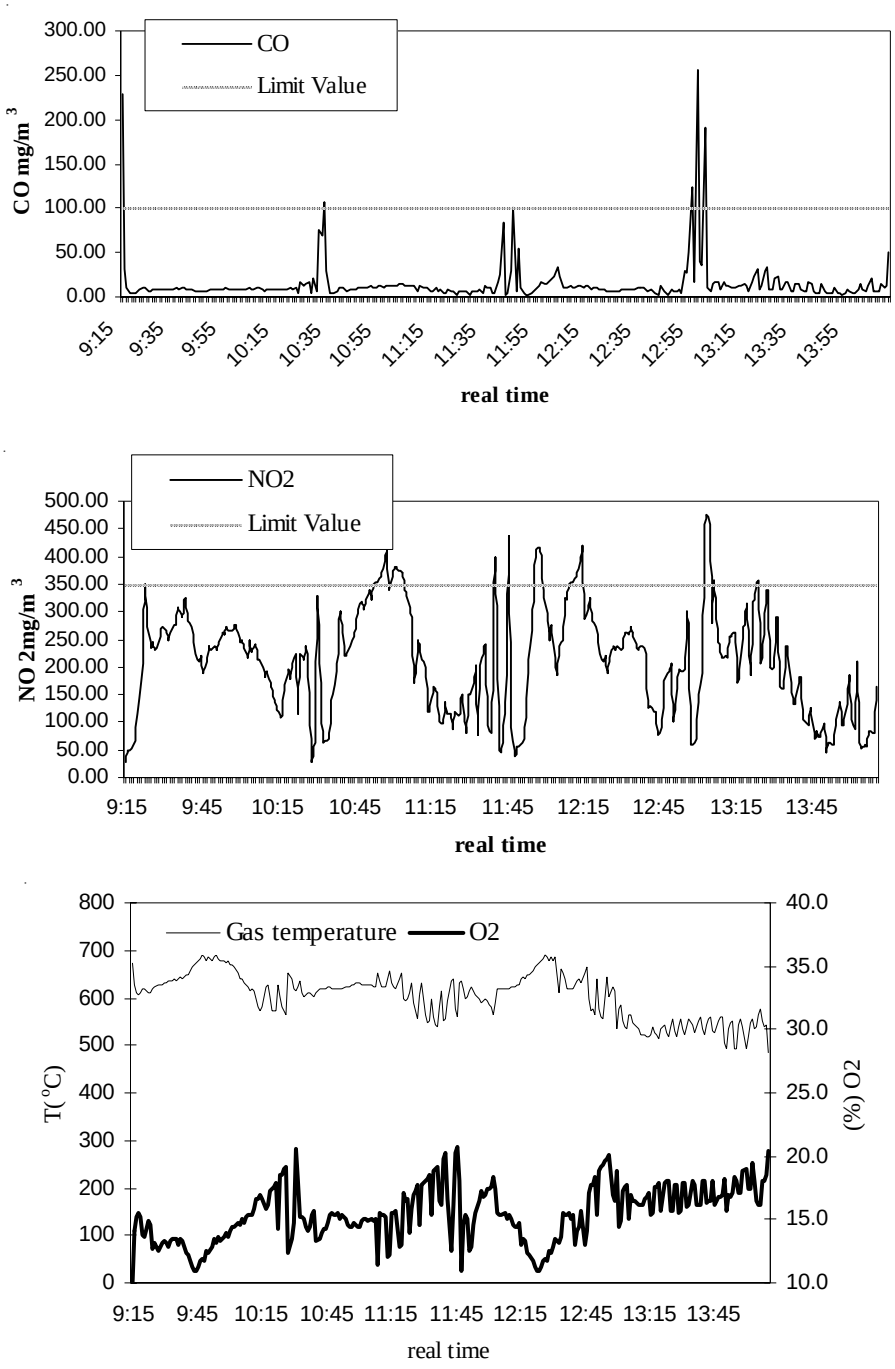


Figure 2. Graph showing emission of harmful gases CO and NO_2, O_2 and gas temperature for one working day with four cremation cycles (I-IV)

CONCLUSION

Satisfactory amount of harmful substance emission is achieved owing to:

- Construction of the furnace with a chamber for secondary incineration of gases,
- Optimization of the process achieved through automatic operation,
- Adhering to the prescribed procedure, including the incineration of caskets made of permitted materials and
- Using gas as energy.

In view of environment protection, emission monitoring is a must. Hereby we understand:

- Continued monitoring of oxygen and temperature of flue gases which is already being carried out, as well as installation of a sensor for continued monitoring of carbon monoxide and
- Regular taking of periodic measurements to monitor the concentration of solid particles, nitrogen oxides, hydrocarbons, hydrochlorides and hydro fluorides, blackening.

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Dubrovnik, CROATIA 6-10 October 2003

REASONABLE LIMITATIONS OF AIR POLLUTANT EMISSION FROM THE EXISTING HEP's THERMAL POWER PLANTS

D Kopjar[1, *], N Barbalić[1], D Mačković[1]

ABSTRACT

In October 2000, the Ministry of Environmental Protection and Physical Planning of the Republic of Croatia initiated the procedure for amending of the Ordinance on Limit Values of Air Pollutant Emission from Stationary Sources. All the stakeholders were invited to submit their comments, proposals, and opinions. The HEP's proposals and remarks mostly focused on the Ordinance provisions that stipulate limitations on emission from the "existing" thermal power plants. These facilities are the core of the HEP's thermal power capacities and thus play an important role in the Croatian economic system. Therefore, the limit values were determined for reasonable retrofits for abatement of air emission of pollutants from the "existing" facilities, and the solutions proposed for determining of adequate and objective emission limit values. The modified Ordinance on Limit Values of Air Pollutant Emission (Ordinance, 2002) has accepted most of the relevant reasons, and the emission limitations set for the existing thermal power plants respected reasonable technical and economic solutions.

INDEX TERMS

Pollutant emissions, air, limit values, Croatia, existing TPPs

INTRODUCTION

The Croatian Ordinance (1998) that came into force in 1999 stipulated the emission limit values (*ELV*) of the characteristic pollutants released from the facilities of Hrvatska Elektroprivreda (*Croatian Power Board)*, HEP. The values

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that applied to the "existing" facilities (built by/under construction in 1998) were to be changed to significantly lower/more stringent standards after July 1, 2004. Considering the present and future operation of the production facilities managed by the Thermal Power Division (TPD), the stipulated changes of *ELV*s had to be highlighted, and the tasks set up to be fulfilled in order to meet the requirements. Attention had particularly to be drawn to the cases when more stringent *ELV*s were stipulated on the basis of nonobjective assessments, so the *ELV*s could not be met by undertaking reasonable (i.e. economically viable) technical measures.

PLACE OF HEP'S TPPS IN THE CROATIAN POWER GENERATION SECTOR

Table 1 enlists all the finished HEP's thermal power generation facilities and their production characteristics. According to the tabulated data, only Plomin 2 TPP and Unit 4 of the TE-TO Zagreb Cogeneration Plant do not belong to the "existing" facilities, which means that the "existing" facilities comprise 78 % of the HEP's fossil electricity generation capacities or about 80 % of total available thermal power.

Table 1. HEP's thermal power generation facilities

Facility	Fuel	Unit	Commissioning, year	Rated output (MWe)	Rated net output (MWe)	Net technical minimum (MWe)	Planned decommissioning, year	Thermal power (MWt)
Sisak TPP	Heavy fuel oil, natural gas, crude oil	Unit A	1970	210	198	90	2013	600
		1						
		Unit B	1976	210	198	90	2017	600
		2						
Rijeka TPP	Heavy fuel oil	Unit 1	1978	320	303	90	2015	900
Plomin 1 TPP	Coal	Unit 1	1976	115	105	60	2015	345
Plomin 2 TPP	Coal	Unit 2	1999	210	192	90	> 2020	525
Jertovec Combined-Cycle Plant	Natural gas, light distillate oil	*GTU 1	1976	31.5	31	8	2012	150
		**TU 1		12.5	11.5	4		
		GTU 2	1957	31.5	31	8		150
		TU 2		12.5	11.5	4		
TE-TO Zagreb Cogeneration Plant	Heavy fuel oil, natural gas	Unit 1	1962	32	25	12	2009	830
		Unit 3	1979	125	100	60	2010	
		Unit 4	trial run	200	195		> 2020	
TE-TO Osijek Cogeneration Plant	Heavy fuel oil, natural gas	Unit 45	1985	45	42	10	2015	200
		GTU 1	1976	25	23.5	2	2011	
		GTU 2		25	23.5	2		
EL-TO Zagreb Cogeneration Plant	Heavy fuel oil, natural gas	TU 1	1970	12.5	6	3.5	2000	550
		TU 2	1980	32	29	5.5	2010	
		***GTP P 1	1998	26	24	1	2020	
		GTPP 2		26	24	1	2020	
TOTAL		-	-	1826.5	1687	-		4850

*GTU – gas turbine unit **TU – turbine unit ***GTPP – gas-turbine power plant

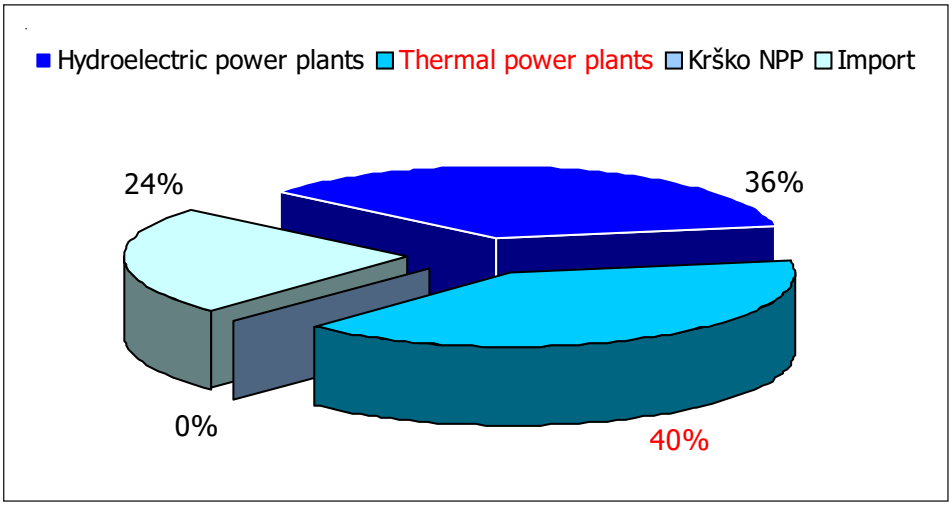

Figure 1. Thermal power plants share in HEP's 2002 electricity production

In 2002, the HEP's thermal power plants generated 5.9 TWh of electricity which comprised 40 % of the HEP's power deliveries (Fig. 1). Additionally, in 2002 these facilities generated approx. 1.2 Tg of process steam and approx. 5.9 PJ of heat. With the exception of electricity generated at the Plomin 2 TPP (22 %), the complete power generation was carried out at the "existing" facilities.

The above overview of the generation capacity and outputs clearly confirms importance of the "existing" thermal power plants for the power supply of Croatia. Therefore, the emission limitations imposed on these facilities have to be carefully set up, considering their technical and economic capacities for abatement of the air pollutant emission. It is particularly important to understand that these are mostly very old, "obsolete" power plants (Table 1), and their fitting with high-efficiency (and consequently expensive) flue gas treatment equipment would be unjustified. It would be justified to adopt reasonable implementation of the so-called primary measures for the air emission abatement. However, the limitations caused by quality of the fuel available at the market should also be taken into consideration. Table 2 shows fuel consumption in 2002, which is nearly a typical year considering shares of individual fuels.

Taking into account the Plomin 1 TPP coal consumption (Plomin 2 TPP is a "new" facility fitted with the flue gas desulfurization plant), and the fuel oil consumption in all the facilities, it is clear that the fuel quality directly affects the particulate matter and SO_2 emission from all the "existing" facilities. Substitution of fuel oil with natural gas (wherever possible, Table 1) and procurement of better quality fuel oil are limited by the market conditions.

Table 2. Fuel consumption in HEP's thermal power plants, 2002

Facility	Fuel oil (tons)	Natural gas (1000 m^3)	Coal (tons)
Sisak TPP	130952	276751	-
Rijeka TPP	276883	-	-
Plomin 1 TPP	712	-	289333
Plomin 2 TPP	1169	-	511040
Jertovec Combined- Cycle Plant	76	41979	-
TE -TO Zagreb Cogeneration Plant	52832	194142	-
TE-TO Osijek Cogeneration Plant	10646	45259	-
Osijek Gas-Turbine Power Plant	9	51841	-
EL-TO Zagreb Cogeneration Plant	29625	164780	-
Sisak District Heating Plant	1260	12882	-
Total	**504164**	**788634**	**800373**

SIGNIFICANCE OF EMISSION FROM THE EXISTING HEP'S FACILITIES

Table 3 shows the emission limit values that were expected to become mandatory for the HEP's thermal power plants after July 1, 2004. Only the "disputable" emission limit values, namely those that cannot be achieved under the current conditions, are tabulated.

To evaluate typical emission values for the existing HEP's thermal power plants, the results of the so-called individual measurements (Ekonerg, 2002) and continuos measurements (HEP, 2001) were used; such "typical" values were compared with the standard values given in Table 3 (Kopjar, Barbalić and Mačković, 2002).

For evaluation purposes, the significance of the emission departure from the *ELV*s from Table 3 was determined by establishing the relation between the mean statistic tendency (mean value or median) of the measurement results and corresponding *ELV*s, and also from the share of emission in excess of the *ELV*s in the total number of the measurement results. These values are calculated and their rank order established as shown in Table 4. If the shares of exceeded *ELV*s

were equal, the cases that correspond with the larger number of the measurement results have been attributed higher significance.
Since the compared ranking orders are not completely identical, the finally accepted order of significance of departure from the *ELV*s is the order of products of the "mean tendency ratio" and the "share of exceeded *ELV*s" (the last column in Table 4).

Table 3. "Disputable" *ELV*s expected to become mandatory for the HEP's thermal power plants after July 1, 2004

Facility /fuel /	Pollutant	*ELV* concentration /(mg/m_n^3)
large furnaces /coal/	particulate matter	100
	NO_x	650
large furnaces /gas/	particulate matter	5
	NO_x	350
large furnaces /heavy fuel oil/	particulate matter	50
	NO_x	450
	SO_2	1700
gas turbines /natural gas/	NO_x	150

Table 4. Order of significance of exceeded *ELV*s according to the mean tendency of the measurement results and share of exceeded *ELV*s in the measurement results

1	2	3	4	5	6	7
Facility /fuel/	Pollutant	Mean tendency and *ELV* ratio	Rank	Share of exceeded *ELV*s	Rank	Final ranking order of the significance of departures from *ELV*s
Plomin 1 furnace /coal/	particulate matter	0.9	5	0.42	5	5
	NO_x	0.7	6	0.13	7	7
furnaces /natural gas/	NO_x	0.5	7	0.29	6	6
furnaces /heavy fuel oil/	particulate matter	3.5	1	1.00	2	1
	NO_x	1.6	4	0.80	4	4
	SO_2	2.0	3	1.00	1	3
gas turbines /natural gas/	NO_x	2.1	2	1.00	3	2

PROBLEM DEFINITION AND FRAMEWORK FOR REASONABLE SOLUTIONS

The values given in columns 3 and 5, Table 4, clearly point to the excessive emission problem that might be faced by the existing HEP's thermal power plants after July 1, 2004. Since the data from the Table 1 indicate these are old or very old facilities, the reasonable solutions might include either implementation of the primary pollutant emission abatement measures or enforcement of the administrative measures, which include stipulating of separate requirements for each case, e.g.

a) combustion improvements (mostly reduction in NO_x and particulate matter emission), which usually include an adequate retrofit of the firing area, including the boiler plant furnace area;
b) fuel quality improvement or fuel replacement (mostly reduction in particulate matter and SO_2 emission);
c) modifications of the Ordinance that would take into account objective possibilities of the "existing" HEP's facilities to comply with more stringent emission standards.

Because of the importance the individual "existing" HEP's thermal power plants have in the power generation and supply and the significance of the departure of their typical values from *ELV*s (Table 3), two aspects have to be considered with regard to meeting of the set up *ELV*s, i.e.:

1. reasonable technical/economic conditions for meeting the *ELV*s,
2. deadlines for coming of the *ELV*s into force.

1. Framework for reasonable technical solutions. According to the present emission status, as shown above, the existing thermal power plants do not meet the set up *ELV*s (Table 3) and they are not achievable by applying reasonable technical and economic solutions (possible exceptions are Plomin 1 TPP and furnaces firing natural gas). Considering share of individual facilities in the power generation, and having in mind their rank order based on significance of their departure from the *ELV*s (Table 4), the furnaces firing heavy fuel oil, the gas turbines and finally coal-firing furnaces (Plomin 1 TPP) are considered as priorities.

Furnaces firing heavy fuel oil. In order to asses whether the measured emissions from the furnaces firing heavy fuel oil are representative, a calculation was made using the emission factors recommended by the *U. S. Environmental Protection Agency* (EPA, 1985) for calculation of heavy fuel oil firing emissions (*residual fuel oil no. 6*) when no emission abatement measures have been taken, depending on the possible mass share of *S* or *N* in the fuel. The following emission values were obtained (Barbalić and Kopjar, 2001):

- particulate matter: $S = 3\ \%$: $c = 355\ mg/m_n^3$
$S = 1\ \%$: $c = 140\ mg/m_n^3$
for $c = 50\ mg/m_n^3 = ELV$: $S = 0.16\ \%$

- NO_x: $N = 0.2$ %: $c = 409$ mg/m$_n^3$ < $ELV = 450$ mg/m$_n^3$
  $N = 0.3$ %: $c = 624$ mg/m$_n^3$ > $ELV = 450$ mg/m$_n^3$
- SO_2: $S = 3$ %: $c = 4897$ mg/m$_n^3$
  $S = 1$ %: $c = 1632$ mg/m$_n^3$
  for $c = 1700$ mg/m$_n^3$ = ELV: $S = 1.04$ %
  for $c = 400$ mg/m$_n^3$ = ELV (*new furnaces*): $S = 0.24$ %

where S and N designate mass shares of sulfur and nitrogen in the fuel oil. Therefore, typical emission values for the "existing" HEP's facilities obtained both from measurements and from calculations using the emission factors exceed the corresponding proposed ('disputable') *ELVs* (Table 3).

According to the calculation results, and regardless of a comparatively higher uncertainty of equations used to determine emission of particulate matter and NO_x (Barbalić and Kopjar, 2001), the below conclusions can be drawn with certainty:

- SO_2 : Emission depends on sulfur content in fuel only. When $ELV = 1700$ mg/m$_n^3$ the fuel oil sulfur content should be maximum 1 %. Thus, the solution is procurement of fuel oil of desired quality. However, the following facts should be born in mind: INA Rijeka Refinery and INA Sisak Rafinery (the only refineries in Croatia) do not produce fuel oil of required quality (sulfur content to 1 %), and construction of a plant for desulfurization of heavy oil components would demand an investment in the range of hundreds million Euro. The production of fuel oil of desired quality by processing of the "low-sulfur oils" is hardly an option because of the price and limited procurement possibilities;

- Particulate matter: Limit value $ELV = 50$ mg/m$_n^3$ cannot be achieved with primary measures. Even if the fuel oil with sulfur content of 1 % by weight was provided, the *ELV* should be set at 150 mg/m$_n^3$, which is still a sufficiently stringent value considering the ambient air quality requirements. However, if the supplied fuel oil sulfur content is up to 3 % by weight only, the limit value must be set at 360 mg/m$_n^3$.

- NO_x: Individual implementation of primary measures should result in abatement of NO_x emission to 40 – 50 % (Rentz *et al.*1996), which is not sufficient for the HEP's thermal power plants to meet the $ELV = 450$ mg/m$_n^3$. Repeated and simultaneous implementation of a larger number of primary measures would probably give results, but the investment costs would be extremely high. Because of typical emission values (Table 4) and unconfirmed justification of implementation of "individual" primary measures, an adequate limit value for NO_x would be 900 mg/m$_n^3$.

Gas turbines. According to the results from Table 4, over 50 % of all measurement results for NO_x emission twice exceed $ELV = 150$ mg/m$_n^3$. The most suitable technique for abatement of NO_x emission in case of retrofits would be the "wet" procedure (injection of steam or water), which reduces the

combustion temperature. At full loading, this procedure enables that separation of approximately 75 % be achieved (Rentz *et al.*1996). Generally, an adequate reduction of NO_x emission would in this case satisfy the *ELV* requirements, but there is a number of elements that might restrict use of the "wet" procedure: possible increase in CO emission, even in excess of the limit values, and demi water use request which significantly increases the NO_x emission abatement costs. Since the number of gas-turbine power plants within the HEP's power generation potential is very small, the investment in these primary measures cannot be technically and economically viable so it would be justified to extend applicability of the earlier set *ELV* – 450 mg/m_n^3 until the end of the operating lifetime of these thermal power plants. Moreover, it would be reasonable to permit more benevolent emission limits, i.e. to allow the *ELV* increase for the gas-turbine combined-cycle units in proportion with turbine exhaust gas heat recovery rates.

Coal firing furnace - Plomin 1 TPP. The Plomin 1 TPP can meet the *ELV* requirements for particulate matter and NO_x with a rather limited implementation of the primary measures. However, such activities on the Plomin 1 TPP should be preceded by an exact determination of the annual use of its capacities and the remaining lifetime. After that, the currently applicable *ELVs* should remain in force until the end of the lifetime of the thermal power plants of this operating category.

2. ELV effective dates. Croatia is party to the Protocol Concerning the Further Reduction of Sulfur Emissions (Protocol, 1998) under which it has assumed the obligations regarding the SO_2 emission reduction compared to the year 1980: 17 % by 2005, and 22 % by 2010. This Protocol recommends the SO_2 emission limits for new facilities (identical to the Croatian *ELVs*). These standards are not mandatory for the existing facilities, so the emission standards for such facilities may be stipulated "as necessary", provided the state fulfils the undertaken obligations for abatement of total SO_2 emission on a national level. According to the ratified Protocol (1998), the year 2005 is one of the "control" years, and it was respected when July 1, 2004 was set as the deadline for change of the *ELVs* for the existing facilities. Finally, the new ordinance on petroleum-derived fuels (Ordinance 2, 2002) stipulates that the limit values for the total sulfur in light, special light, medium, heavy and extra heavy fuel oil should be below 1 % by weight after July 1, 2004. That was taken as the upper limit for the fuel oil sulfur content with which the *ELV* requirement for SO_2 can be met by the fuel oil firing furnaces.

Proposal of Reasonable *ELV*s for the Existing HEP Facilities and *ELV*s Finally Accepted in the Ordinance (2002)

This section of the paper elaborates the reasonable emission limits for the existing HEP facilities that would be possible and/or technically and economically viable,

i.e. *ELVs* achievable by implementation of such primary measures for air pollutant emission abatement that do not demand modifications in the facilities, installation of new or modification of the existing equipment, namely the primary measures that do not demand capital investments into the "existing" facilities. This is the only reasonable solution considering the remaining lifetime of these "obsolete" plants. On the other hand, such solution relies on the current standardization practice of the European Union which, after setting up the generally applicable emission limitations for the "existing" facilities, regularly refers to numerous exceptions (sometimes even by name) that are permitted less stringent emission limitations and longer periods to comply with the generally applied limit values (Council Directive, 1992; Directive, 2001). Such a reference to the European Union practice becomes even more important when substantiated by comparisons with other relevant and meaningful indicators used by the European Union members (economic potential, gross national product, technical tradition, and the like). These need not be detailed in this paper, and there is specially no need for referring to generally known facts on the balance of the transboundary movement of characteristic pollutants and the difference of the essential indicators of "specific emission" of pollutants into the air (such as per capita, per surface area) from the EU countries. The Table 5 is a brief presentation of the considerations elaborated in this section, with tabulation of *ELV* – reasonable (*ELVR*), that should remain in force for a limited period of time – until the end of the lifetime for an adequate thermal power plant operating category. The data given the Table 5 lead to the conclusion that this "transitional" period would in general last until the year 2017 when the operating lifetime of all the "existing" HEP facilities should end. It is a suitable coincidence that the same year (2017) is a deadline for adjustment of the "existing" facilities under the new European Union Directive (Directive, 2001) on the limitation of emissions into the air from large combustion plants.

Ultimately, advocating of setting reasonable *ELV*s for the "existing" HEP's thermal power plants resulted in the *ELV*s as stipulated by the Ordinance Amendment (Ordinance, 2002): the authorities have accepted the arguments that application of radical technical improvements would be unjustified for the old facilities. Therefore, the "existing" thermal power plants have been stipulated the *ELV*s equal to or even less stringent than the *ELVR*s from Table 5. However, the authorities have not accepted the proposed *ELV*s effective deadline (2017), but have decided that the *ELV*s stipulated for the "existing" thermal power plants shell remain effective until December 31, 2008. Thus, the "existing" thermal power plants will operate without any problems until 2009, and after that date they will either have to meet the ELVs applicable to the "new" thermal power plants or limit their operating capacities (up to 2000 hr/year or up to total 30,000 operating hours), as stipulated by the Ordinance (2002).

Table 5. Reasonable ELVs for the existing HEP's thermal power plants

Facility /fuel/	Pollutant	*ELVR* concentration / (mg/m_n^3)	Effective date	Application conditions
large furnace /coal/ Plomin 1 TPP	particulate matter	200	2015	-
	NO_x	1 200		
	SO_2	2 000		
large furnaces /natural gas/	particulate matter	10	2017	-
	NO_x	700		
large furnaces /heavy fuel oil/	particulate matter	150	2017	guaranteed $S \leq 1\%$ by weight in fuel
	NO_x	900		-
	SO_2	1 700		guaranteed $S \leq 1\%$ by weight in fuel
gas turbines /natural gas/	NO_x	450	2020	-

CONCLUSION

The HEP's "existing" thermal power plants are extremely important for the Croatian power supply: in 2002, they generated 5.9 TWh of electricity, 1.2 Mt of process steam and 5.9 PJ of heat. The measurements have confirmed that none of the "existing" HEP's facilities meets the pending more stringent *ELVs* expected to come into force on July 1, 2004 under the Ordinance (1997). Coming of such *ELV*s into force would imperil normal operation of some 90 % of the HEP's generating facilities. Their rather short remaining lifetime demands that the solution for the abatement of the air pollutant emission be sought within the framework of the primary measures only, which should not incur high investments. For the provisions of the Ordinance amendments on the emission limitations that were in preparation the current objective possibilities of the "existing" HEP's facilities had to be respected, so appropriate *ELV*s and deadlines for their changes had to be set up. The reasonable solution was: Setting up of *ELV* respecting the objective/reasonable possibilities of implementation of the (primary) measures for abatement of the air pollutant emission. These are reasonable *ELV*s as tabulated in Table 5, along with their effective periods depending on the remaining operating lifetime for individual operating categories of the HEP's thermal power plants.
The proposed *ELV*s also comply with the EU standards applied to the "existing" thermal power plants. Considering importance of the HEP' facilities for the power supply of Croatia, the issue of adequately set up *ELV*s for the "existing" thermal

power plants in Ordinance (2002) gave finally immediate and reasonable solution that is based on the proposals elaborated herein. However, the proposed *ELV*s effective date for the "existing" thermal power plants (2017) was not accepted, and the closer deadline was set up (December 31, 2008).

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

PARTICLE EMISSION MEASUREMENT FROM CEMENT FURNACE STACK

G Pašalić*, Z Mikšik and Z Kovačević

ABSTRACT

In this paper practical problems of particle emission measurement from cement furnace stack and power plant stack have been presented. A description of problems encountered while providing measurements under different disturbances caused by technological process are given. Results of different measurements on the same cement furnace stack with two different types of stack gas particle filters (electrostatic precipitator and fine mechanical filter) have been presented and discussed.

INDEX TERMS

particle concentration measurement, measurement accuracy, electrostatic precipitator, cement furnace stack, technological conditions

INTRODUCTION

Gravimetric measurement of particle concentration in smoke gas is performed for the purpose of emission source control or control and calibration of the continuous emission monitoring system. Although the requirements for performing these two types of measurements differ, the problems encountered while performing measurements and analyzing results are common to both types of measurement.

While performing control measurements or calibrations of optical instruments for continuous monitoring of particle concentration, a higher accuracy of measurement and a higher number of samplings is required, which in practice made the detection of phenomena which affect the accuracy of measurement

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results easier. Correct performance of installed equipment for continuous monitoring of particle concentration is of great significance, since the collected data can easily give insight into the state of technological process and parameters which affect the accuracy of gravimetric measurement. By using these data we attempted to improve determining of sampling parameters and measurement accuracy. The same experiences can be, by this same analogy, also applied to gravimetric measurements at emission sources without installed devices for continuous monitoring of emission, which are subject to the same technological conditions during the performing of measurement.

METHODS

By performing gravimetric measurements of particle concentration at emission sources, such as power plant stacks and cement furnace stacks in cement factories, we detected a repetition of the same factors which affect the accuracy and correctness of performance of the measuring procedure, and which are not in their entirety included in the standard descriptions of the measuring procedure. We performed measurements in accordance with the ISO 9096, EN 13284-1 (method 17) and VDI guidelines (VDI2066, VDI3950) by using the automatic gravimetric filling instrument "SICK GRAVIMAT SHC-501". This measuring instrument enables isokinetic sampling with angle correction of smoke gas flow and fast positioning of the measuring head on the measuring axis.

By careful selection of the sampling period we took into consideration the factors dependant on measuring equipment and emission source. The determination of the minimum sampling period was mostly based on the quantity of samples necessary for required accuracy, although it can also depend on the periodical variation of measured particle concentration. The maximum sampling period is limited by the capacity of the filter of the sampling head and by particle concentration, but it also depends on the stability of the technological process, since too long measurement period may include irregularities which are not typical or prevent the accurate calculation of concentration from the collected sample. To a great extent, accuracy and dispersion of measurement results depend on the adequate selection of the sampling period.

A great flow velocity of smoke gas, mostly at larger stack diameters, can cause significant oscillations of the measuring head of the instrument for gravimetric sampling at higher lengths of the measuring probe. In some cases, we had to additionally secure the measuring instrument to facilitate a more accurate measuring of velocity and angle of flow.

It was proven that disturbances in the performance of the filtration unit, particularly electrostatic precipitator, can lead to a short-term increase in particle concentration. If there is a disturbance during measurement in more measuring points of the same stack section, there occurs a significant error, since the previously measured points are not in the same operation regime, thus rendering

averaging of results pointless. Even a sudden short-term increase in particle concentration at the input of the electrostatic precipitator causes a disturbance in filter performance, which manifests itself at the output in the sudden increase of particle concentration. Exceeding maximum particle concentration that can be registered by the instrument for continuous emission monitoring leads to a loss of data from the instrument for continuous emission monitoring. The mean value of the concentration calculated on the basis of these data is in such case not usable for comparison with the gravimetric measurement. If this happens during calibration, it results in a significant measurement error, therefore the measurement must be repeated. In practical measurements in cement furnace stacks at the time of electrostatic precipitator failure, an enormous increase in particle concentration was registered, exceeding the measuring range of the installed monitoring equipment manifold. Such short-term exceeding of emission concentration may go unnoticed, since their amplitude is not visible, whereas gravimetric measurement will show a significantly higher mean value of particle concentration. Gravimetric measurement during calibration in such cases will show a significant deviation of values measured in these conditions from the mean value of other measurements.

The stability of the technological process is of crucial importance to the measuring process. Changes in the production process reflect directly on the measurements of emission, therefore it is necessary to ensure timely information about instabilities or changes in the operation regime of the plant prior to measurement, and after measurement gather all relevant data for the assessment of usability of each individual sample. Unforeseen changes in the operation regime, which often occur in the performance of cement furnaces, can compromise the relevance of individual measurements, and sometimes it is necessary to repeat the whole measuring procedure.

For the safety of measurements, we tried to have the number of samples collected during measurement in plants with greater changes in operation regime always higher than the minimum number of measurements required by the standard in order to have the sufficient number of measurements for relevant accuracy after elimination of incorrect measurements.

During control calibration of the instrument for continuous measuring of particle emission it is necessary to perform measurements in several points of the instrument's measuring range, which requires a change of the operation regime of the plant. Measurements in thermo-electric power plants showed that it is sufficient to change the operating power of the plant to the values of approximately 25%, 50% and 90% of its capacity. The problem is generally that the change in power can be realized only after adequate coordination with technological requirements, with the measurement performable after the full stabilization of the operation regime of the plant. Measurements in cement furnace stacks in cement factories do not require extensive preparations for the operation regime change, but the stability of working conditions immediately after the change is

problematic and permanent supervision of the status of technological conditions during measurement is required.

Periodical changes in particle concentration and other parameters in smoke gas are consequential to periodical operation of automatic instrument for firebox or filter cleaning, and other periodical technological processes. The repetition interval of these disturbances ranges from several minutes to several hours. The diagram of the change in particle concentration in Fig. 1 clearly illustrates a typical periodical change in particle concentration in a cement furnace stack. The oscillations of measured momentary values of particle concentration amount to approximately 50 % of the maximum value, which cannot be neglected. Prior to every measurement we attempted to determine the interval of such processes, and during measurement in more measuring points to coordinate the measurement so that it includes the full number of intervals in each sampling, or to perform the sampling always in the same stage of the process.

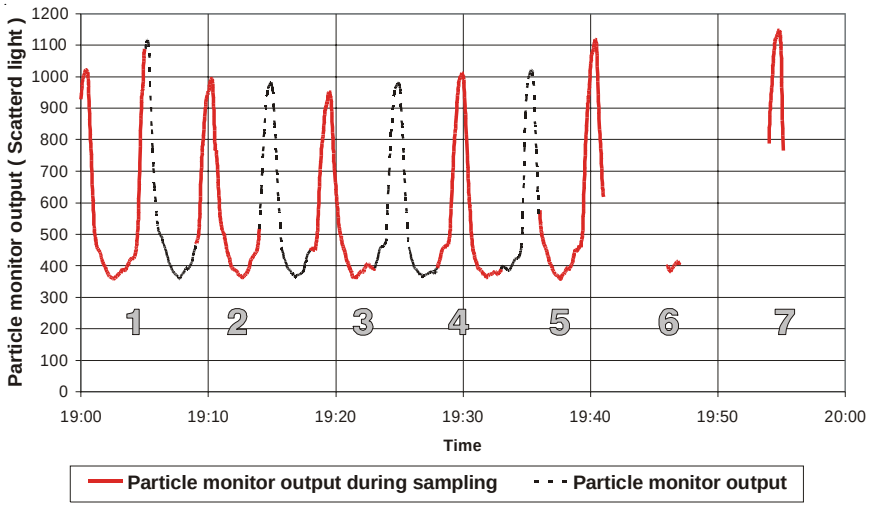

Figure 1. Particle concentration changes during measurement.

RESULTS

Example in Fig. 2 shows the measuring results of the control calibration of the instrument for monitoring concentration of particle emission in a cement furnace stack by gravimetric method. In Fig. 1 there are time diagrams of change in particle concentration during sampling in the same measuring point (diagram parts 1 to 7). It is evident that particle concentration changes periodically, with the repetition period of 5 minutes. The measurements marked 1 to 5 were performed by sampling in the duration approximately similar to the interval of concentration change, whereas the measurements 6 and 7 were performed by

sampling in the duration of half the interval during minimum (measurement no. 6) and maximum (measurement no. 7) concentrations of particle emission. From Fig. 2 it is evident that deviations of all measurements from the calculated calibration line are within acceptable limits. It is interesting to note that points 6 and 7 lie on the same line, which can be calculated by averaging other measurements. In this case, a shorter synchronized sampling gives equally good results as taking a larger number of samples and averaging them. Simultaneously, the performance of the calibrated instrument can be checked for concentration values above and below the mean value without intervening in the operation regime of the plant. If the sampling had been performed without the knowledge about the periodicity of concentration change, the achieved results would have shown significantly higher deviations from the mean value, and the measurement error could have been reduced only by taking a larger number of samples and lengthening the sampling period.

Changes in emission concentration during measurement in some measuring points of the same section, which are later used for calculation of the mean value of the concentration, lead to an increase in statistical deviation and reduce the accuracy of measurement. Temporal changes of the distribution of particle concentration can be avoided by careful coordination of performance time of measurement and the technologically conditioned changes of the operating conditions of the plant.

Measurements in larger stacks and canals are performed in more segments of the same cross section in order to include the unevenness of particle distribution

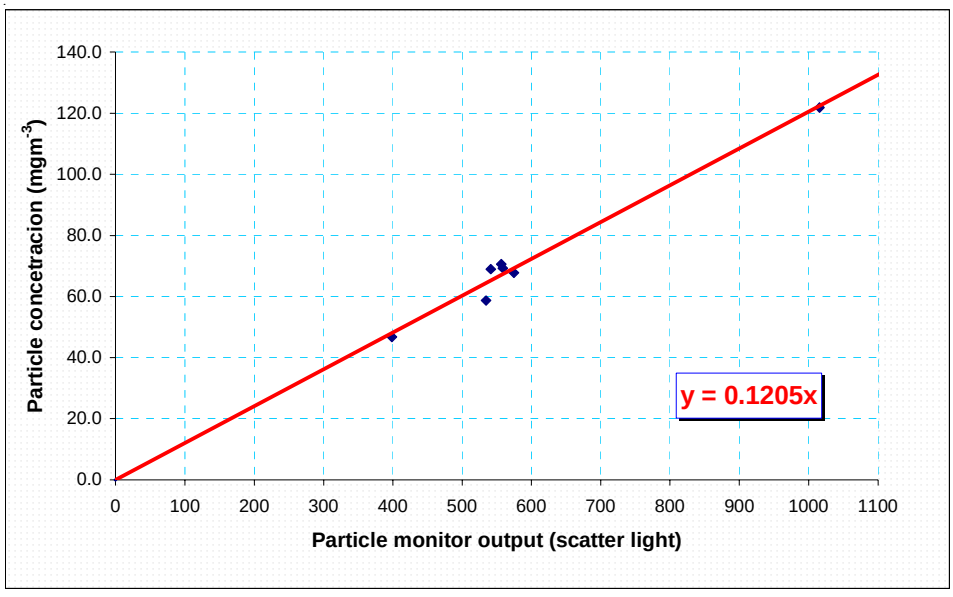

Figure 2. Calibration curve for particle emission monitoring instrument.

by the averaging of results in all segments. With horizontal smoke canals frequently there exist significant differences in concentration and size of particles on the vertical axis of the section, and their distribution depends on the flow velocity of smoke gas and other factors which determine the conditions of separation and agglomeration of particles. The impossibility of simultaneous measurement in all segments of the canal section necessarily leads to measurement error caused by a temporal change in the distribution and concentration of particles in the period from the start to the end of the series of measurements, which include one measurement value of the concentration for the given section.

In the practice it is useful to analyze collected results in order to determine unhomogeneity and temporal changeability of particle concentration in segments of the section. During the calibration of the system for continuous monitoring of particle emission it is possible to calculate a better accuracy of the calibration curve if it is linear and if the characteristics of the instrument for continuous monitoring of particle emission allow for it. This is achieved by the calculation of partial calibration lines for each segment of the measured section, and then averaging their coefficients. This can partially eliminate the influence of fluctuations of particle concentration during measurement. Fig. 3 shows the results of calibration in the conditions where, due to a large diameter of the stack, the measurement was performed in four measuring points, in two vertical diameters of the stack, and in three different operation regimes of the plant. During the measurement there occurred changes in the concentration and distribution of particles, therefore the results of the measurement shown in the figure in the form of calibration line of the calibrated instrument show greater

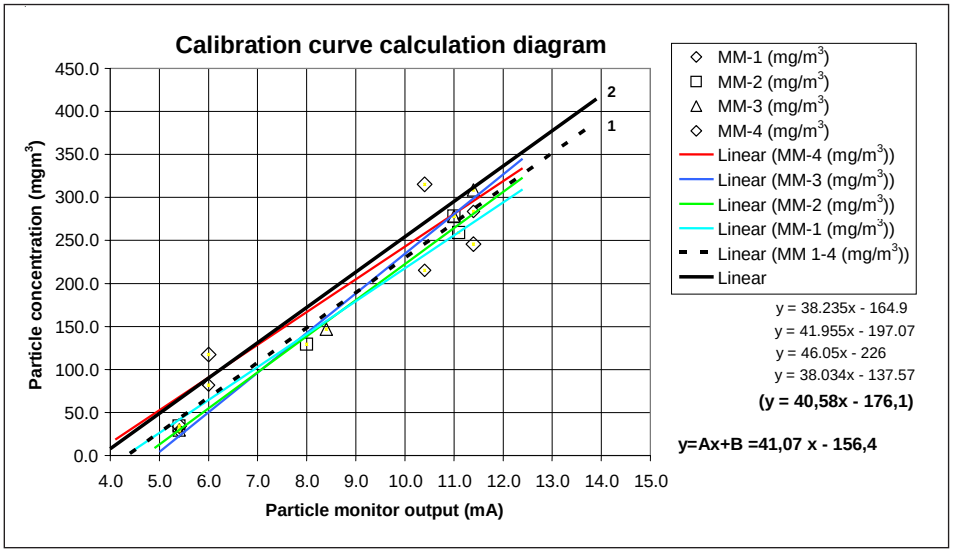

Figure 3. Comparison of calibration curve diagram for different sampling axis

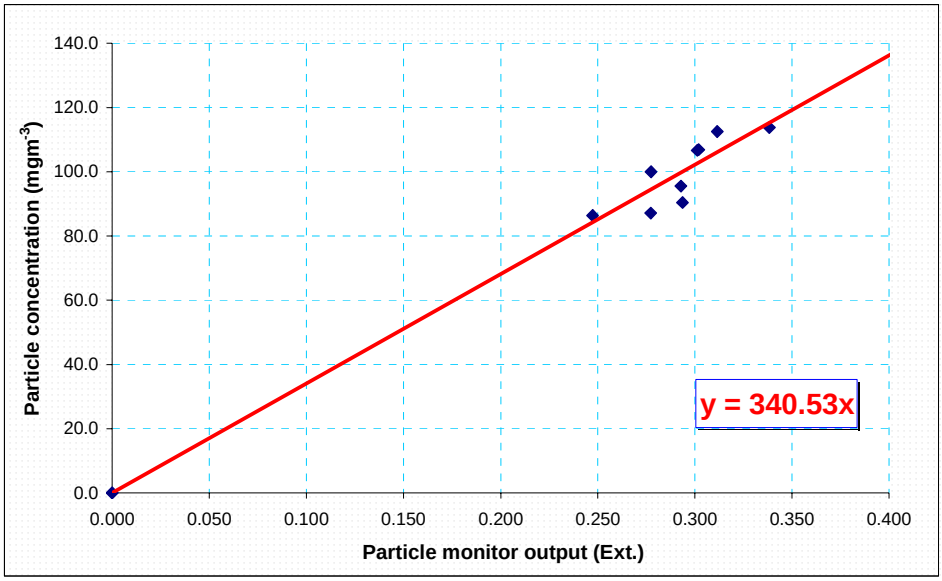

Figure 4. Calibration curve for particle emission monitoring instrument mounted on cement furnace stack with electrostatic precipitator.

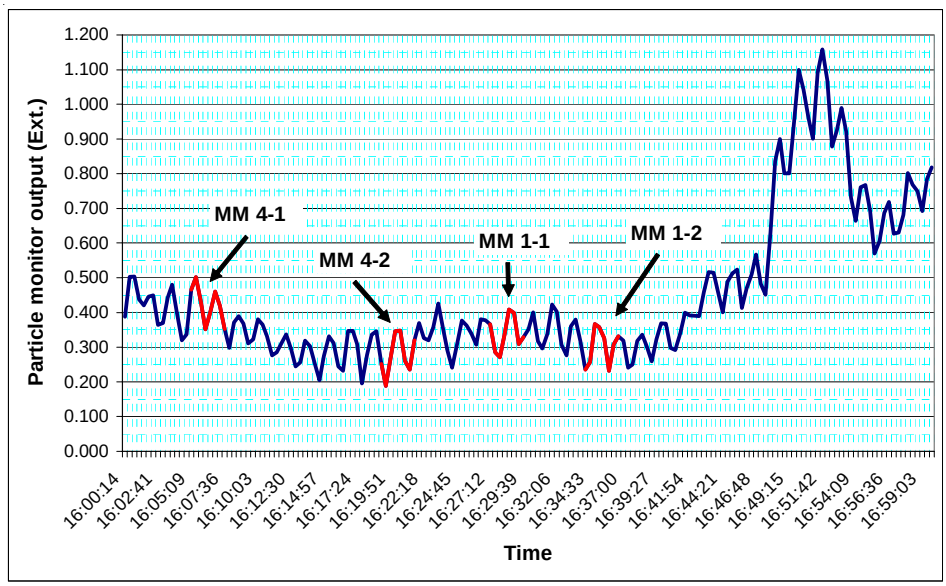

Figure 5. Particle concentration changes during measurement shown on Fig.4.

deviations from the mean value. Line 1 is the result of the averaging of measured values of all measurements, whereas line 2 shows the mean value of the calibration lines calculated and shown for each measuring point. In case of stable particle

concentrations during measurement, these two lines would overlap into the same calibration curve, and their difference in this case would indicate a measurement error caused by unstable operation regime of the plant.

Based on the example of two gravimetric calibrations of the same instrument for continuous measurement of particle emission concentration we will consider the possibility of avoiding the influence of disturbances caused by the characteristics of the plant on the results of the calibration.

A periodical fluctuation of particle concentration of approximately 50% of measurement value and a sudden increase in concentration to almost triple value are evident. This calibration was performed in the plant equipped with an electrostatic precipitator, whose periodical change of efficiency is the probable cause of the fluctuations of particle concentration. After the electrostatic precipitator was replaced by mechanical bag filters due to technological requirements, the calibration of the same instrument was repeated. Fig. 6 shows the results of this calibration, and from the diagram in Fig. 7 it is evident that particle concentration is significantly less changeable than when the electrostatic precipitator was used. If the results of the calibrations in Fig. 4 and Fig. 6 are compared, we can see that in both cases there is about equal dispersion of measured values, which is the result of taking into consideration parameters of the technological process and avoiding the sampling in the period of instable operation of the plant.

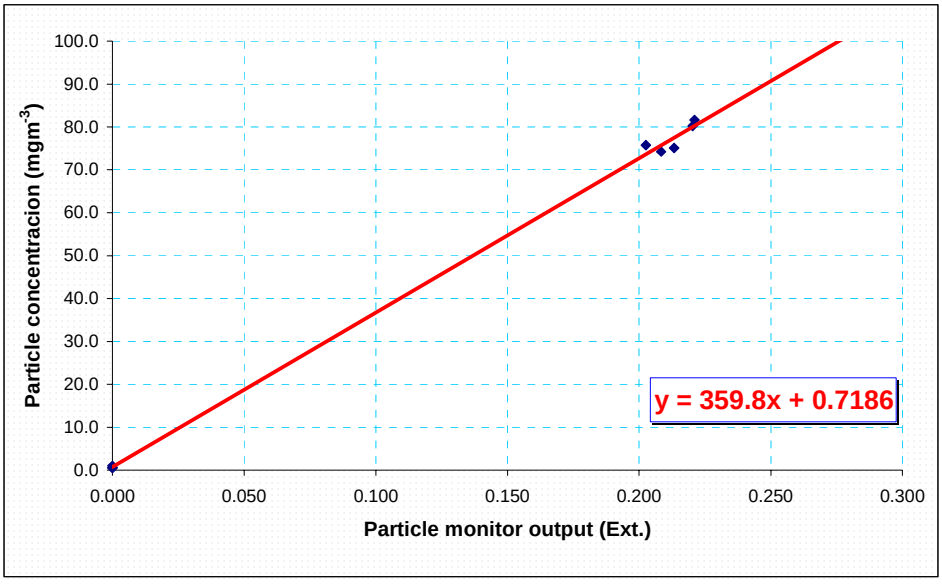

Figure 6. Calibration curve for particle emission monitoring instrument mounted on cement furnace stack with mechanical bag filters.

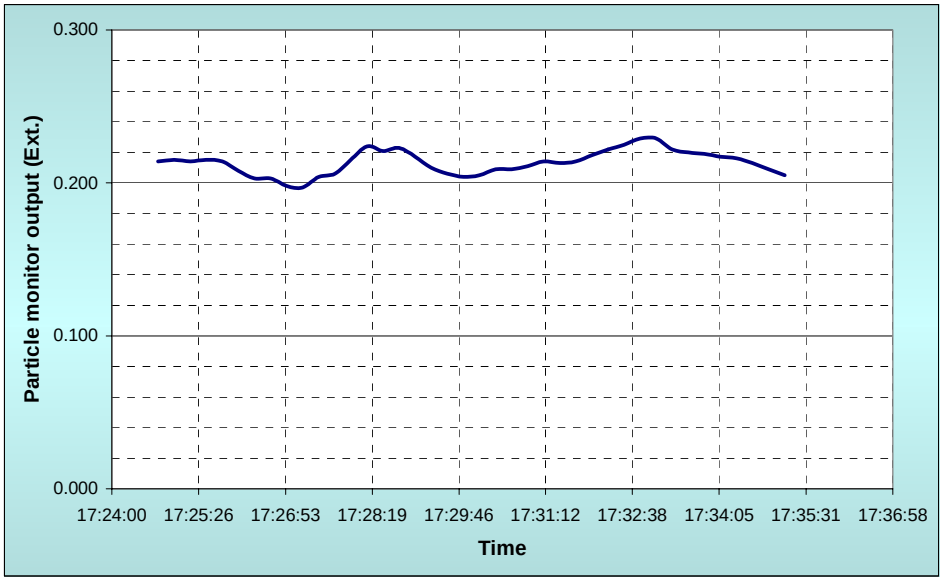

Figure 7. Particle concentration changes during measurement shown on Fig. 6.

CONCLUSION

Measurements of particle emission concentrations and calibration of equipment for continuous measurement are subject to a number of influences which can reduce the accuracy of measurement, and which are part of emission source structure and therefore unavoidable. Studying of such influences opens up a possibility for a more accurate performance of measuring procedure and reduction of the number and costs of unnecessarily performed, useless or inaccurate measurements.

The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

USE OF GAUSSIAN PLUME MODEL FOR CALCULATION OF EFFECTIVE DOSES RECEIVED BY THE POPULATION AROUND NPP "KOZLODUY"

Z Paskalev[1, *] and D Apostolova[2]

ABSTRACT

Radioactive fall-out from Nuclear powers releases small quantities of a wide variety of radioactive materials at each stage in the nuclear fuel cycle. Nuclear power stations release radioactive isotopes , which find their way throung food to humans.They may lead to human exposure by several pathways: external irradiation from radioactive materials deposited on the ground, inhalation of airborne radioactivity, and ingestion of radioactive materials in food and water.For the public the global yearly average dose is 0.008 mSv.

In this study are presented the results fore determination of effective doses obtained by the population around Kozloduy NPP was used the calculated concentration of the releases radioactive isotopes in the atmosphere air and over the ground surface.

Doses from artificial radiation are, for most of the population, much smaller than those from natural radiation but they still vary considerably according to the rocks and soils of the area (1,20 mSv/y – 15,6 mSv/y).

INDEX TERMS

Radioactive fall-out, Nuclear Power Plant releases, Dose to individuals, Vertical and Horizontal dispersion of radionuclides

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INTRODUCTION

Estimates of the equivalent dose to tissues within human respiratory tract and other organs from internal end external exposure are needed in the assessment of health risks associated to the radioactive pollution of the environment (around uranium mines).
The important problem is the estimation of the radiation risk for population living around nuclear power station.

AIM OF THE STUDY

In this study we estimate the effective dose received of population living around the distance 30 km to the Kozloduy NPP from external and internal exposure of ionizing radiation.

MATERIALS AND METHODS

For determination of effective doses obtained by the population around the Kozloduy NPP was used the calculated concentration of the radiological activity in the air (Bq m^{-3} at downwind distance x, crosswind distance y, and height z), and over the ground surface, using the following equations:

Elevated Source, Elevater Receptor

(source height = $h(h_{eff})$] receptor height = z)

$$\chi = (x, y, z) = \frac{Q}{2\pi\sigma_y\sigma_z\bar{u}}\left[\exp\left\{-\frac{(h+z)^2}{2\sigma_z^2}\right\} + \exp\left\{-\frac{(h+z)^2}{2\sigma_z^2}\right\}\right]\left[\exp\left\{-\frac{y2}{2\sigma_y^2}\right\}\right]$$

χ (x, y, z) air concentration (Bq m^{-3} or Ci m^{-3}) at downwind distance x, crosswind distance y, and height z;

$\dot{Q}$ Activity release rate (Bq sec^{-1} or Ci sec^{-1})

σ horizontal dispersion parameter (m)

σ_z vertical dispersion parameter (m)

$\bar{u}$ mean inverse wind speed (m sec^{-1})

$$\left(\frac{1}{\bar{u}}\right) = \frac{1}{N}\sum_{i-1}^{W}\frac{1}{u_1}$$

Elevated Source, Elevated Receptor, Centerline

(source height = $h(h_{eff})$; receptor height = z; y = 0)

$$\chi = (x,0,z) - \frac{\dot{Q}}{2\pi\sigma_y\sigma_z\bar{u}}\left[\exp\left\{-\frac{(h+z)^2}{2\sigma_z^2}\right\} + \exp\left\{-\frac{(h-z)^2}{2\sigma_z^2}\right\}\right]$$

Elevated Source, Ground – Level Receptor

(source height = $h(h_{eff})$; receptor height, z = 0)

$$\chi = (x,y,0) = \frac{\dot{Q}}{\pi\sigma_y\sigma_z\bar{u}}\left[\exp\left\{-\frac{h^2}{2\sigma_z^2}\right\}\right]\left[\exp\left\{-\frac{h^2}{2\sigma_z^2}\right\}\right]$$

Elevated Source, Ground – Level Receptor, Centerline

(source height = $h(h_{eff})$; receptor height = 0; y = 0)

$$\chi = (x,0,0) - \frac{\dot{Q}}{\pi\sigma_y\sigma_z\bar{u}}\left[\exp\left\{-\frac{h^2}{2\sigma_z^2}\right\}\right]$$

Approximate Maximum Concentration:

$$\chi_{max} \quad \frac{2\dot{Q}}{\pi e\bar{u}h^2}\left(\frac{\sigma_z}{\sigma_y}\right)$$

where **e** is the base of natural logarithms (e = 2.71 + …). This maximun occurs for $\sigma_z = h/\nu_2$. The distance at which ht maximun occurs can be read off the graphs for σ_z versus distance.

Ground–Level Source, Ground–Level Receptor

(source height , h = 0; receptor height, z = 0)

$$\chi = (x,y,0) - \frac{\dot{Q}}{\pi\sigma_y\sigma_z\bar{u}}\left[\exp\left\{-\frac{y^2}{2\sigma_z^2}\right\}\right]$$

Elevated Source, Elevated Receptor

(source height = $h(h_{eff})$; receptor height = z)

$$\chi(x,y,z,t) - \frac{Q}{(2\pi)^{3/2}\sigma_{xl}\sigma_{yl}\sigma_{zl}\bar{u}}\left[\exp\left\{-\frac{(h+z)^2}{2\sigma_{zl}^2}\right\} + \exp\frac{(h-z)^2}{2\sigma_{zl}^2}\right].$$

$$\left[\exp\left\{-\frac{y^2}{2\sigma_{yl}^2}\right\}\right]\left[\exp-\left\{\frac{\left(x-\bar{u}t\right)^2}{2\sigma_{xl}^2}\right\}\right]$$

where σ_{xl}, σ_{yl} and σ_{zl} are instantaneous dispersion parameters in the x, y and z directions rather than the 15 – 20 minute average parameters normally used, and Q is the total activity released rather than the activity release rate.

Elevated Source, Ground–Level Receptor

$$\chi(x,y,0,t)-\frac{Q}{(2\pi)^{1/2}\pi^{3/2}\sigma_{xl}\sigma_{yl}\sigma_{zl}\bar{u}}\left[\exp\left\{-\frac{h^2}{2\sigma_{zl}^2}\right\}\right]\left[\exp\left\{-\frac{y^2}{2\sigma_{zl}^2}\right\}\right]\left[\exp-\left\{\frac{\left(x-\bar{u}\right)^2}{2\sigma_{zl}^2}\right\}\right]$$

Ground–Level Source, Ground–Level Receptor

$$\chi(x,y,0,t)-\frac{Q}{2^{1/2}\pi^{3/2}\sigma_{xl}\sigma_{yl}\sigma_{zl}\bar{u}}\left[\exp\left\{-\frac{h^2}{2\sigma_{yl}^2}\right\}\right]\left[\exp-\left\{\frac{\left(x-\bar{u}t\right)^2}{2\sigma_{xl}^2}\right\}\right]$$

Ground–Level Source, Ground–Level Receptor, Centerline

$$\chi(x,0,0,t)-\frac{Q}{2^{1/2}\pi^{3/2}\sigma_{xl}\sigma_{yl}\sigma_{zl}\bar{u}}\left[\exp-\left\{\frac{\left(x-\bar{u}t\right)^2}{2\sigma_{xl}^2}\right\}\right]$$

Fulmigation (Trapping) Inversion at Height H (H > h)

$$\chi_F(x,y,0)-\frac{\dot{Q}}{(2\pi)^{1/2}H\sigma_y\bar{u}}\left[\exp\left\{-\frac{y^2}{2\sigma_y^2}\right\}\right]$$

Use of a semi-infinite cloud approximation and the ground-level radionuclide concentration for estimating the gamma and beta doses rate from an elevated source (stack of NPP-effective release height) can seriously underestimate the doses close to the release point before the plume reaches the ground. The values

of vertical and horizontal dispersion coefficient were determined for strong, moderate, neutral, and slight atmospheric stability at 10^3 to 10^5 meters from source (effective release height).

The annual average release of noble radioactive gas from the Kozloduy NPP was 251769 GBq (0,96% of the norm); the total long lived beta aerosols released in the atmospheric air were 1186 MBq (0,14% of the norm), and the total emission of I-131 was 3260 MBq (0,62% of the norm) /Table 1, 2, 3/.

Table 1. Released in the atmosphere air the noble radioactive cases from NPP Kozlodui (GBq)

Month	Stack 1	Stack 2	Stack 3	Stack 4	Stack 5	% norm
I	10720	7370	5618	394	2302	1,2
II	7870	7200	3499	942	1862	1,0
III	9020	7280	3471	695	1729	1,0
IV	8360	7020	4443	274	2102	1,1
V	8130	7410	475	257	1744	0,8
VI	6969	7304	495	326	1682	0,8
VII	7272	7810	403	1099	1569	0,8
VIII	7386	7323	2257	975	1581	0,9
IX	7310	6880	4367	709	2229	1,0
X	7000	6930	2793	1142	2024	0,9
XI	9260	6100	4498	702	2001	1,0
XII	7130	6810	6672	191	2165	1,0
All	**96645**	**38991**	**7706**		**22990**	**0,96**

RESULTS

Mean annual absorbed dose and annual effective dose from background exposure for Bulgarian population are:

- External 711 μGy/a or 738 μSv/a
- Internal 191 μGy/a or 1550 μSv/a
- TOTAL 902 μGy/a or 2288 μSv/a
- Lung 1228 μGy/a
- Annual collective effective dose for Bulgarian population from background exposure is 19800 man.Sv/a.
- Weighted mean annual effective dose for NPP operation is 3,7 mSv/a.
- Annual collective effective dose for the Kozloduy NPP exposure is 30 man.Sv/a.

Table 2. Released in the atmosphere air the radioactive beta–derosoles from NPP Kozlodui (MBq)

Month	Stack 1	Stack 2	Stack 3	Stack 4	Stack 5	Stack6	% norm
I	34	87	4	3	11	4	0,2
II	28	13	5	4	11	5	0,1
III	37	40	6	5	10	7	0,2
IV	30	26	9	4	12	6	0,1
V	29	28	5	4	13	7	0,1
VI	27	32	4	4	15	6	0,1
VII	27	40	5	5	15	6	0,1
VIII	26	44	7	6	15	7	0,2
IX	26	37	11	8	17	5	0,2
X	23	40	4	24	26	7	0,2
XI	23	26	4	9	24	5	0,1
XII	25	35	4	4	16	5	0,1
All	**335**	**448**	**68**	**80**	**185**	**70**	**0,14**

Table 3. I-131 release in the atmosphere from NPP Kozlodui (MBq)

Month	Stack 1	Stack 2	Stack 3	Stack 4	Stack 5	% norm
I	74	72	15	4	11	0,4
II	39	97	7	4	10	0,4
III	47	100	6	6	8	0,4
IV	45	81	652	4	16	1,9
V	42	418	19	3	15	1,1
VI	37	161	13	2	22	0,5
VII	51	58	12	8	22	0,3
VIII	36	293	13	12	21	0,8
IX	40	143	47	11	23	0,6
X	41	67	15	13	23	0,4
XI	59	33	7	10	23	0,3
XII	40	63	11	5	30	0,3
All	**551**	**1586**	**817**	**82**	**224**	**0,62**

CONCLUSION

The results of the analysis show that the total effective doses (from internal and external gamma-beta exposure) obtained by the population around the Kozloduy NPP were very small- 0,15% to natural background.

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Monitoring and Measurement

The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

AREA SATURATION MONITORING OF ATMOSPHERIC POLLUTANTS BY MEANS OF PASSIVE SAMPLERS AND DIFFUSION DENUDERS

I Allegrini, F Costabile*, F De Santis and A Ianniello

ABSTRACT

Conventional monitoring techniques intended for the evaluation of atmospheric pollution in urban or industrial sites are characterised by high time resolution. In fact, they use automatic analysers characterised by sufficiently fast response, accuracy and reliability. However, due to the high costs for the equipment and maintenance, they are not very suitable if an extensive monitoring program is required. In such cases, the use of simple, inexpensive, yet accurate measurement provided by alternative methods may be preferred. In fact they could simultaneously allow the measurements over a high number of monitoring sites, thereby allowing the so-called "saturation monitoring" in which the spatial coverage of the experimental observation is very high. Saturation monitoring is fulfilling several practical requirements such as a better knowledge about spatial distribution of pollutants and a better recognition of the environment when preliminary assessment of the distribution of atmospheric pollution is needed, especially when a network of fixed stations is planned. However, since saturation monitoring is using relatively inexpensive techniques, it can be also conveniently adopted in situations where financial resources for extensive monitoring of atmospheric pollutants are limited. This is the case for most developing Countries. Several techniques may be employed for saturation monitoring. This paper describes some example of air quality monitoring in urban sites by using a combination of passive samplers and of diffusion denuders. Passive samplers are used for integrated monitoring over a long period of time (typically one month) and are particularly suitable for criteria pollutants with high integration time

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limits (for example: annual average) are required. Diffusion denuders are very suitable for daily measurements of important pollutants such as sulphur and nitrogen dioxide. A proper sampling line made with two denuders coupled to a small impactor allows the simple measurement of daily averages of nitrogen dioxide, sulphur dioxide and particulate PM_{10}. Technical specification of the sampling apparatuses will be given as well as the results obtained in measurement campaigns carried out in selected locations in Italy.

INDEX TERMS

Diffusion Denuders, Passive Samplers, Saturation Monitoring, Air Pollution Assessment.

INTRODUCTION

Saturation monitoring in air pollution assessment consists of a series of measurements addressed to a better understanding of the spatial distribution of pollution over a specific area. In fact, the concentration data usually gathered from monitoring network may be expressed as:

$$C_i = \int_{t_1}^{t_2} C_i(x, y, z, t)dt$$

Where x, y and z are geometric coordinates of the sampling site and t the time, with t_1 and t_2 the integration times of the monitoring device. If $(t_2 - t_1) <$ minutes, then the monitoring is carried out as real time monitoring. This is the case of automatic instruments, which are usually employed in classic networks. If $(t_2 - t_1 >$hours or days, then monitoring is characterized by a high integration time and the response (C_i) is defined as integrated concentration. Of course, real time monitors should be preferred since they provide a high time resolution. However, time integrated monitoring offers an interesting alternative since it employs sampling and analytical methods that are characterized by a low operating cost. Thus, the total cost of few automatic monitoring stations could be competitive with several integration monitoring stations. This will allow a better representation of atmospheric pollution since the space integration may be carried out in a more detailed way. This is the source of the term *Saturation Monitoring*, where saturation indicates that the spatial details of pollution distribution are complete and that additional data in space are not required. On the contrary, automatic monitors are limited in numbers, thus spatial integration is carried out by modeling or other statistical averaging techniques that may give unreliable results.
Although based on different principles, saturation and automatic monitoring are not in competition. In fact, automatic monitoring stations provide information on the time evolution of atmospheric pollution, while saturation stations provide

details about the spatial distribution, thus a combination of both seems to provide the best answer to the need of environmental assessment in an area where atmospheric pollution may be a problem. However, while automatic monitors are widely used, saturation monitoring with integration devices is not very common. This is mainly due to the fact that monitors have been fully characterized in terms of data quality, while integration devices are still in the evaluation phase. In addition, although the former require a higher investment cost, the latter require high labor cost, thus economic balance toward saturation monitoring is depending upon the labor cost of the Country where the sampling needs to be carried out. Clearly, for developing Countries, integration monitoring can be carried out at very reasonable cost, thus a better characterization in terms of reliability is the key element for a wide use of such alternative monitoring techniques, especially in developing Countries.

This paper describes the last experiences carried out on passive samplers and diffusion tubes which are two possible candidates for a widespread saturation monitoring of air pollution in urban areas. In addition, the paper shows how a simple configuration of diffusion tubes allows the direct measurement of most important air pollutants.

Passive samplers and diffusion denuders are based on the same principle: pollutant molecules diffuse on a suitable reactive layer, which acts a physical or chemical sink for the species of interest. This will cause a concentration gradient that removes pollutants molecules from an air stream. In the diffusion denuders, the air is moving through a channel (Cylindrical or annular) having the internal walls coated with the reactive substance by means of a suitable pump, while in the passive sampler, molecular diffusion only provides the driving force for moving pollutant molecules on the reactive layers. Thus, passive sampling may be extended to several weeks, while for diffusion denuders it is limited to a maximum of 1 day or so. In diffusion denuders the air flow rate may be as high as 30 L/min, while passive samplers show an "apparent flow rate" of the order of few mL/min, thus they show less sensitivity. However, thanks to the higher exposition time, such a lower sensitivity may be counterbalanced to practical satisfactory figures. Depending upon the chemical species to be measured, passive samplers show sensitivities of less than 1 $\mu g/m^3$ for an exposition time of 1 month while for diffusion tubes such a sensitivity levels is reached for sampling periods ranging from 1 to several hours.

METHODS AND RESULTS

Passive samplers have long been used for the assessment of atmospheric pollution. However, their use have been severely limited by their poor performances in terms of reliability for the long term sampling of several species. In fact, after a certain sampling time, the reactive substrate is usually depleted, thus the advantage of using such device (sufficiently long sampling time) is lost. In order to overcome

such difficulty, a relatively new design for a passive sampler was developed. This resulted into the new passive sampler ANALYST, basically a badge sampler, which was shown to be very suitable for routine monitoring of several pollutants. In fact, Analyst provides sufficiently high apparent flow rate (about 8 mL/min) coupled with a high operative capacity. This allows long time exposition, which, for Benzene, may be as high as 6 months. Such a high integration time might be seen as a drawback. However, it should be recalled that health effects of several atmospheric pollutants are associated to long-term effects. In fact, recent Directives on Air Quality following the Framework European Directive 96/62, define limits that, in several cases (Sulfur Dioxide, Benzene, Nitrogen Dioxide), are based on annual averages. Therefore, it is clear that the use of passive samplers on long term monitoring may provide long term concentration averages at reasonable costs and efforts.

Such samplers were thoroughly characterized in terms of accuracy, sensitivity and comparability with the standard reference methods. Results, which are reported elsewhere, shows that the total uncertainty associated to the measurement is on the order of 15%, compared to measurements carried out with the reference method. A special attention was addressed to the capacity, i.e., the ability of the sampler in up taking pollutant molecules without significant degradation of the performances. Such experiment was carried out for more than one year in an urban location where series of passive samplers were simultaneously exposed for the measurement of Benzene. They were exposed for one, two, four, six and twelve weeks and data were evaluated comparing integral data with the sum of individual samplers exposed for shorter periods of time. Such comparison show that no degradation of performance occurred after eight months of exposure to an average concentration of Benzene of few $\mu g/m^3$, thus showing good performances for long term sampling.

As an example of area saturation monitoring, Figure 1 shows the results of a monitoring campaign carried out near an oil refinery on the Adriatic Sea, Italy. Nitrogen Dioxide, Sulfur Dioxide, Benzene, Toluene and Ammonia were monitored by means of analyst passive samplers for several months over about 60 monitoring sites. Interpolation was provided by means of Krieging technique. As it is shown in the Figures, sulfur dioxide is distributed near the refinery, while ammonia show maximum values West of the plant, where farming activities are prevailing. Nitrogen dioxide is almost evenly distributed, indicating that the traffic source near the refinery is significant. It should be stressed that, beyond the environmental significance of the results, relatively few measurements are able to provide similar detailed spatial distribution of most important air pollutants, either released by the plant or present on the area as background pollutants. Thus, a very clear picture of environmental impact is easily obtained.

Passive samplers can very efficiently provide spatial saturation monitoring for several species relevant to atmospheric pollutants and their effects on environment and public health. However, as said above, they are not very effective in providing

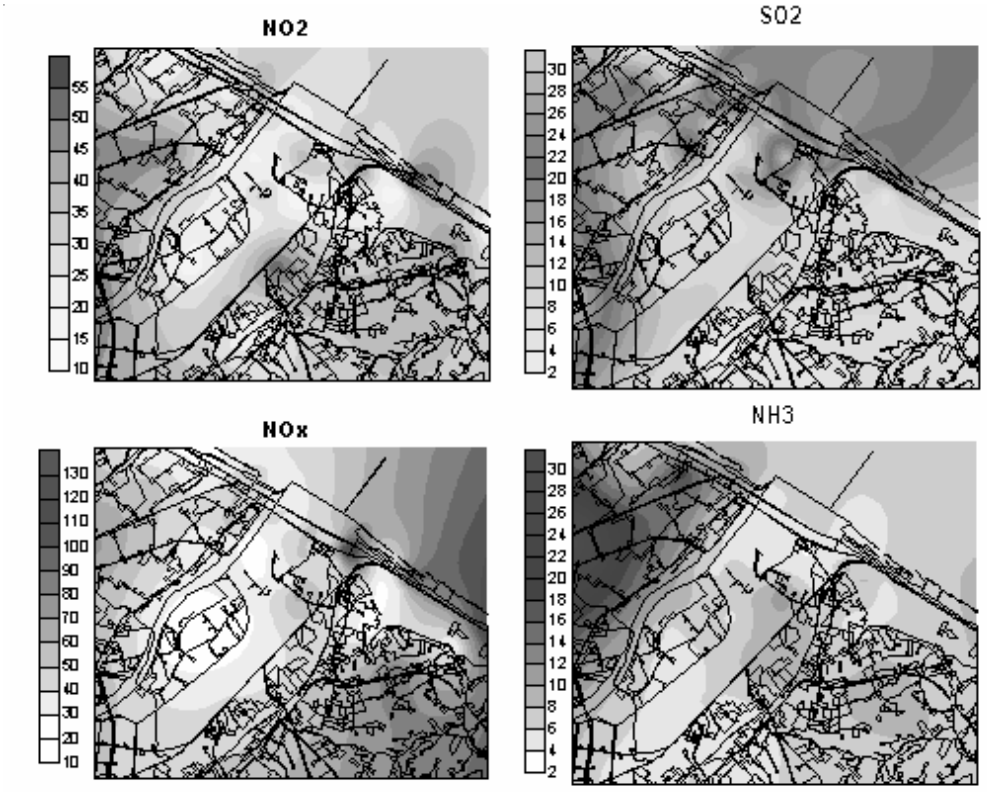

Figure 1.

information related to the time distribution of pollutants in a given area. For such a goal, the development of new apparatuses based on diffusion denuders may provide the proper tools. Unfortunately, diffusion denuder usually provides the determination of one species. Thus, an efficient use of this technique would require the simultaneous determination of several species. Earlier experiences suggested that a combination of annular diffusion tubes coupled with a filter pack would meet the requirements for the simultaneous determination of several species of environmental significance. However, since the technique was developed for measurements in remote locations, its use was only limited to some specific scientific purpose. In order to develop a simple multiparametric system based on diffusion denuders, a new design was proposed. As it is shown in Figure 2, it consists of a line made up of two denuders in series. The first is coated with sodium carbonate, which absorbs sulfur dioxide. The second denuder is coated with alkaline carbon which was shown to be very efficient for the collection of Nitrogen Dioxide. After the second denuder, the airstreams, containing particulate matter, passes through an inertial impactor providing a cut size of 10 um at the nominal flow rate of 2 L/min. After impaction, the PM_{10} particulate is collected on a 37 mm diameter filter, weighed according to a standard gravimetric procedure

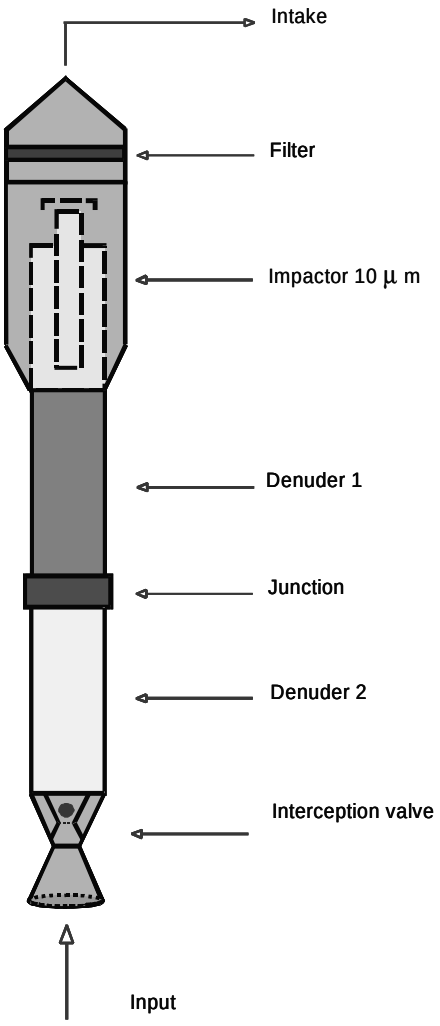

Figure 2.

by using a high sensitivity balance (1 μg). After sampling, the denuders are extracted with water and analyzed according to ionic content by means of ion chromatography. Sulfur Dioxide is converted into sulphate, while Nitrogen Dioxide on carbon coating is quantitatively converted into Nitrite. In conclusion, two IC analysis and a standard weighing steps provide the measurements of three of most important air pollutants. The sampling procedures is carried out by means of a small sequential sampler which is able to collect pollutants over 8 sampling line for a 1 week unattended operation. After one week, the denuder lines are removed and analyzed according to the procedures given above, providing the average daily concentration of the pollutants.

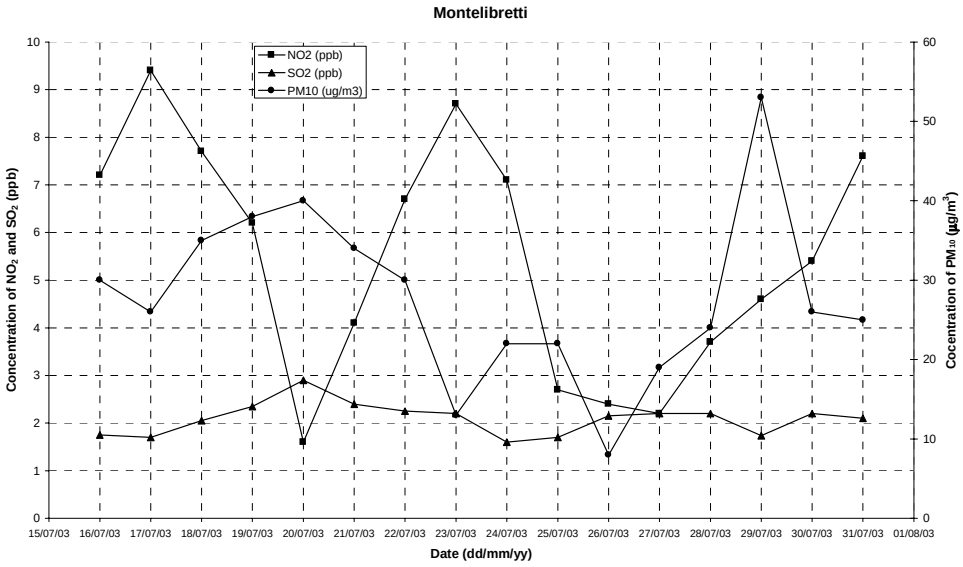

Figure 3.

Figure 3 shows an example of application of this technique in sampling pollutants in a monitoring station located 20 km NE of Rome in the area where the Institute is also located. Sampling was carried out for two weeks and daily average concentrations of pollutants were obtained. The results, which will be presented and discussed in more details elsewhere, show how the technique is effective for a simple and reliable assessment of atmospheric pollution in a given location.

CONCLUSIONS

Diffusive sampling through passive apparatuses or denuders provides a very effective tool for saturation monitoring for atmospheric pollutants of environmental significance. The use of such devices may be an important complement to existing monitoring network where they may be conveniently used to track pollutants in locations not served by fixed stations. In addition, since the logistic requirements for diffusive sampling are very limited, the additional advantage of simple and easy re-location of the monitors is clearly seen. An addition advantage is due to the fact that diffusive sampling allows the determination of species, which are not easy to detect with automatic monitors. For example, Hydrogen Sulphide, Ammonia and Nitric Acid are just few cases. The use of passive samplers may open new opportunities in the studies related to emission, transformation and deposition of atmospheric pollutants in urban, industrial and remote areas, thus more research is needed to improve their performance and more applications are sough for a widespread use of the devices, especially in developing countries.

The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

THE INFLUENCE OF WEATHER TYPES ON SUSPENDED PARTICLE CONCENTRATIONS

I Bešlić*, [1], K Šega[1] and Z Bencetić Klaić[2]

ABSTRACT

The influence of weather types on concentrations of airborne particle fractions PM_{10} and $PM_{2.5}$ is presented. Samples were collected on Whatman EPM 2000 glassfiber filters, 47 mm in diameter, at the measuring site located in Northern, residential part of Zagreb during the period 1 August 1999 - 31 July 2002. For this purpose weather type classification by Poje (1965) is used. The groupation of weather types in six groups (E. Lončar and V. Vučetić, to be published) shows significant agreement with particle concentrations. Weather types characterised with a high pressure, low winds and stable, long-lasting temperature inversions are related to higher particle concentrations. On the other hand, lower concentrations are accompanied with the strong winds and humid and cold air advection during the summer.

INDEX TERMS

PM_{10}, $PM_{2.5}$, Weather types, Analysis of Variance

INTRODUCTION

The main shortages in collection of total suspended matter are undefined upper particle size level, local origin of particles and weak correlation between particle concentrations and health effects. Recently, due to better insight in the health effects, collecting of PM_{10} and $PM_{2.5}$ particle fractions was introduced. This study

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investigates dependence of daily concentrations of PM_{10} and $PM_{2.5}$ on the weather types, which characterize weather conditions of a single day integrally. The purpose of this investigation is to predict the air pollution levels as well as a risk of population or specific population subgroups.

METHODS

Low Volume Samplers – Ingenieurburo Sven Leckel, collected daily samples of PM_{10} and $PM_{2.5}$. These samplers satisfy European norm EN 12341. Samples were collected on Whatman EPM 2000 glassfiber filters, 47 mm in diameter, at the measuring site located in the northern, residential part of Zagreb during the period 1 August 1999 - 31 July 2002. In the same period daily weather types were determinated on the basis of the surface pressure field in one of the synoptic termines (0, 6, 12 UTC). For this purpose weather type classification by Poje (1965), which distinguishes 29 different weather types, was used. Weather types were separated in six groups (regimes). Each regime consists of weather types with similar weather conditions, as it is shown in table 1.
In order to investigate the dependence of suspended particle concentrations on weather types, analysis of variance was used.

Table 1. Weather types separated into six groups (regimes).

Regime	Description
Radiative (Rad)	High pressure and stable weather conditions. Periodic weak winds with alternating direction. Maximal contribution of local factors.
High pressure ridge (g)	Transitional state of high pressure, but with cloudy and rainy weather.
Precipitative (Pre)	Warm and humid advection with cyclonic characteristic. Substantial convection with cloud and rain formation.
Advection from SE Europe (SE)	Cold advection in winter period. Persistent inversion.
Advection from NW Europe (NW)	Cold advection in warm period. Convective clouds and rain formation.
Windy (Wind)	Cold advections with strong winds. Intense horizontal and vertical air mixing.

RESULTS

The annual course of absolute frequencies of weather type regimes is shown in Figure 1.

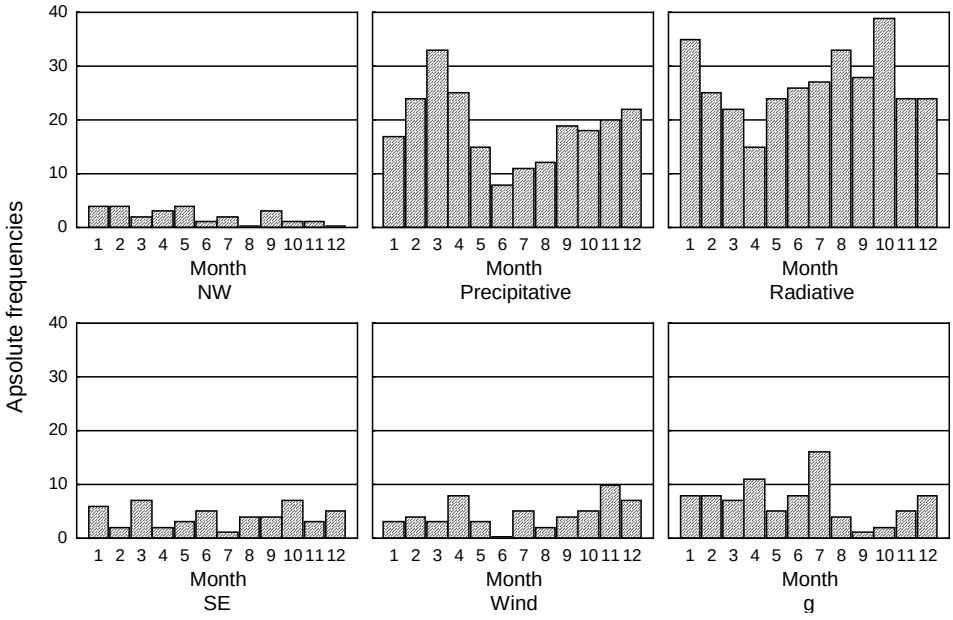

Figure 1. The annual course of absolute frequencies of weather type regimes for Zagreb during the period 1 August 1999 - 31 July 2002. Radiative and precipative regimes were the most frequent during the measuring period

Results of analysis of variance are shown in table 2. They indicate significant differences between particle concentrations for different weather regimes for both particle fractions. Comparison of mean values of both suspended particle fraction concentrations for different weather regimes is shown in Figure 2.

Table 2. Analysis of variance for grouped weather types during the period 1 August 1999 - 31 July 2002. F is variance ratio, and p is significance level. Analysis of variance points out the significant differences between particle concentrations measured in different weather regimes, for both particle fractions.

	PM_{10}	$PM_{2.5}$
F	10,34	8,35
p	<0,01	<0,01

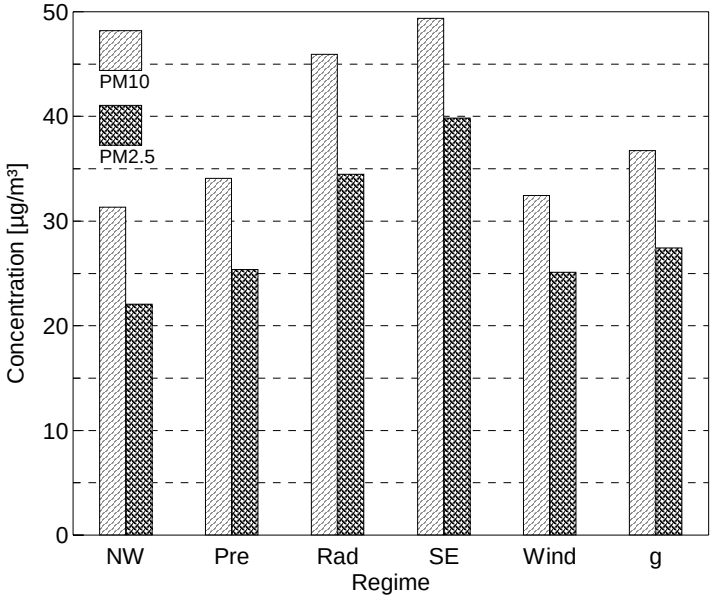

Figure 2. Mean values of suspended particle concentrations. PM_{10} concentrations are higher then $PM_{2.5}$ for all weather regimes. The highest and the lowest concentrations are obtained for SE and NW regimes, respectively

Concentration distributions for weather regimes with the high particle concentrations are shown in Figure 3.

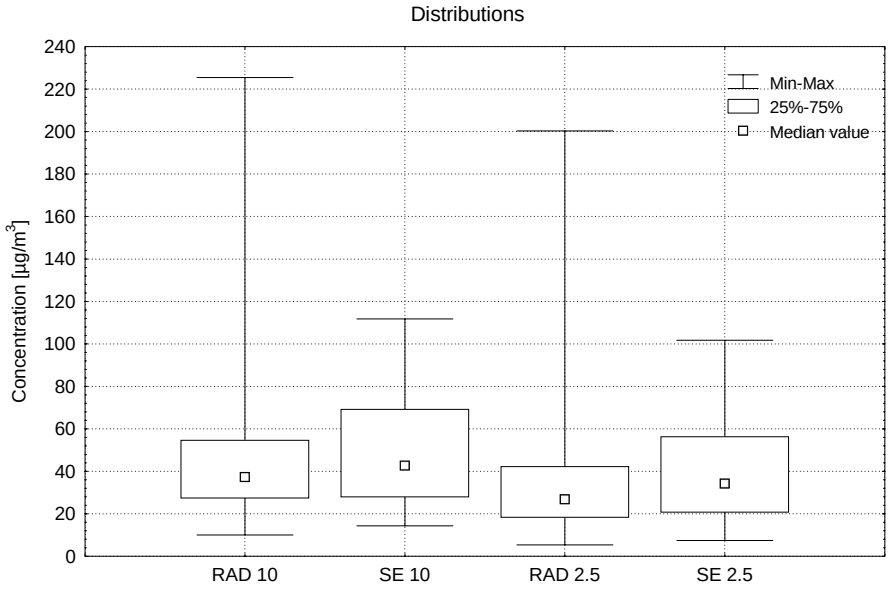

Figure 3. PM_{10} and $PM_{2.}5$ concentration distributions for radiative and SE regimes.

There was no significant difference between median values of concentrations for both particle fractions during the radiative and SE regimes. However, lower maximum values of particle concentration and wider quartile range was observed during the SE regime, compared to the radiative regime.

DISCUSSION

Radiative and precipitative regimes were the most frequent during the measuring period. Similar results were obtained for 20 year period (Lončar E, Vučetić V. 2003, Bencetić Klaić Z. 2001). This fact points out that three-year period was sufficient for our investigations.

Analysis of variance shows statistically significant differences in particle concentrations for different regimes. Consequently, comparison of mean values of suspended particle concentrations was derived, and it is shown in Figure 2.

High particle concentrations during SE regime show significant particle advection from SE direction. An industrial area is located SE of the measuring site. This turned out to be the main cause of high concentrations during this SE regime. Persistent inversions, which characterise the SE regime only, disable vertical air mixing and ventilation.

High particle concentrations during radiative regime are result of very stable weather conditions without rain and/or significant wind speed, which are typical for high pressure field.

Low concentrations during NW regime suggest a dominant influence of local topography (Medvednica mountain is located NW of measure site). Low particle concentrations can also occur due to the cold advection during a warm part of a year. This process is favourable for the development of turbulence. As a result, a convective clouds are formed and rainy weather occurs. Both, intensive air mixing and rain, which washes out the particles, dilute the particle concentrations.

Significant horizontal and vertical air mixing are the main causes of low particle concentrations during the windy regime. This regime is characterised by cold advection.

Precipitative regime is characterised with convective processes with pronounced particle lift-up, and formation of clouds and rain. These processes wash out particles from the atmosphere. Therefore, low particle concentrations are expected.

Particle concentrations during g regime are low compared to the radiative regime from which g regime was extracted. Ridge of high pressure has no characteristics typical for the radiative regime. During the g regime, cloudy and rainy weather conditions are persistent, which results in low particle concentrations.

Lower maximum values of particle concentrations and wide quartile range (C_{75}-C_{25}) in SE regime, opposite to the radiative regime, are evident from picture 3. Persistent inversions do not allow pollution input from outside of inversion region. This distribution is the characteristic of SE regime only, and confirms the hypothesis of permanent particle advection from the industrial area.

CONCLUSIONS

The level of suspended particle concentrations depends on weather types. Knowledge of weather type enables a rough prediction of concentration level of airborne particles.

Investigation shows high particle concentrations during a stable weather conditions, long-lasting inversions and advections from SE. On the contrary, low particle concentrations occur during significant vertical and horizontal air mixing, convective processes, as well as during the cloudy and rainy weather.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

BROADBAND EXTINCTION SPECTROSCOPY TECHNIQUE FOR REMOTE SENSING OF AIR POLLUTION

A Borghese*

ABSTRACT

A novel instrument is described, which constitutes a versatile tool for remote sensing of most gaseous pollutants and suspended aerosols of environmental interest.
It works on the operating principle of spectrophotometry, which measures the spectral attenuation of broadband light travelling across open paths of atmosphere. The spectral coverage extends from far ultraviolet ($\lambda \approx 200$ nm) down to near infrared ($\lambda \approx 1100$ nm), as determined by the spectral emission of a special light source, the point-like plasma resulting from laser-induced optical breakdown[1].
The technique operation has been demonstrated in a lab-scale configuration[2] to allow the remote, istantaneous and multi-species detection of both gaseous and aerosol pollutants, such as NO_2, SO_2, O_3 and elemental carbon (EC), organic carbon (OC), ammonium nitrates/sulphates, respectively, as well as of ambient temperature and relative humidity.
Applications have been so far carried out on different length scales at once, ranging from A) below 10m-long optical paths for the detection of exhausts emissions of cars and combustors, B) short-range (10m-100m) open path recordings of traffic pollutants and tropospheric O_3 daily evolutions, up to C) medium-range (100m-1000m) sounding of NO_2 and water vapor concentrations.
The instrument, currently under development for field campaigns, can be quickly tailored as well for applications of 2-D wide-area monitoring of air pollution in urban, residential and industrial sites, with the aid of a network of passive retroreflectors.

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INDEX TERMS

Remote sensing, Ultraviolet extinction spectroscopy, Particulate matter

STATE-OF-THE-ART

Standard or žreference' methods for detection and measurement of air pollutants rely mostly on sampling-based point-sensors, basically a set of instruments for the chemical analysis of air samples, each dedicated to a single species. Although highly sensitive and accurate, such methods suffer from the needs of local sampling, off-line analysis and time-delayed results, as well as high investment and maintenance costs.

On the other hand, more advanced methods are increasingly being considered, which are based on optical techniques and show more powerful features of local and wide-area remote sensing, real-time, multi-species detection, along with very high benefits/costs ratios. Last-generation passive/active spectrophotometers , on one side, and laser-based Lidar sensors, on the other, constitute typical examples of advanced air quality monitors.

However, both still present some limitations, due to their operating principles, since they are sensitive either to particles (e.g. sun spectrophotometers, Mie Lidars) or gases (e.g. Dial, Doas), in any case only to a limited number of species.

Here, we report on a measurement principle and technique, based on the well-assessed extinction spectroscopy, aimed at extending the operating specifications of conventional spectrophotometry, on one side, and of DOAS-like sensors, on the other side, featuring in addition some properties of Lidar techniques.

BROADBAND EXTINCTION SPECTROSCOPY TECHNIQUE

The Extinction Spectroscopy technique is based on the Lambert-Beer law, which relates the light intensities at wavelength λ, respectively incident $I_0(\lambda)$ and transmitted I_T, across a medium of lenght L along the propagation axis of the light. Its simplest formulation has the expression:

$$I_T(\lambda) = I_O(\lambda) \cdot \exp(-\alpha_{EXT}(\lambda) \cdot L) \quad (1)$$

where $\alpha_{EXT}(\lambda) = \alpha_{ABS}(\lambda) + \alpha_{SCA}(\lambda)$ is the extinction coefficient of the medium, and $\alpha_{ABS}(l)$ and $\alpha_{SCA}(l)$ are the absorption and the scattering contributions to $\alpha_{EXT}(\lambda)$.

The experimental measurement of the two spectra $I_T(\lambda)$ and $I_0(\lambda)$ allows one to retrieve from Eq.(1), given L, the spectral distribution of the extinction coefficient $\alpha_{EXT}(l)$.

In turn, this quantity can be expressed in terms of the number concentrations N_i and the extinction cross-sections $s_i(l)$ of the species involved:

$$\alpha_{EXT}(\lambda) = \Sigma_i N_i \cdot \sigma_i(\lambda) \quad (2)$$

Actually, for size-polidispersed particles populations , the term $N_i \cdot \sigma_i(l)$ is replaced by an integral expression over the size distribution function.
The values of the number concentrations N_i of the individual species can be retrieved by means of an inversion procedure (i.e. solution of the 'inverse problem'), once the $\alpha_{EXT}(\lambda)$ has been measured experimentally and the identity of the species is known, in terms of the absorption cross-sections $\sigma_i(\lambda)$ of the gaseous species and of the complex refractive indexes of the particles populations.
To solve the inverse problem means to find the solutions of a Fredholm integral equation of the second kind, which constitutes an 'ill-posed' problem. However, it can be treated by using numerical procedures of errors minimization and solutions regularization, as well as imposing constraints of mathematical and physical nature to the solutions.
The Extinction Spectroscopy technique is used in a variety of schemes and applications, e.g. the Atomic Absorption Spectroscopy, the Sun Spectrophotometry, the Differential Optical Absorption Spectroscopy, etc.
The technical configuration of the Broadband Extinction Spectroscopy technique, reported on here, has the peculiar features of providing quantitative, istantaneous, remote and simultaneous multi-species measurements of both gaseous pollutants and particulate matter concentrations; in the latter case, it provides in addition estimates of the size distribution functions of aerosols with different chemical compositions.

THE REMOTE SENSOR

A. THE TRANSMITTER

According to the operating principle outlined above, the technique requires a transmitter TX of a broadband light source, with an outgoing emission spectrum $I_O(\lambda)$, and a receiver RX of a transmitted spectrum $I_T(\lambda)$, resulting from the optical attenuation through a prefixed open path in the atmosphere.
In conventional spectrophotometers, the light source is either natural (e.g. sun, moon, stars) or an arc-lamp, typically a high-pressute Xe lamp. In the present case, the light source is a very hot, bright and short-lived plasma, resulting from the laser-induced optical breakdown of a gaseous medium. The emiiting plasma shows the following peculiar characteristics : A) a broadband spectral continuum, extending from deep ultraviolet ($\lambda \approx 200$ nm) down to near infrared (($\lambda \approx 1000$ nm), corresponding to a plasma peak temperature of nearly 100,000 K; B) a point-like spatial extension, with size $d \approx 300\ \mu m$ and a volume $v_{\xi} \approx 10^{-2}$ mm^3; C) a temporal duration $t_d \approx 50$ ns (FWHM) and risetime $t_r \approx 3$ ns. The above mentioned features, considered individually or as a whole, constitute premium factors for the operating specifications of the measuring system.
The source system is constituted by a Q-switched Nd-YAG compact laser head, a short-focal-lenght focusing lens, a paraboloidal mirror for collimating and launching the probe light.

B. THE RECEIVER

The receiver RX collects the light transmitted over the measuring path, by means of a paraboloidal mirror, provides its spectral dispersion by means of either diffraction gratings or quartz prisms, and acquires and stores the corresponding spectra by means of an intensified and gatable CCD.
The operation with diffraction gratings is typical. However, the use of small-angle quartz prisms for spectral dispersion, not discussed here, provides important advantages over the conventional grating-based schemes.

C. THE INTEGRATED SYSTEM

In a reference configuration, the transmitter TX and the reicever RX are positioned at opposite ends of the optical path, of given length L. However, in pactical schemes the two parts reside in the same assembly and use is made of a retroreflector, placed on the far side of the optical path, in order to fold the light beam, coming from the transmitter, back to the receiver.
This second configuration is much more practical and feasible, since it involves a precious compactness , and in addition it provides an increased sensitivity, for a given length L, due to the round trip of the measuring light.
The main drawback of the configurations cited above is the difficulty or even the impossibility of acquiring the reference (or incident) light $I_O(\lambda)$, as well as instrumental response and efficiencies..
A third configuration is preferred, which involves the use of two retroreflectrors RR_1 and RR_2, positioned respectively at the two distances L_1 e L_2 ($L_1 < L_2$). As a result, it can be easily shown that the extinction coefficient $\alpha_{EXT}(\lambda)$ is given by

$$\alpha_{EXT}(\lambda) = 1/2(L_2 - L_1) \cdot \log (I_1/I_2) \qquad (3)$$

wherein there is no dependence on $I_O(\lambda)$ and on instrumental factors, since they cancel out by properly aligning the retroreflectors on nearly the same optical path.
Equation (3) constitutes the working relationship of the measuring system.
The extension of the technique to a number of retroreflectors greater than two is immediate and opens up the possibility of single-shot, space-resolved measurements, averaged over optical paths of length $(L_{n+1} - L_n)$, with n=1, 2, 3… belonging to the same radial direction.
Finally, the disposition of more such groups of retroreflectors at different horizontal angles allows 2-D spatial mapping of areas, as wide as several squared kilometers, just by means of one central sensor.

D. SPECIFICATIONS

The optical technique described here can detect remotely and measure quantitatively the number and mass concentrations of both

a) gaseous species, such as. NO, NO_2, SO_2, O_3, O_2, NH_4, H_2O and
b) particulate matter, namely: elemental carbon, organic carbon, ammonium nitrates/sulphates, water (haze), dispersed in the size range 3 nm – 3,0 μm.

The detection sensitivity varies for individual species, as it is a function of the values of the absorption/extinction cross-sections and of the optical path length L.

E. APPLICATIONS

As of this writing, a number of applications has been already demonstrated in a variety of measuring schemes, which can be categorized according to the extent of spatial ranges accessed.

Preliminary measurements have been carried out over path lengths of few up to tens of meters, in a composition-controlled, confined atmosphere, in order to check the system specifications in a gaseous medium with well-known species concentrations, as shown in Fig. 2 .

Next, investigations have been carried out over optical paths of few meters, on the air-diluted exhausts, flown in the optically explored pipe shown in Fig. 2, and emitted by internal combustion engines of vehicles, driven at the chassis dynamometer. Such measurements have led to the time-resolved detection of nitrogen oxides (NO and NO_2) and carbon-containing particles (EC and OC) as combustion by-products, in a variety.of operating conditions and of vehicle typologies and engines, thus providing useful emission data bases for subsequent inversions in unconfined urban atmosphere.

Main applications of concern to this Conference refer to the measurement of some relevant atmospheric pollutants in urban areas. Ozone, organic carbon, elemental carbon and nitrates/sulfates particles have been detected (see Fig. 3) and their temporal variations have been followed over full day cycle as well as over a much longer time range (two weeks). Figure 3 reports on the extinction spectra in the wavelength range 200 nm – 500 nm integrated over a 200-long optical path of urban atmosphere. The experimental extinction spectrum turns out to be fitted fairly well by an inverted spectrum, contributed A) by a number of known gaseous and particulate species, each at the indicated concentration, and B) by a class of organic nanoparticles, as observed in flames and at the exhausts of combustion systems (see Fig. 4).

We are currently planning and preparing field campaigns, aimed at demonstrating the 2-D mapping capabilities of the remote sensing technique, reported on here.

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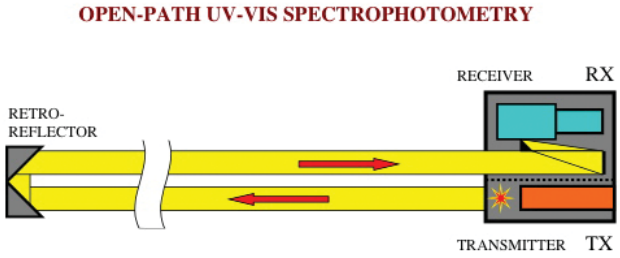

Figure 1. Optical Lay-out of the Remote sensor, including the Transmitter and the Receiver (on the right side) and a Retroreflector at a distance L (on the left side)

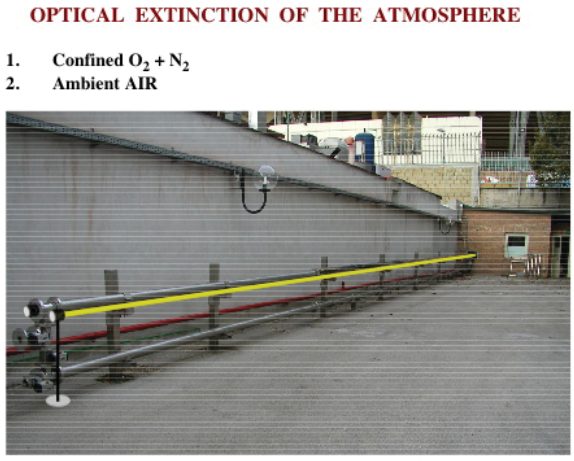

Figure 2. Photograph of the apparatus for optical studies on confined and composition-controlled atmospheres. The yellow line indicates the optical path in unconfined atmosphere.

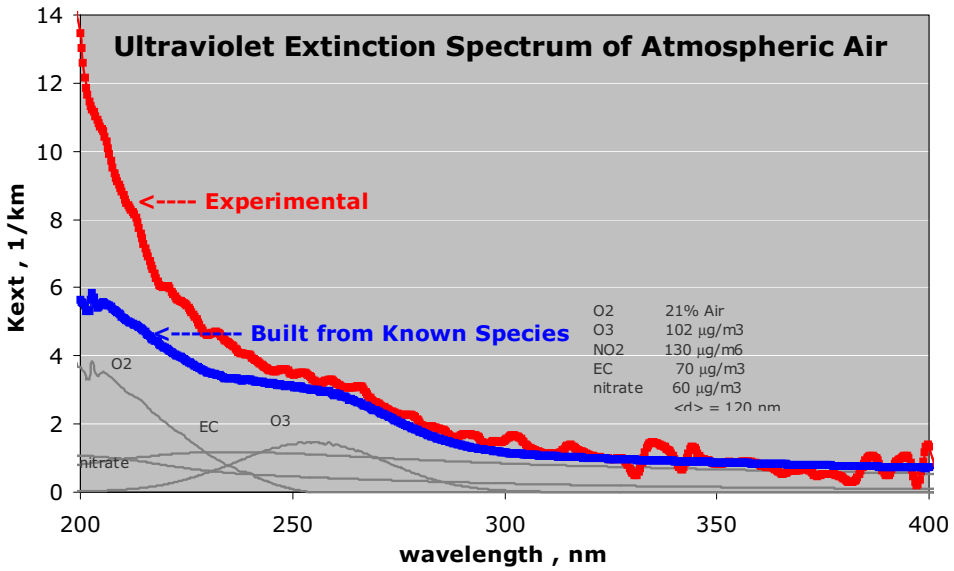

Figure 3. Experimental extinction spectrum (red) of urban atmosphere, integrated over 200 m. The spectrum contributed by known species id shown in blu. Individual contributions are shown in gray.

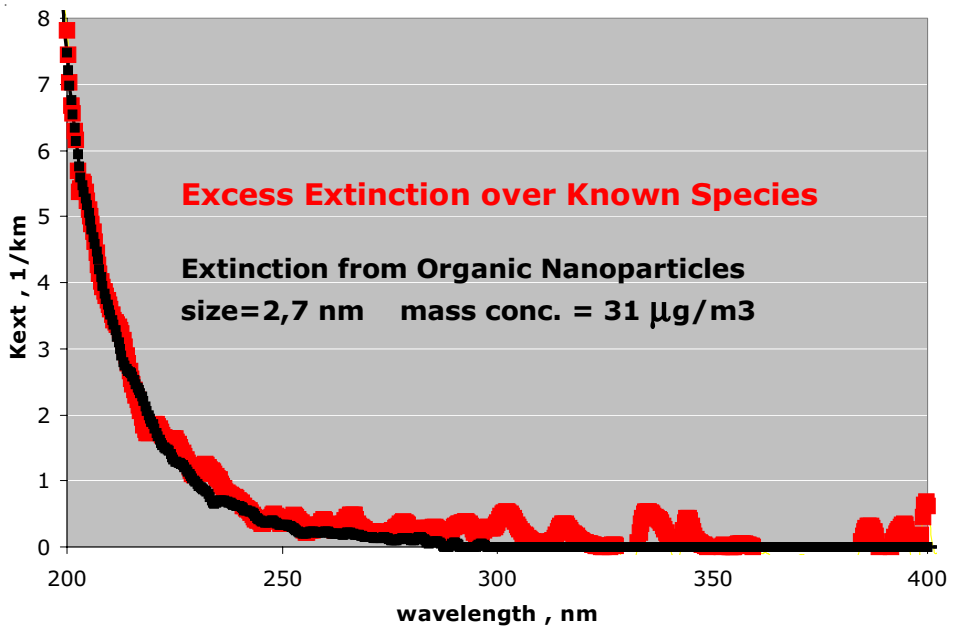

Figure 4. *Excess* extinction spectrum (red) over that due to known species, compared with that of organic carbon nanoparticle, as observed in flames and combustion systems.

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MONITORING OF MERCURY AND OTHER HEAVY METALS DEPOSITION IN SAVONA (ITALY)

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ABSTRACT

This work presents some information on heavy metal monitoring data collected at the Italian Mediterranean Riviera. Atmospheric trace metals (Co, Cd, Cu, Ni, Pb, Hg and Zn) concentration in air (particulate) and in rain water (particulate and dissolved) in a North-West Italy coastal town were monitored for 17 months. The highest trace metal concentration in aerosol samples are linked to particular anemological conditions, and can be related to local or long range transport processes. On the other hand, highest levels in rain samples are associated with small rainfall events, and do not significantly depend on the wind direction.

INDEX TERMS

Air pollution, atmospheric deposition, dry fluxes, rainwater pollution, trace metals, wet deposition.

INTRODUCTION

Heavy metals in the atmosphere derive from anthropogenic (e.g. combustion of fossil fuels and solid wastes, specific industrial emissions) and natural sources (e.g. soil suspension, volcanic emissions).
Due to its volatility mercury has a peculiar role in micro pollutants contamination. Its dominant fraction (> 80%) in the atmosphere consists of volatile gaseous elemental mercury, which can be widely dispersed and transported thousands of

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miles from source emissions, while the remaining fraction is particulate mercury. Heavy metals when either bound to airborne particles or in the gaseous form, are readily removed from atmosphere by precipitation or they are dry deposited to the earth surface giving rise to environmental problems. The input of trace metals from the atmosphere is particularly important for the biogeochemistry of a semi-enclosed sea like the Mediterranean (Guerzoni et al., 1999).
This work presents some information on heavy metal concentrations and deposition fluxes collected in Savona, about midway between Genoa and Nice on the Italian Riviera. The influence of seasonal weather and wind direction has been investigated in order to identify the role of particular local source and long-range transport phenomena.

EXPERIMENTAL

This study was performed in Savona, a town of 60,000 located on the coast of the Ligurian Sea about 45 km west of Genoa (Lat. 44° 18' 25"N; Long. 8° 28' 49"E). The location of the measurement site is represented in Fig. 1. Measurements were taken at the Interuniversity Centre of Environmental Monitoring Research (CIMA) of the University of Genova. The Centre is situated in a residential area at about 5 km from the town centre and 5 km from a coal power station. A highway runs at a few hundreds meters from CIMA; the Mediterranean Sea is at about the same distance. The sampling station was set up at about 6 m above the ground.
Air samples were collected by means of a high volume sampler with a flow of about 30 l min^{-1} and were filtered through Nucleopore filters with a pore-size of 0.45 mm. Rain samples were collected by exposing to the rainfall a funnel (with surface area of 0.05 m^2) connected to a 7.5 l bottle. Rain samples were filtered on 0.45 mm pore-size filters. Particulate collected on filters and filtered rainwater were analysed separately. The station was equipped with standard meteorological

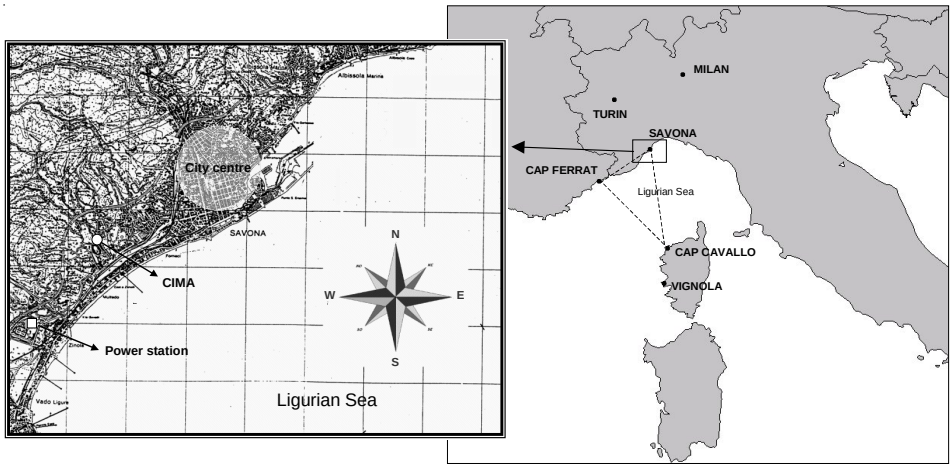

Figure1. Location of Savona and other Ligurian Sea sampling sites

instrumentation to monitor wind direction, wind speed, humidity and temperature. Instantaneous wind direction and wind velocity were elaborated by a computer to give hourly averages. Air and rain samples were analysed for Hg, Zn, Cd, Co, Cu, Ni and Pb. Prior to analyses, aerosol and rainwater filters were treated with 50 ml of deionised water, added with 5 ml of sulphuric acid and 5 ml of nitric acid in an ultrasonic shaker for two hours. Measurements of heavy metal content were performed with a 746 VA Metrohm Trace Analyzer polarographic instrument equipped with a Metrohm 747 VA Stand.

RESULTS AND DISCUSSION

Table 1 list averages and standard deviations of aerosol concentration data collected over one-month periods from May 2000 to July 2001 for all metals considered in this work (Hg, Zn, Cd, Co, Cu, Ni and Pb). Zn and Hg present the highest average concentrations, while Cd and Co show the lowest levels. Table 2 reports data on heavy metal concentrations in rain water. Town and highway vehicular traffic, sea and the power plant located 5 km South West of the sampling site are the major local source of heavy metal pollution for the town of Savona. Each source contribution can be evaluated through the analysis of measured heavy metal concentrations in relation to the daily prevalent wind direction:

i) when wind prevalently blows from North-North West (generally for about 16-20 hours per day) heavy metals produced by anthropogenic sources (i.e. Cd, Zn, Hg, Zn and Cu) show peaks that can be ascribed to emissions from the industrial region located North of town or, considering transport mechanisms at longer scale, from towns and industries of Piemonte and Lombardia regions or France;

Table 1. Monthly averages and standard deviations of heavy metal concentrations in air (ng Nm^{-3}).

	Zn		Hg		Pb		Cu		Ni		Cr		Co		Cd	
	mean	sd	mean	sd	mean	sd	mean	sd	mean	sd	mean	sd	mean	sd	mean	sd
May 2000	428	320			80	80	39	21	88	43	39	22			0.2	0.0
June 2000	518	278	181	63	49	32	45	18	87	49	36	22			1.0	0.1
July 2000	304	154	111	27	66	39	45	25	51	39	20	10			0.9	0.2
August 2000			94	29	95	9	34	11			62	9			0.7	0.2
September 2000	278	162	25	29	51	15	54	32	56	31	46	21			1.0	0.6
October 2000	288	156	3	2	48	13	58	30	45	19	19	7			1.3	0.5
November 2000	159	111	23	20	26	11	18	12	25	18	12	6	0.5	0.5	0.6	0.5
December 2000	53	27	13	12	21	7	10	5	28	22	4	1	3.5	3.1	0.5	0.4
January 2001	157	95	2	1	30	13	40	23	31	18	5	1	0.1	0.0	1.5	0.4
February 2001	197	120	5	4	45	27	29	10	21	21	7	2	2.9	0.8	0.6	0.5
March 2001	174	105	13	13	32	13	22	11	18	14	5	2	0.4	0.9	0.3	0.3
April 2001	471	264	218	219	98	28	126	121	70	53	19	23	0.2	0.1	1.1	0.2
May 2001	471	277	188	236	72	32	67	52	52	33	47	24	4.2	3.5	0.9	0.5
June 2001	533	365	202	189	61	14	77	29	68	26	38	27	3.7	6.4	1.1	0.6
July 2001	612	393	211	98	81	13	64	9	88	32	72	58	2.1	1.3	1.0	0.7
June 2000- May 2001	279		73		53		46		44		23		1.7		0.9	

Table 2. Heavy metals concentrations in rain water (mg l^{-1})

Rain event	Rain height (mm)	pH	Cd (µg/L)		Pb (µg/L)		Cu (µg/L)		Zn (µg/L)		Ni (µg/L)		Co (µg/L)		Hg (µg/L)	
			F	P	F	P	F	P	F	P	F	P	F	P	F	P
1	2.9	n.d.	n.d.	n.d.	n.d.	n.d.	82	226	942	2581	n.d.	n.d.	n.d.	n.d.	0.8	2
2	35.6	n.d.	n.d.	n.d.	n.d.	n.d.	55	150	493	1350	n.d.	n.d.	n.d.	n.d.	0.7	2
3	0.55	n.d.	n.d.	n.d.	n.d.	n.d.	173	475	2101	5757	n.d.	n.d.	n.d.	n.d.	0.5	1
4	1	4.3	0.4	1	12	32	591	1618	184	504	10	29	0.0	n.d.	3.1	8
5	1.8	6.3	0.7	2	6	17	62	171	111	303	6	15	0.0	n.d.	2.0	5
6	1	6.5	0.6	2	2	5	191	522	105	287	7	18	1.7	5	0.3	1
7	30	5.9	0.7	2	3	8	174	477	100	273	2	6	n.d.	n.d.	0.7	2
8	40	6	0.4	1	3	8	22	60	81	223	1	3	2.1	6	0.5	1
9	110	6.8	0.2	0	29	79	48	131	278	761	n.d.	n.d.	5.3	15	6.5	18
10	20	6.2	0.2	1	21	58	39	106	267	732	22	60	0.7	2	3.7	10
11	120	6.7	0.6	2	11	30	14	37	203	555	23	62	1.8	5	8.0	22
12	120	6.7	0.6	2	21	57	36	98	197	540	8	21	1.3	4	2.3	6
13	5	6.1	0.4	1	17	46	138	378	172	472	5	15	0.8	2	0.6	2
14	20	6.5	0.3	1	17	48	52	141	205	561	39	107	0.0	0	8.5	23
Average	36		0.4	1	13	35	120	328	388	1064	12	34	2	5	3	7
Standard deviation	36		0.2	0.5	9	24	148	406	541	1484	12	33	2	4	3	7

Legend: F: filtrate; P: particulate; n.d.: not determined.

ii) when the wind blows from the South for more than 12-15 hours per day or has a strong component from east, higher levels of Hg, Co, Ni and Cd are detected. This fact can be ascribed to the high Hg and Cd and other metals content of the sea spray ("maritime effect", GESAMP, 1989), generated by bubble bursting processes, which brings aerosol coming from the sea surface micro-layer, which is enriched in trace metals respect to the bulk sea water, into the atmosphere (Cambray et al., 1975);

iii) it is not possible to evaluate the specific contribution of the power plant, although it seems to affect atmospheric base levels because wind is seldom coming from South West. When the wind is from South-South East, the global circulation has a cycling character, which may enable an air mass circulation above some continental industrialised areas located in the North West of Italy (Lombardia and Piemonte) before transiting over the Ligurian sea.

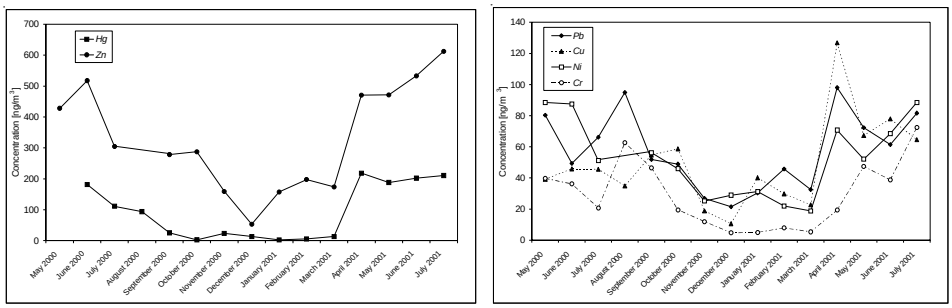

Figure 2. Time series for heavy metals monthly average concentrations

Typical seasonal patterns of heavy metal concentration in air are shown in Fig. 2, which reports the evolution over time of monthly average concentrations of Zn and Hg in air daily samples. All other metals show similar patterns. Lowest concentration levels are observed in autumn and winter, while highest concentrations are measured in late spring and summer. This is in agreement with studies carried out over the western Mediterranean Sea reporting that concentrations exhibit a seasonal pattern inversely related to the frequency and the amount of rainfall such that the highest concentrations are observed between May and October (GESAMP, 1989). During these months dry weather conditions with low wind intensity and air circulation prevail over rainy periods. Under these conditions local sources (i.e. vehicular traffic, maritime effect, and power plant) may cause high atmospheric concentrations.

As previously observed by Georgii et al. (1984) and Ambe and Nishikawa (1986), concentrations are highest during the initial stages of a rainfall event and consequently in small events. The changes in concentration during a single event were not determined in this study, but a wide range of precipitation volumes were collected from individual events, allowing to point out the relationship between rain volume and rain water concentration. The variation of the sum of all trace metal concentrations considered in this study with the rain volume (express in term of height of precipitation, mm) is plotted in Fig. 3. It can be observed in this figure that higher concentrations are associated to smaller rainfall events. According to Baeyens et al. (1990) the hyperbolic-like relationship obtained by plotting concentration in rain versus precipitation volumes (Fig. 3) reflects the fact that the higher the precipitation volume is, the more the dissolved metal concentration in rain water will tend to the initial or cloud vapour concentration.

However, the hyperbolic relationship suggests that the maximum scavengeable amount is reached immediately after rain started. As far as trace metal deposition per event is concerned, the greater volume tends to compensate for the lower concentration and the highest depositions are generally observed with the largest.

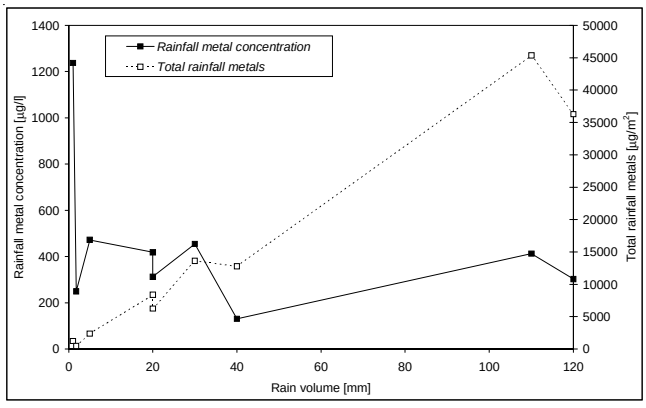

Figure 3. Relationship between trace metal concentration and deposition with rainfall amount

Analysis carried out on the particulate collected with rain samples shows that for metals such as Cu, Pb, Zn and to a lesser extent Ni, mostly originating from anthropogenic sources, wet inputs are essentially in dissolved form, particularly under pH values of 5 (the insoluble fraction in rain water is generally less than 5%). In contrast with the results of Pleij and Munthe (1995), Hg was prevalently found in the particulate form, rather than in the dissolved form. This result can be explained by the proximity of the power plant to the sampling station and because particulate Hg falls down to the soil very close to the emission source, whilst gaseous mercury can be transported up to several (hundreds to thousands) kilometres. Previous studies performed at Cap Ferrat and Tour du Valat in France (Guieu et al., 1997), and at Vignola, Cap Cavallo and other sites in Corsica (Migon et al., 1993) may be used together with data collected in this work to characterise heavy metal pollution in the Ligurian Sea (see Fig. 1). A comparison of data collected in this work and data reported for other sites in the Ligurian Sea is made in Table 3. Concentration levels found in Savona are higher than those reported for other coastal sites of the Ligurian Sea. Levels measured in this work agree with those reported for other coastal sites, and are generally higher than those found in other urban sites, in particular for those metals whose reemission from sea surface due to the maritime effect is not negligible (ATMOS, 1984).

Table 3. Heavy metals concentration in the air (ng Nm^{-3}) and in rain water ($\mu g\ l^{-1}$) in northwestern Mediterranean sites

	Air concentration			Rain water concentration	
	Cap Ferrat[a,b]	Cap Cavallo[a]	Vignola[a]	Cap Ferrat[b]	Tour du Valat[b] (France)
Cd	0.28-0.36	0.66	0.11	0.11-0.45	0.14±0.28
Co	0.17	-	-	0.04	0.2
Cu	3.6-6.2	2.1	1.9	2.15-3.1	1.3±1.2
Hg	-	-	-	-	-
Ni	2-2.8	-	0.97	0.34-0.76	0.5±0.5
Pb	32.7-58	15.9	8.8	2.7-4.6	2.2±2.9
Zn	26.9-41	19.1	11.8	8.6	7.0±8.6

[a] Sandroni and Migon, 1997
[b] Guieu et al., 1997

A detailed analysis of each metal level shows that average values of Cd and Co concentrations and ranges of variability are similar to those reported for other coastal sites, though slightly higher than those reported for other urban sites. Cu and Ni concentrations agree with levels reported for other urban atmospheres. Hg and Zn rain contents are markedly higher than other sites. In particular, Hg data collected in this work are one order of magnitude higher than values commonly quoted in the literature. Pb concentrations are in the range of values reported for both urban and coastal sites.

CONCLUSIONS

This study presents data regarding air and rainwater quality in a town in the North Mediterranean coast of Italy. Results are comparable to those reported for other urban and/or coastal sites, although Zn and Hg present higher levels are comparable to those sometimes found in industrial areas. An analysis of the anemological characteristics of the sampling sites in relation to the potential contamination sources, shows that the highest concentrations of heavy metals (Hg and Zn in particular) detected in this study are due to long distance transport effects. As large ranges of variability were found, it can be pointed out that heavy metals presence is highly influenced by meteorological and anemological conditions. During later spring and summer high atmosphere stability and low wind velocity are more frequent and rain events decrease markedly in number, promoting particles settling from the upper layers of the atmosphere and resulting in higher levels of concentration respect to winter and autumn ones, as experimentally proved in this work.

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ANALYSIS OF AIRBORNE MICROORGANISMS IN THE SURROUNDING OF COMPOSTING FACILITIES

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ABSTRACT

Emission and dispersal of microorganisms and odours from composting plants were studied in a 3-year project at nine different composting plants in Germany. Measurements were carried out under so called *'normal-case'*, i.e. typical local climate conditions and working activities within the plants, and *'real worst-case'* conditions ('drainage flow' conditions) being characterized by the translocation of cold air mostly a night containing large amounts of bioaerosols. Highest concentrations of microorganisms were observed during turning of compost with a maximum of 2.4 x 10^6 cfu m^{-3} for thermophilic actinomycetes. The other groups of microorganisms were detected in concentrations of about 10^5 cfu m^{-3}. During shredding of fresh organic material the concentrations of all microorganisms reached 10^4 cfu m^{-3}. Here odour concentrations turned out to be highest (up to 1,367 odour units (OU) m^{-3}). At plants equipped with a biofilter (odour reduction) a decrease in OU by a factor of 10 was observed. In the surrounding of the plants, highest concentrations ranged between 10^1–10^3 cfu m^{-3} upwind and from 10^1 - 10^4 cfu m^{-3} downwind. The specific local meteorological situations must be considered carefully in advance and during sampling. Especially 'drainage flow' situations can lead to high microorganism concentrations (> 10^4–10^5 cfu m^{-3} of thermophilic actinomycetes and thermophilic fungi) in the surroundings of composting plants.

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INTRODUCTION

Microorganisms and odour emissions from composting plants are regarded as a nuisance, especially for residents living close to such plants. Composting plants and waste treatment plants in general can emit high numbers of pathogenic and non-pathogenic microorganisms of different groups and taxa. Microorganisms can cause allergies, be infectious or may produce toxins. Therefore, emissions from composting facilities are critically evaluated and regarded as potential health hazards by residents being exposed to bioaerosols and odours. With respect to specific local climatic conditions, concentration of microorganisms and odours, as well as the odour perception and the presence of MVOC were studied in a 3-year project at nine different composting plants and in their surroundings in Germany. Measurements were carried out at several facilities differing in their type of process engineering and topography of the landscape. The dispersal of microorganisms and odours was studies depending on activity within the plant, wind direction, wind speed, and microclimatic circumstances.

MATERIAL AND METHODS

In 2000 and 2001 sampling of airborne microorganisms, microbial volatile organic compounds (MVOC) and assessment of odour perception was performed at nine different composting plants and in their surrounding. Sampling within the plants was performed during activities such as turning and sieving of compost but also at static piles and biofilters. Sampling sites in the surrounding of the plant were situated in increasing distances from the plants, either downwind in the prevalent wind direction or in the direction of residential estates.

Sampling, identification, and quantification of airborne microorganisms

Airborne microorganisms were sampled in four replicates using Sartorius MD-8 sampler (Sartorius, Germany) equipped with gelatine filters (3 μm pore size) on days with low air humidity and All Glass Impinger (AGI 30) at times with higher air humidity. Gelatine filters were transferred to 10 ml of sterile 0.9% NaCl with 0.01% Tween 80 on site. The tubes containing the gelatine filters were transported to the laboratory and kept in the refrigerator overnight at 4°C. On the next day the gelatine filters were melted in a water quench at 35°C. The air samples were plated by dilution in steps up to 10^{-4} on different media: 1. Cfu of mesophilic fungi were assessed on dichloran glycerol 18% agar (DG 18, Oxoid) with 100 ppm chloramphenicol after 7 days of incubation at 25°C. 2. Thermotolerant fungi were assessed on malt-extract agar (MEA) at 45°C after 3 days of incubation with Petri dishes packed in plastic bags. 3. Actinomycetes were quantified on glycerin-arginin agar with cycloheximid after incubation at 50°C for 14 days. 4. Bacterial counts were assessed on casein soja peptone agar (CASO, Oxoid) agar at 36°C after 7 days of incubation.

Measurements of odour intensity emitted from sources within composting plants

Air samples of both raw and cleaned air were taken in polycarbonate foil sampling bags (Kalle, Wiesbaden, Germany) and analyzed by 'olfactometry' according to the German guideline VDI 3881 (Anonymous, 1986a; 1986b; 1987; 1989). Samples were analysed by using a TO 6 olfactometer (Ecoma Emissionstechnik und Consult Mannebeck, Honigsee, Germany). The odour threshold value of air samples was determined by stepwise dilution with pure air. The maximum dilution that can provoke a malodour is defined as 1 odour unit (1 OU). The odour concentration was measured in OU m^{-3}. The numerical value of the odour concentration is thus a multiple calculated from the odour threshold value.

Chemical analysis and exposure assessment of MVOC

Exposure assessment of MVOC was performed at three out of nine plants. Seven compounds were analysed and quantified, i.e. 3-methylfuran, 3-methyl-1-butanol, dimethyldisulfide, 2-heptanone, 1-octen-3-ol, 3-octanone, 3-octanol. Samples were sorbed on Orbo 92 by active sampling (0.5-1 L min^{-1}) using suction pumps (SKC 224PCXR7 and SKC 224PCXR8) and elution was done by ultrasonic treatment in 500 μl dichloromethane for 30 min. Samples were analysed by gas chromatography (Hewlett Packard, HP 5890 Series II) in combination with mass spectrometric detection (Hewlett Packard, MSD 5972). The column was a Restek DB-VRX.

RESULTS

Concentration of microorganisms in air

On sampling sites within the facilities concentrations of airborne microorganisms ranged between 10^2 and 10^5 cfu m^{-3}. Lowest values were mostly found on the biofilter whereas highest values were found during turning of compost. In most cases, concentrations of bacteria (36°C) and actinomycetes (45°C) exceeded those of mesophilic (25°C) and thermotolerant fungi (37°C), but on the biofilters the different groups of microorganisms were mostly found in similar concentrations. During sieving, concentrations of thermophilic actinomycetes (45°C) ranged one order of magnitude higher than those of thermotolerant fungi (37°C), whereas during turning of compost the thermotolerant as well as the mesophilic (25°C) fungi and the bacteria (36°C) exceeded the numbers of actinomycetes one order of magnitude. In distances up to 300 m, numbers of bacteria and mesophilic fungi were found to be 2 to 3 orders of magnitude lower compared to the concentrations near the sources of emission. Concentrations of bacteria slightly decreased further in distances greater 300m and ranged three orders of magnitude below the emission values in 800m distance. Thus, concentrations reached values measured at the reference sites in upwind direction. Concentrations of thermotolerant fungi and thermophilic actinomycetes were 1 to 2 orders of magnitude lower in distances of up to 300 m, 2 to 3 orders of magnitude were

reached in distances greater 300m (Fig. 1). In most cases, concentrations of thermophilic miroorganisms in distances > 300m were similar to those found at reference sites, with a few exceptions concerning the numbers of thermotolerant fungi. The results presented for plant 3 (Fig. 1) are representative of those found in other facilities.

Emission of odour compounds from biofilters and diffuse sources

Biofilters of three composting facilities had been investigated for the reduction of odours by comparing odour concentrations in raw and cleaned air. In *plant 1, 2*, and *3* odour concentrations in raw air ranged between 1,000 and 10,000 OU m^{-3} (odour units), in cleaned air between 100 and 1,000 OU m^{-3} (Fig. 2). In most cases, the biofilters reduced odour concentrations by 1 to 1.5 orders of magnitude. In the facility *3* odour concentrations emitted from diffuse sources, i.e. the compost pile and during sieving, ranged between 10 and slightly above 100 OU m^{-3}. Thus, odour emission from biofilters slightly exceeded that of diffuse sources (Fig. 2). However, in facility 5 it turned out that odour concentrations emitted from piles and during sieving varied depending on the degree of decomposition and type of activity. Sieving of fresh compost emitted considerably higher odour concentrations than sieving of ripened compost (Table 1). During turning of the pile highest odour concentrations of 3,979 OU m^{-3} were reached. Depending on the sampling date, in *plant 6* highest concentrations of odours were reached during shredding of biowaste and turning of compost, followed by sieving (data not shown). Considerably lower concentrations (1 to 2 orders of magnitude) occurred at the static pile, which was similar in *plant 5* (Table 1). It can be concluded that in case of emissions from static piles odour concentrations remain below those known for biofilters. On the other hand during activities such as turning of compost, sieving and stacking of piles odour concentrations can be exceeded by 1 to 2 orders of magnitude compared to static piles.

Incidence of odour perception in the surrounding of the plants

In *drainage flow* situations the incidence of odour perception decreased from between 80 to 100 % (25m respectively 50m distance) to below 10% in 870m distance from the plant. In case of thermal airflow, the incidence of odour perception near the plant was lower (50 to 60% in 200 m distance) compared to drainage flow situations and the incidence of odour perception reached 20 to 30% in 870m distance. In case of thermal airflow a typical compost odour was detected in slightly higher percentages even within a near residential area (distance >1300 m).

By comparing *real worst case* and *normal case situations*, it gets obvious that the incidence of odour perception near the plants is higher under *real worst case* conditions.

Under normal case conditions, percentages of odour perception decreased somewhat more slowly with growing distance from the plant.

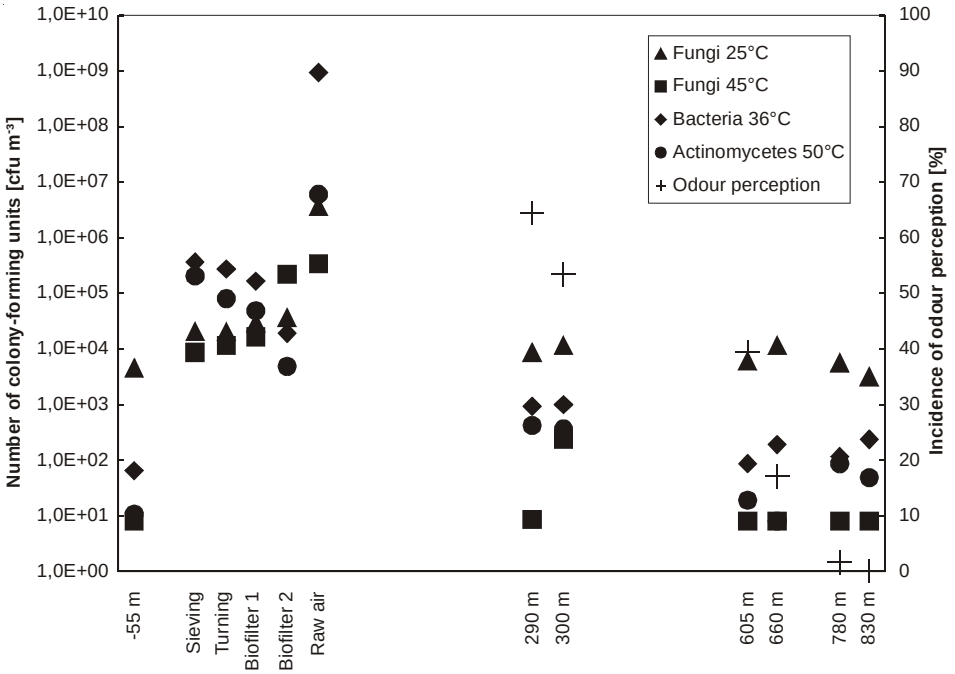

Figure 1. Concentration of airborne microorganisms (Plant 3, 1st sampling on 14 Aug 2001)

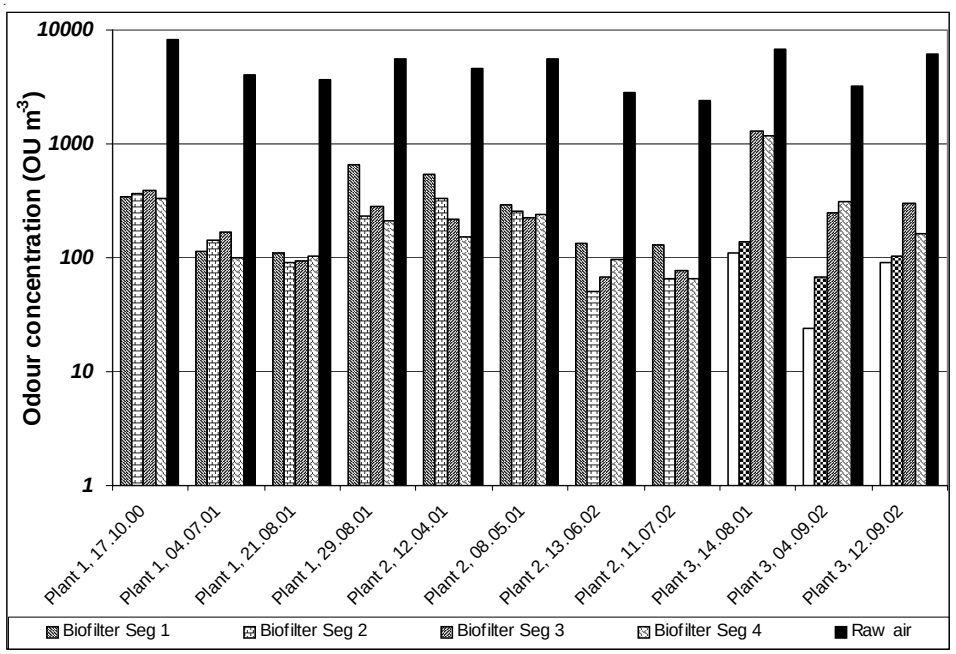

Figure 2. Odour concentrations in raw and cleaned air in the plants *1*, *2*, and *3*. The two columns on the left showing data of plant 3 represent data assessed at compost piles and during sieving.

Table 1. Odour concentrations emitted from different sources and activities in plant *5*

Date of sampling:	25.06.01		01.08.01		26.06.02		10.10.02	
Concentration in [OU m^{-3}]:	Mean value (n=3)	Max.	Mean value (n=3)	Max.	Mean value (n=8)	Max.	Mean value (n=8)	Max.
Sampling site:								
Sieving of ripened compost	414	512						
Sieving of fresh compost			1,137	1,253	4,479	12,274	9,069	16,384
Static pile	56	64	82	99				
Turning of pile	3,000	3,979	809	1,117				
Pile after turning	1,128	1,579	251	256				

Occurrence of MVOC in the surrounding of plant *3*

During the first sampling in plant 3, concentrations of 3-methyl-1-butanol were approximately three-fold higher at the sampling site in 300 m distance than in distances greater than 600 m. Concentrations of MVOC in 600 and 800m distance did not differ significantly (Fig. 3). Concentrations of 2-heptanone did not differ between the different sampling site including the reference site (Luv). During the second sampling in plant 3, highest concentrations of MVOC were found at the sampling sites in greater distance from the facility, although the incidence of odour perception decreased constantly with increasing distance from the plant. Similar data were found for other facilities. Consequently, a causal relation between odour perception/concentration and the occurrence of the specific MVOC measured here seems to be unlikely. This conclusion can not be drawn in general as the number of replicates was relatively low (n = 2 to 4) for each plant.

DISCUSSION

In most cases concentrations of microorganisms reached the level of the reference site in distances above 600 to 800 m. However, cfu numbers of thermotolerant fungi were partly higher at the reference sites compared to the natural background level. It must be taken into account that due to topography and vegetation the reference site at certain facilities was located too close to the plant, so that dispersal of plant specific bioaerosols even in upwind direction can not completely be dismissed. Odour concentrations emitted from static piles remained below those measured for biofilters. However, during activities such as turning of compost, sieving and stacking of piles odour concentrations were exceeded by 1 to 2 orders of magnitude compared to static piles. Consequently, the quality of odour emitted from such plants may change throughout the day, as activities such as turning, sieving and stacking of piles is done during the work day, whereas the biofilter is also working at night. This means that malodorous emissions during drainage flow situations originate mainly from the biofilters, whereas the typical compost odour is perceivable throughout the day. When *real worst case* and *normal case* situations were compared significant differences concerning the incidence of odour

perception in the surrounding of composting plants did not get obvious. The percentage of odour perception near the plants was somewhat higher under *real worst case* conditions, which is obviously due to the meteorological situation. During drainage flow conditions atmospheric layering is more stable (e.g. stability class I) than during the day (e.g. stability class V) and air exchange between different layers of the lower atmosphere is reduced.

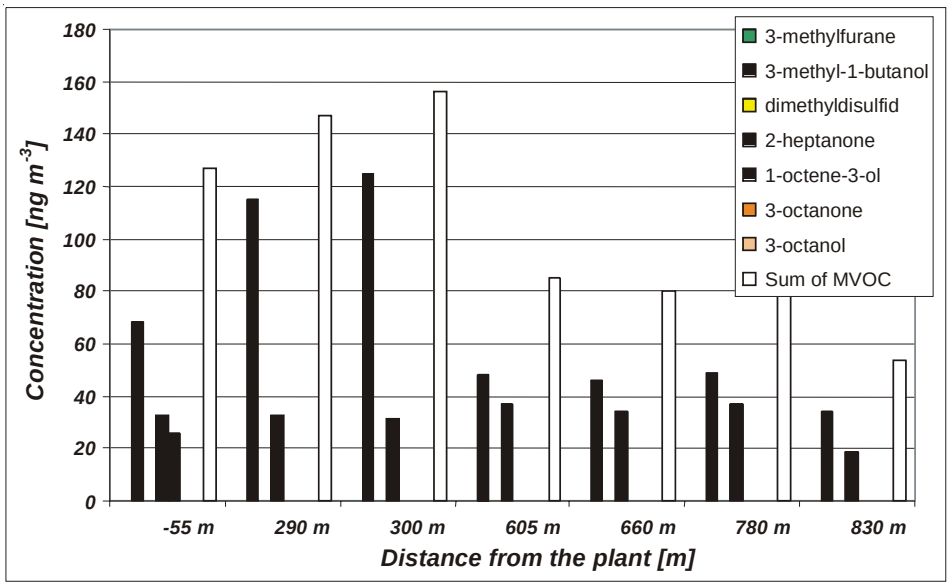

Figure 3. Concentration of MVOC measured at the different sampling sites in the surrounding of plant 3 (1st sampling on 14 August 2001). Only three out of seven compounds were detected: 1-octene-3-ol, 3-methyl-1-butanol and 2-heptanone.

Consequently, percentages of odour perception are likely to be higher as diffusion of malodorous air is reduced. A general coincidence between the concentrations of MVOC, microorganisms, and the odour perception could not be observed, although in some cases concentrations decreased likewise (plant 3).

CONCLUSIONS AND IMPLICATIONS

Thermotolerant fungi and actinomycetes can serve as indicators for the dispersal of compost-specific bioaerosols into the environment. Significant differences in the dispersal of microorganisms and odours between *real worst case* and *normal case* situations could not be observed. The incidence of malodours in distances greater than 800 m from the facility ranges below 10% regardless of the type of process engineering or the climatic situation. In general, topography has a greater impact on the air flow during drainage flow situations, whereas under normal case situations wind-dispersal is more relevant.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

CHARACTERIZATION OF THE BACKGROUND CONCENTRATION IN AN INDUSTRIAL AREA

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ABSTRACT

In a large industrial area the background concentrations of several pollutants, provided by natural sources, are normally negligible when compared with the contribution from anthropogenic sources, but in presence of volcanic emissions or natural particles from dry regions they could be relevant in some circumstances. This is the case of one of the largest Italian industrial area in Sicily, located on the east cost, close to the Etna volcano and sometimes exposed to desert storm from north Africa.
In view of stringent air quality standards to comply with, mainly in terms of PM_{10}, the background concentrations for some representative pollutants has to be characterized in order to adopt efficacious action plans in meteorological critical conditions.
This study started through the statistical analysis of air quality data collected by a fixed measurement station network, which has been monitoring the area for many years, and will continue with the chemical characterization of airborne particles.

INTRODUCTION

For the purpose of the European Directive 99/30/EC, which establishes limit values in ambient air for sulphur dioxide, nitrogen dioxide, oxides of nitrogen, particulate matter and lead, *pollutant* is defined as "*any substance introduced directly or indirectly by man into the ambient air and likely to have harmful effects on human health and/or the environment as a whole*". On the other side the limit values "*fixed on the basis of*

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scientific knowledge with the aim of avoiding, preventing or reducing harmful effects " do not distinguish the sources of pollutants, either anthropogenic or natural.
The same Directive, in the case of SO_2 and PM_{10}, says that where the limit values are exceeded due to natural events (volcanic eruptions, seismic activities, geothermal activities, wind-land fires, high wind events or the atmospheric re-suspension or transport of natural particles from dry regions) which result in concentrations significantly in excess of normal background levels from natural sources, Member States shall provide the necessary justification to demonstrate such excess.
For geographical area where the contributions of natural sources and/or natural events to the air quality may be significant their quantification on spatial and temporal scale is quite complicated. Furthermore, the "normal" background levels due natural sources have not necessary to be steady-state when more or less frequent natural events may occur. In any case, the difficult to inform the public about these circumstances and convince it that even when the limits for human health protection are exceeded there is nothing to worry about or to comply with being mainly due to natural sources and/or events.
This problem has been approached for a large industrial area located along the east cost of Sicily in Italy (Fig. 1) where particles containing sodium chloride derived from sea spray are certainly always present together with volcanic particles from Etna, which is about 60 kilometres far by air and has been quite active in the last few years and particularly in 2002. Furthermore, the area suffers of non infrequent sand storm from north Africa.
This paper refers on the first results of a study which started recently with the aim to understand the rate of the phenomena involved, mainly concerning PM_{10} concentrations, to "weight" somehow the different contributions from anthropogenic and natural sources and/or events, to characterize the background concentrations.

GEOGRAPHICAL AREA UNDER INVESTIGATION

In the industrial area under investigation, whose extension may be considered of about 150 Km^2, there are several industrial factories, mainly for chemical and petrochemical productions. The air quality is monitored through a 12-station network (set up in 1975 by CIPA, a consortium of local industries) which analyses several pollutants as SO_2, H_2S, NO, NO_x, NO_2, O3, CH4, NMHC, THC, PM_{10}, benzene, toluene and some other organic compounds. The network includes three meteorological stations for the continuous monitoring of conventional parameters other then with RASS and SODAR for the measurement respectively of the vertical thermal gradient and the vertical profile of the wind direction and velocity.

AIR QUALITY DATA ANALYSIS

Air quality data, collected in 2002 at five stations (Melilli, Augusta, Belvedere, San Focà, Faro Dromo in Fig. 1), of sulphur dioxide (on hourly averaged base) and PM_{10} (on bi-hourly averaged base) have been assembled and averaged in 16

sectors corresponding to the wind directions that together with the wind speed have been measured at the CIPA station.
Looking at the case of figure 2, it may be observed that the prevailing wind (~ 47%) blows from NW to SW (sectors 11 to 14), while the wind blowing from East (sectors 4 to 7), which makes the location downwind the industrial sources, accounts only for about 28%. The average wind velocities on their turn show less differences having values from 2,2 to 3 m/s. Only for two directions (sectors 11 and 15) the average velocity has been less then 2 m/s.
The higher SO_2 concentrations, measured at Melilli station, in the range from 20 to 45 $\mu g/m^3$, are measured for wind blowing from east side, that is in circumstances clearly downwind to industrial sources. For wind blowing from the opposite directions, that is from open country, concentrations fall down of 1/3 to 1/8 to about 5-6 $\mu g/m^3$. Quite different is the situation for PM_{10}, since the average concentration of about 41 $\mu g/m^3$ for wind blowing from the sectors 11 to 15 is exactly the same for wind blowing from the remaining sectors. The maximum average corresponds to wind from SW direction which is not downwind to any anthropogenic source. Therefore for PM_{10} there is no evidence, as in the case of SO_2, that a prevailing contribution may come from industrial sources.

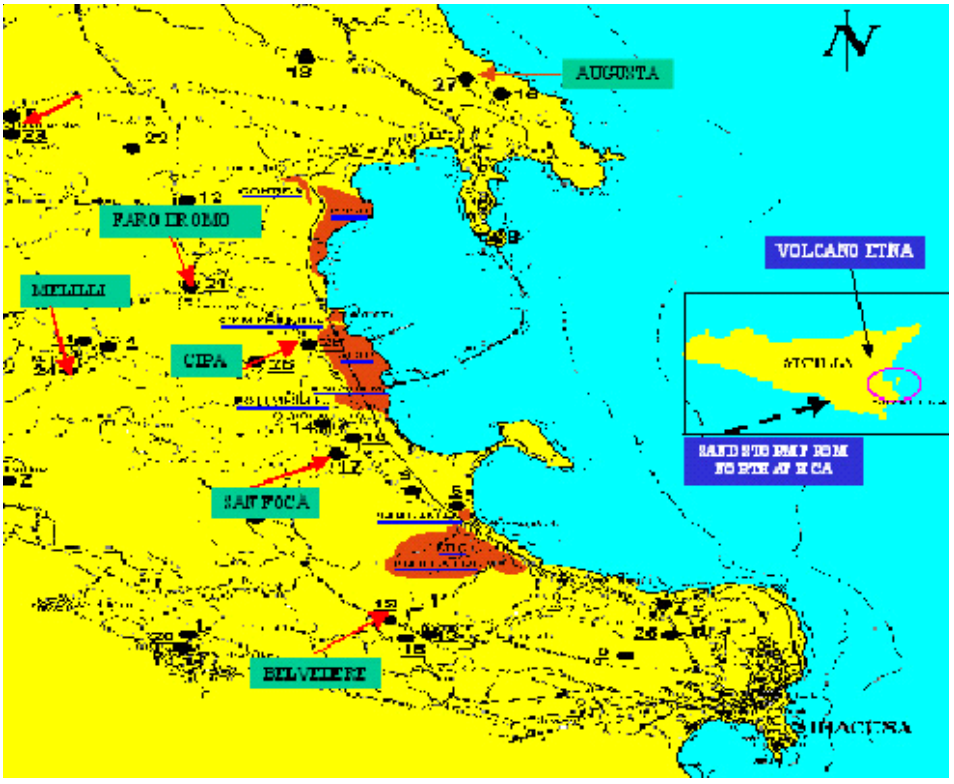

Figure 1. Industrial area and air pollution network in Siracusa, ITALY

Similar considerations may be obtained from fig. 3, which refers to PM_{10} and SO_2 measured at Augusta station, located along the NE direction with respect to the industrial sources (that is downwind to sectors 9 to 12). Wind direction and wind velocity are the same then in Melilli. SO_2 concentrations are quite low (2 to 4 $\mu g/m^3$) for any direction, while PM_{10} concentrations are in same range then in Melilli (29 to 53 $\mu g/m^3$ with an average of 36 $\mu g/m^3$). One again there is no evidence of prevailing or even substantial contribution from industrial sources.

The same analysis has been done on the data collected at stations San Focà, Farodromo e Belvedere, and the conclusions have been reached, that SO_2 is clearly due to industrial sources while PM_{10} averaged concentrations, between 35 and 39 $\mu g/m^3$, do not exhibit any prevailing direction.

The same data for SO_2 and PM_{10} for the five stations mentioned before have been assembled in a cumulative frequency distribution in Figs. 4 and 5. It is clear that the wide differences of the SO_2 behaviour (sharp slope of the curves, irrelevant values for more then 70 % of the time) depends on the place, its distance from the industrial sources, the probability that the location is downwind those sources. On the contrary the behaviour of PM_{10}, which shows weak slopes, log-normal distributions, few anomalous very high or very low values, seems typical of natural phenomena due to natural scattered sources.

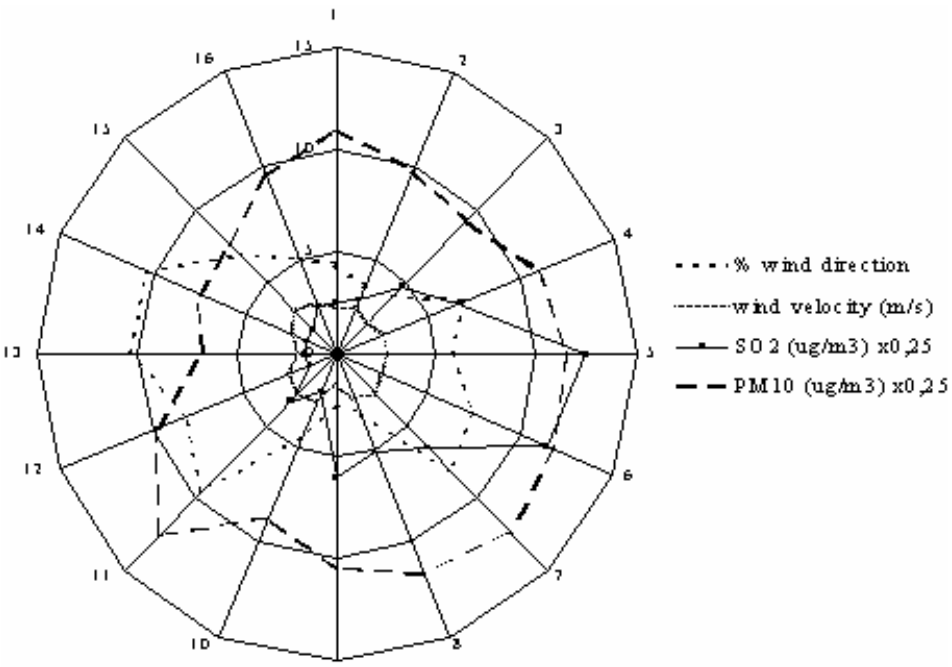

Figure 2. Melilli station

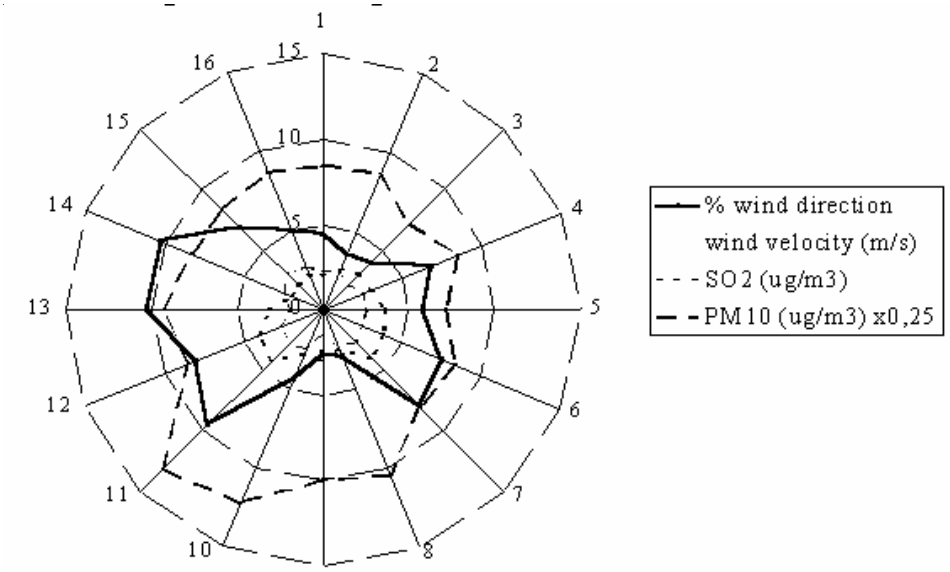

Figure 3. Augusta station

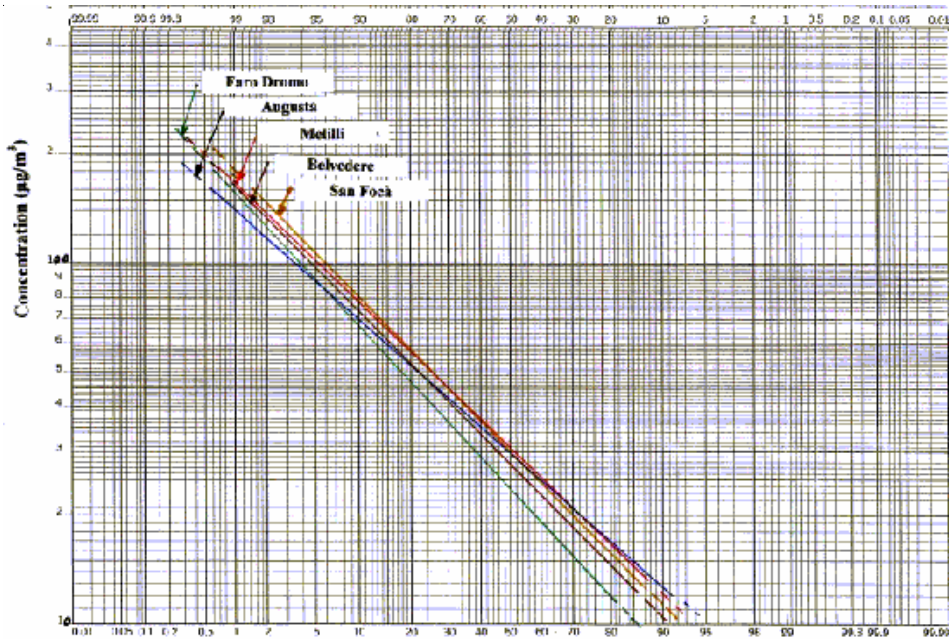

Figure 4. Cumulative frequency distributions for PM_{10} – Year 2002

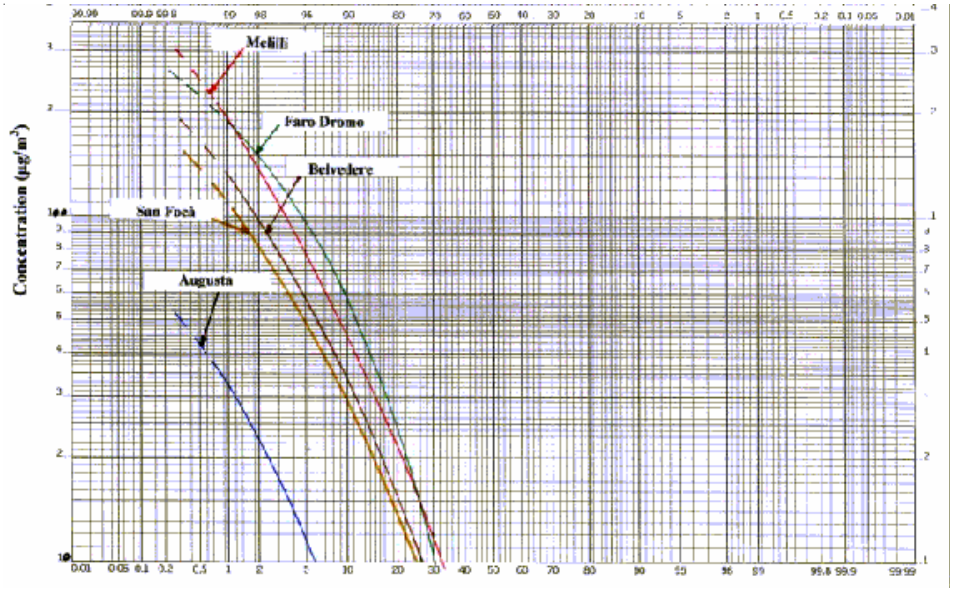

Figure 5. Cumulative frequency distributions for SO_2 – Year 2002

NATURAL SOURCES AND EVENTS

Sand storms

From 12th to 14th April 2002 the wind has been blowing from SW to N persistently for almost 48 hours. The SO_2 concentrations measured at the five stations were very low, with an average of 3 $\mu g/m^3$, while the PM_{10} concentrations were very high with an average of 190 $\mu g/m^3$, about five times higher then the annual average. This was clearly a sand storm from north Africa. Similar events happened in short extend in May (8th to 9th), with averaged concentrations less then 10 $\mu g/m^3$ for SO_2 and about 130 $\mu g/m^3$ for PM_{10}, in July (23rd to 25th), with averaged concentrations about 35 $\mu g/m^3$ for SO_2 and around 100 $\mu g/m^3$ for PM_{10}, in November (13th to 17th), with averaged concentrations less then 4 $\mu g/m^3$ for SO_2 and about 60 $\mu g/m^3$ for PM_{10}. Of course these kind of events depend on different parameters as wind persistence, wind velocity, humidity, distance covered by the sand clouds before reaching the Sicilian area.
CIPA is going to adopt a specific software in order to quantify this transboundary transport which concerns other sites in the Mediterranean area [(1)].

Volcanic gases and particles from Etna

There is no evidence of a contribution of Etna to the ground-level SO_2 concentrations. The sulphur dioxide discharged from Etna, with moderate activity, has been evaluated [(2)] in about 4100 t/day. It is a big amount compared with about 170 t/day discharged by the industrial sources located in the area under

investigation, but the natural source which releases at an altitude of about 4000 m produces insignificant concentrations at 60 Km downwind compared with the possible maximum concentration which a single not too high chimney may generate.
A contribution to PM_{10} concentrations is more evident with high value up to 170 in Melilli and 240 in Farodromo on July 24th, more then 100 in the same stations on August 5th to 6th. The main and continuous Etna activity has been from the end of October to the end of December, but fortunately in this period of the year the wind blows vary rarely from north so very few and short episodes could be related to volcanic emissions. In any case this circumstance is not such to exclude the presence of volcanic particles in the industrial area since their lifetime may last up to few weeks.

Particles from sea spray

A significant contribution to PM_{10} from sea spray is very likely, due to the rocky and indented coast.
Looking at Fig. 2 (Augusta station) the PM_{10} concentrations for wind blowing from sea side (N to S) are not too much different from those corresponding to wind blowing from land (S to N).

CONCLUSIONS

There are geographical areas where a background concentration has to be intended as a floating value during the year rather then a steady-state condition, due to significant natural sources, more or less frequent natural events or possible transboundary transportation of pollutants. The issue is very important for the PM_{10} air quality characterization in a large industrial area where the limit values established by an European Directive at the moment are exceeded, and the action plans to implement in order to lower the concentrations them within January 1st 2005 are not easy to define since they seems to be due, in a significant contribution, to natural sources and/or events.
From the first results of the research previously discussed it came out the need to characterize the chemical composition of the airborne particles first of all in terms of metals, as traces of volcanic emissions, sodium chloride coming from sea spray, mineral material from re-suspended coarse fraction. Also a software is going to be arranged in order to evaluate the transboundary transport of sand from North Africa.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

TROPOSPHERIC OZONE IN CROATIA

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ABSTRACT

Tropospheric ozone in Croatia has been measured on various locations since 1975. These locations includes sites as Puntijarka (where ozone is measured continuously since 1989) and the town of Zagreb, Split, Šibenik, Zadar, Dubrovnik and Osijek. Short measurements campaigns took place along the Adriatic coast at Rovinj, Omišalj, Mali Lošinj, Zavižan, Iž, Makarska and Hvar. Analysis of ozone distribution and daily and seasonal variation based on monitoring from several urban and rural locations is given. Short term measurements along the Adriatic coast have shown that there is a negative north to south gradient in ozone concentration as predicted by model calculations. Long range transport (Rovinj, Mali Lošinj, Zavižan) was observed as well as local photochemical production even at the remote Adriatic island (Iž) far from pollution sources.

INDEX TERMS

Tropospheric ozone measurements, Croatia, daily variation

INTRODUCTION

Ozone in the troposphere is considered a pollutant causing plant damage, material damage, adverse health effects, visibility reduction, greenhouse effect and overall increase of the oxidation capacity of the atmosphere (Crutzen, 1998). It has been reported that in the past one hundred years the ozone concentration near the ground has more than doubled and is still rising (Bojkov, 1986; Volz, 1988; Finlayson-Pits, 2000). Long-term measurements are therefore underway to assess this trend. Ozone concentrations monitored at any tropospheric site are influenced by i) chemistry i.e. the composition of air and insolation, ii) topography, especially

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altitude, type of terrain, vegetation etc and iii) meteorological parameters, in particular temperature, wind speed and direction, seasonal variation, and clouds. Consequently, assessment of all factors influencing the ozone concentration at a particular site requires complete knowledge of these factors not only for the site but also for the surroundings; this is achieved through measuring campaigns which involve simultaneous use of ground station, aircraft (and balloons) and satellite observation over a shorter period of time. Less demanding, but also very useful is monitoring of ozone and selected species important for ozone formation and destruction together with meteorological parameters within a network of fixed stations. Such data give clues on the regional dependence, daily, monthly and seasonal variations as well as on trends of ozone concentration. Experimentally and financially ozone concentrations are easiest to monitor, and such data collected over longer periods of time at representative sites are often the only parameters available for comparative analysis. Tropospheric ozone in Croatia has been measured on various locations since 1975. These locations includes sites as Puntijarka (where ozone is measured continuously since 1989) and the town of Zagreb, Split, Šibenik, Zadar, Dubrovnik and Osijek. Short measurements campaigns took place along the Adriatic coast at Rovinj, Omišalj, Mali Lošinj, Zavižan, Iž, Makarska and Hvar.

METHODS

Ozone has been monitored with commercial Dasibi and Environment monitors, which have been regularly checked and calibrated.

RESULT AND DISCUSSIONS

At the Puntijarka site located about 10 km north of the city of Zagreb on the ridge of mountain Medvednica (45.90^{o} N; 15.97^{o} E, 980 m a.s.l.) ozone monitoring has been continued giving now a fourteen years data series of continuous measurements at this site. Analysis shows that at Puntijarka there is a negligible diurnal variation (Fig. 1) and seasonal cycle with a broad summer maximum (Fig. 2). In comparison with previous measurements (Butković, Cvitaš, Džepina et al., 2002) it seems that, during the last three years, summer maximum occurred earlier (i.e. in June instead of July or August).

Nevertheless, this behaviour is typical for relatively remote and elevated station, which can be considered as representative for regional level. The city of Zagreb and other sources of primary pollutants only weakly influence the Puntijarka site (Cvitaš, Kezele, Klasinc et al., 1995) and to the north of the mountain there is an agricultural area with no significant industry.

Concerning the trend there is at the Puntijarka station an indication that the exponential rise observed for boundary layer ozone in this century in Europe is slowing, if not descending in the 1990's, after having reached a maximum in 1992/1993. The least squares statistical analysis of the years 1990 – 2002 conforms either with no

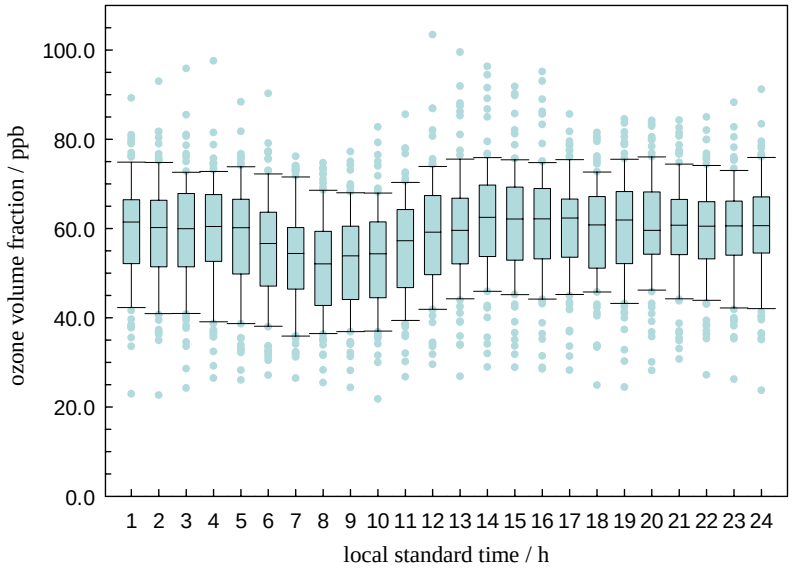

Figure 1. Diurnal variation of ozone volume fractions at Puntijarka for summer months 2003 (May – August). Box boundaries indicate 25th and 75th percentile, whiskers above and below the box indicate 10th and 90th percentile and outlaying points are ploted.

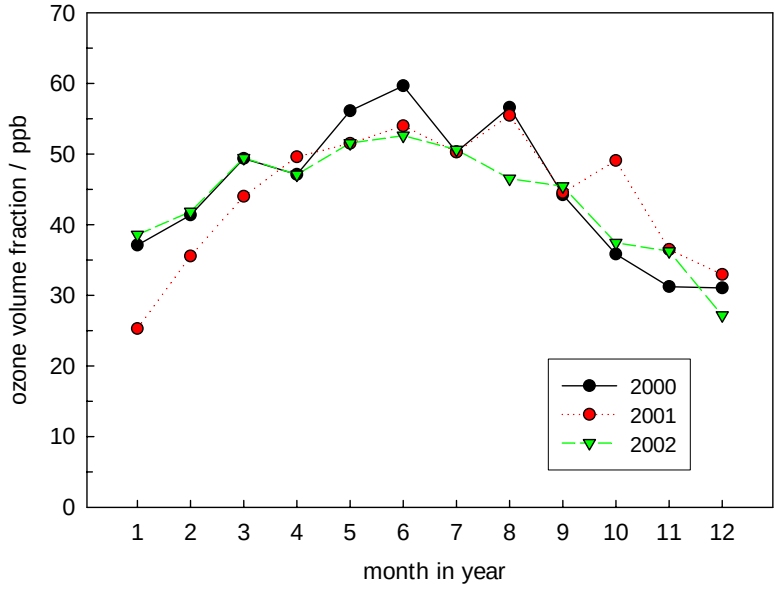

Figure 2. Seasonal variations of ozone volume fractions for three recent consecutive years at Puntijarka.

increase of ozone volume fraction or a slight decrease of 3 ppb per decade (Figure 3). A possible reason for the general trend could be the depletion of ozone in the lower stratosphere resulting in a decreased input to the troposphere by diffusion and intrusion, but more probably also to the dramatic changes in Croatian industry and transportation (strong reduction of air traffic over Zagreb) during the last decade.

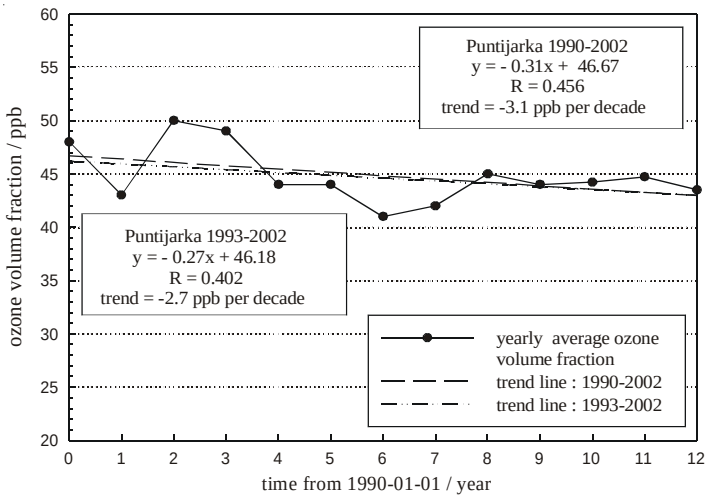

Figure 3. Average yearly ozone volume fractions and regression analysis for Puntijarka station

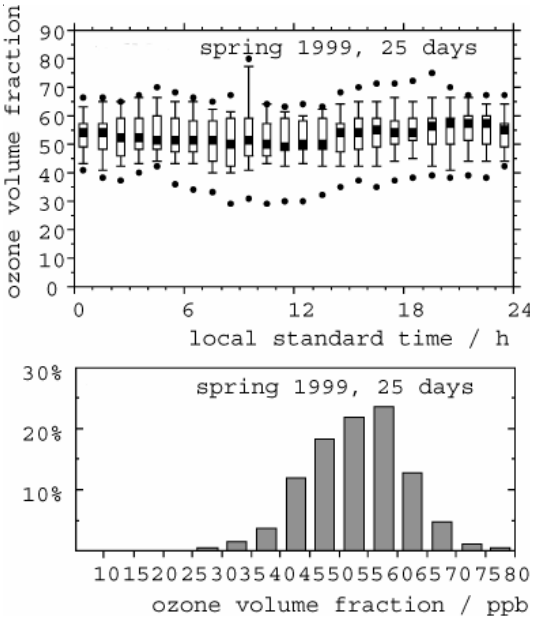

Figure 4. Distribution of hourly average ozone volume fraction at Zavižan

Data for Zavižan on the Velebit Mountain (44.80° N, 15.00° E, 1670 m a.s.l.) are typical for an isolated and elevated site with a somewhat high mean value of 45 ppb (higher than the estimated average continental background in the boundary layer). Owning to instrumental failure data for 1999 are restricted only to the early spring period (Fig. 4), but they show an even higher mean value in comparison with the 1998 summer season.

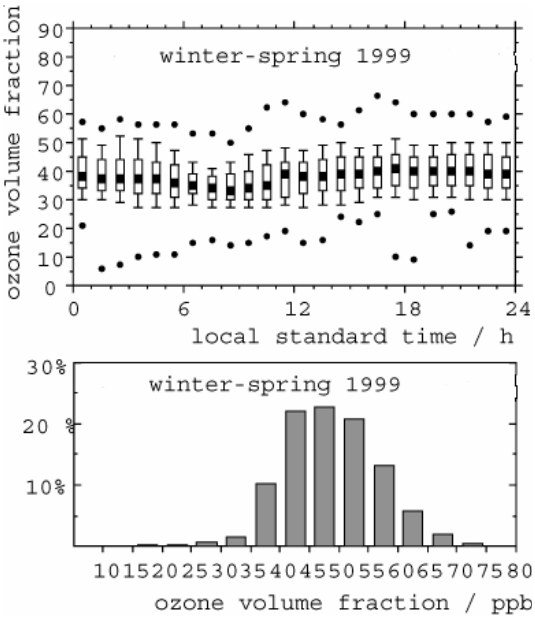

Figure 5. Distribution of hourly average ozone volume fraction at Srđ

The data from the location Srđ above Dubrovnik (42.65° N, 17.45° E, 412 m a.s.l.) show negligible average diurnal variation with a mean value of 38 ppb (Fig. 5). Wind sector analysis shows that distributions of ozone concentrations are similar for different sectors. This measurements in the southern Adriatic at Srđ show lower ozone levels than those found in the central and northern regions (Cvitaš, Kezele and Klasinc, 1997) which is in agreement with most model computations (Simpson, 1991).
Data for Mali Lošinj an island site isolated from any close pollution sources yield a summer mean value of 41 ppb (Fig. 6). A polar plot of relative deviations from average diurnal behaviour and corresponding wind direction show that at Mali Lošinj the average ozone value is higher when the wind blows from the south-western than from the eastern sector (Fig. 7). For the summer 1999 data show negligible diurnal variation in comparison with previous summer seasons but relatively higher ozone values are again connected with southern and western winds. This conclusion is in accordance with our previous results and can be best visualised by a quantile - quantile plot (Fig. 8).

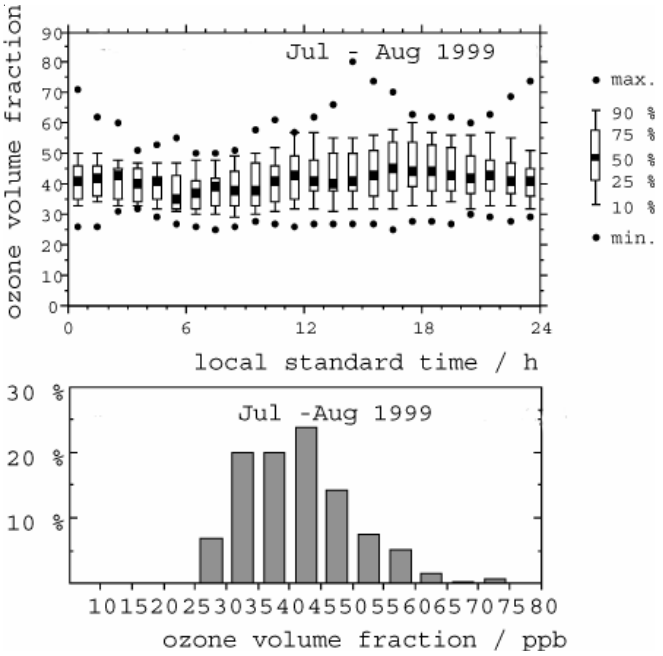

Figure 6. Distribution of hourly average ozone volume fraction at Mali Lošinj

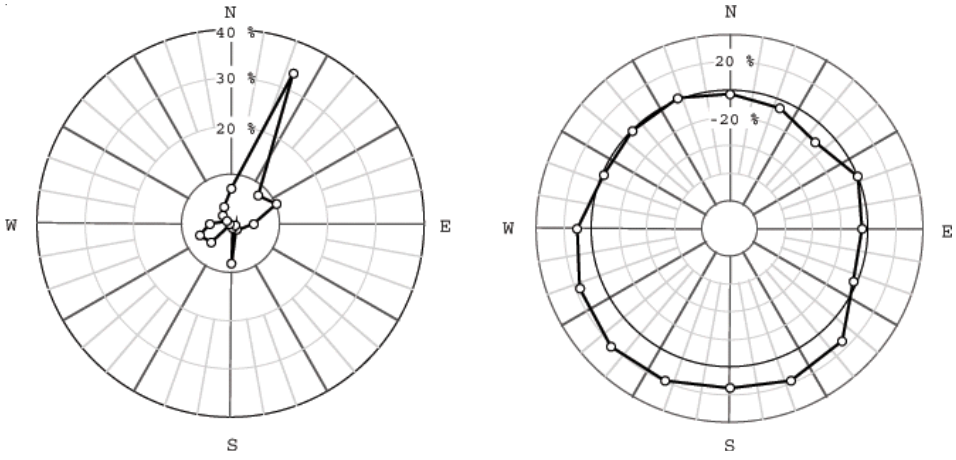

Figure 7. Left: wind rose for 37 days monitoring period in July – August at Mali Lošinj Right: relative deviation from average ozone concentrations for the same period at Mali Lošinj

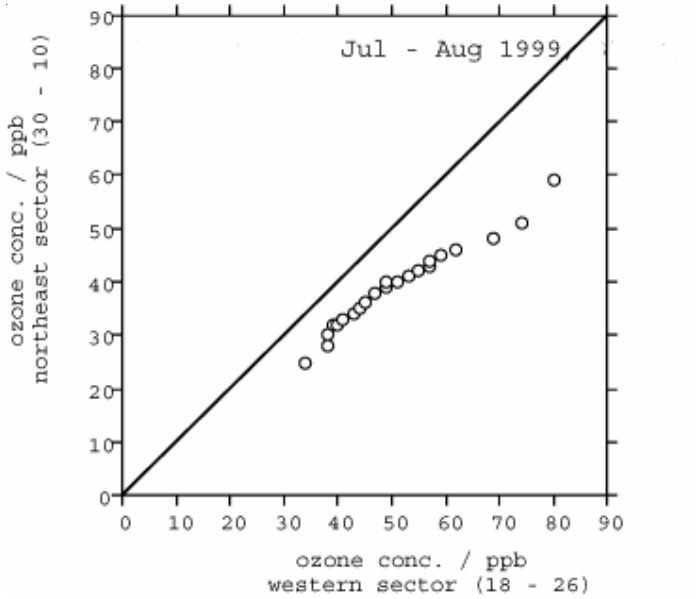

Figure 8. Quantile – quantile comparison for two selected wind sectors at Mali Lošinj

CONCLUSION

Measurements at Puntijarka station which can be considered as relatively clean site show seasonal variations of ozone volume fractions with broad summer maximum. Spring maximum which is reported for the northern midlatitude free troposphere (Monks P. S., 2000) is not found in our measurements. Last three years summer maximum show shifting from July and August to June. Trend analysis of thirteen years ozone time series show slight decrease in ozone values of 3 ppb per decade. Many years of summer measurements at different locations along the Adriatic coast give us evidence of north to south gradient in ozone concentrations in that region.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

PHOTOCHEMICAL Pollution INDICES: AN ANALYSIS OF 12 EMEP STATIONS

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ABSTRACT

Indices were devised to classify air pollution monitoring sites according to the type of expected photochemical pollution. The indices are based on two contributions: one due to the ratio of daily maximum-to-minimum ozone volume fractions and the other to observed peak values. The two contributions are combined by multiplication. The type of station is mainly described by the mentioned ratio incidence of ozone volume fractions exceeding the limit of 80 ppb. Twelve monitoring stations of the EMEP network were classified according to this index into three groups: clean, medium and polluted, based on the data for the growth seasons (April through September) 1997 to 2000.

INDEX TERMS

Tropospheric ozone, photochemical pollution, air pollution index

INTRODUCTION

There is no doubt that many urban areas and rural regions experience excessive concentrations of oxidants in the atmosphere during summer months. The main contributor to such kind of pollution is ozone formed in the atmosphere from its precursors under the influence of solar radiation. The observed severe episodes were termed photosmog. Various effects have been ascribed to such kind of photochemical pollution: oxidation of sensitive materials e.g. rubber, harmful effects on plants causing decolouration and lower crop yields (Musselman and Massman, 1999) irritation effects and lower performance in humans such as

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irritation of eyes and respiratory system and poorer results in sport competitions during photosmog episodes (Lippmann, 1991). In some countries expected pollutant concentrations or volume fractions in ambient air are reported together with meteorological data, particularly when air quality standards are likely to be violated, to indicate the degree of well being when residing outside.

It is not easy to find a simple representative value to describe photochemical pollution, a complex state in ambient air involving various trace species at excessive concentrations. Furthermore these concentrations as well as their ratios often tend to vary dramatically during 24 hours of the day.

It is the aim of the present article to analyze different patterns of behaviour of the leading species in photochemically polluted air, namely ozone, in order to find a simple way of classifying types of monitoring sites and extent of expected photochemical pollution. Another advantage of choosing ozone is that it is relatively frequently and reliably monitored at many stations.

STATIONS

Twelve stations from the EMEP network were selected for the analysis mainly for some comparative features with the monitoring sites in Croatia. They are listed in Table 1 together with their geographical coordinates. The geographical locations are also indicated on the map in Fig. 1. Among the stations there is only one at high altitude (Krvavec, 9), two are at medium altitude (Kosetice, 6 and Payerne, 10) while all the others are at low altitudes.

Table 1. EMEP monitoring stations selected for the analysis

No.	Station, country	Latitude	Longitude	Altitude
1	Bottesford, GB	52,56° N	0.49° W	32 m
2	Vezin, BE	50.30° N	4.59° E	160 m
3	Neuglobsow, DE	53.09° N	13.02° E	62 m
4	Diabla Gora, PL	54.09° N	22.04° E	157 m
5	Jarczew, PL	51.19° N	21.59° E	180 m
6	Kosetice, CZ	49.35° N	15.05° E	534 m
7	K-Puszta, HU	46.58° N	19.35° E	125 m
8	Illmitz, AT	47.46° N	16.46° E	117 m
9	Krvavec, SI	46.18° N	14.32° E	1720 m
10	Payerne, CH	46,48° N	6.57° E	510 m
11	Peyrusse Vielle, FR	47.22° N	0.06° E	236 m
12	Montelibretti, IT	42.06° N	12.38° E	48 m

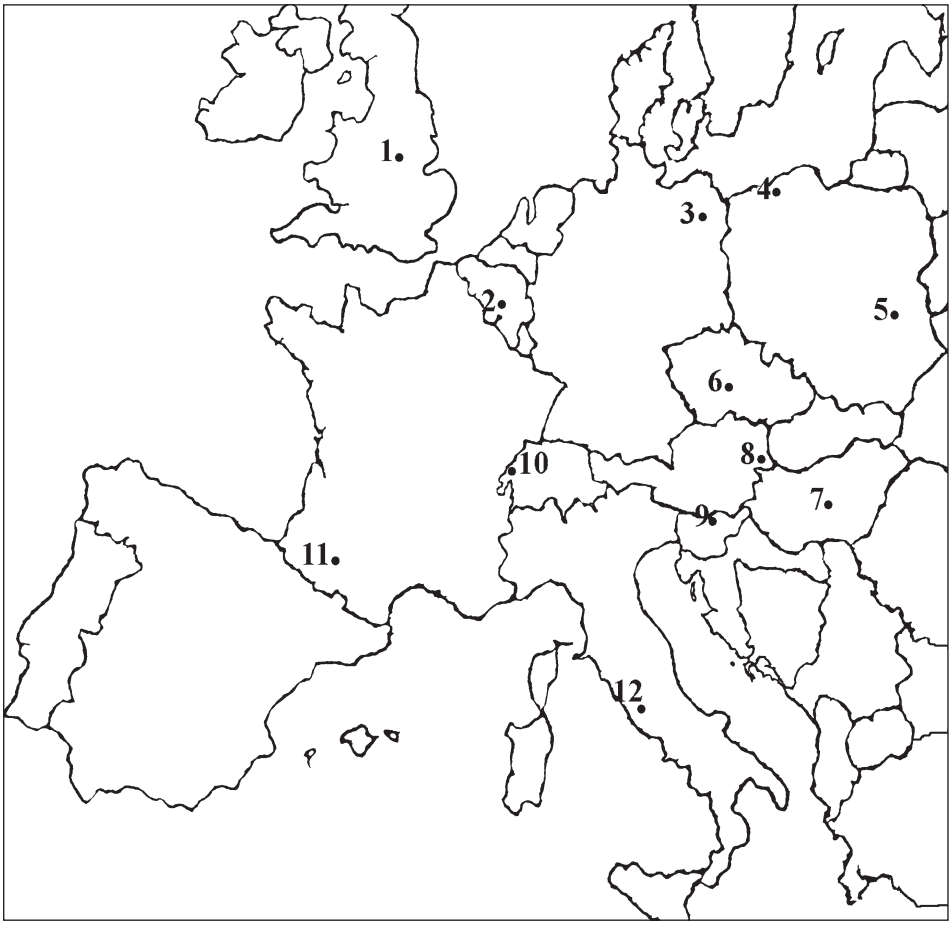

Figure 1. Location of the investigated European stations:1 - Bottesford, 2 - Vezin, 3 - Neuglobsow, 4 - Diabla Gora, 5 - Jarczew, 6 - Kosetice, 7 - K-puszta, 8 - Illmitz, 9 - Krvavec, 10 - Payerne, 11 - Peyrusse Vielle, 12 - Montelibretti

Mass concentrations for ozone in micrograms per cubic metre are available on the Web (www.nilu.no/projects/ccc/network.html) and we have chosen the summer periods (1 April to 30 September) of four years 1997 to 2000 for the analysis. More recent data are not available for all stations.

METHOD

Relatively comprehensive information on ozone behaviour at a particular site can be obtained by plotting average daily behaviour (Butković *et al*., 1990), or even better by plotting the so called box and whiskers diagrams (Jeftić and Cvitaš, 1991). However such plots require significant work to produce and relatively high background knowledge to understand.

Much simpler would be giving just the average value of all the measured hourly average volume fractions. The daily, weekly, or monthly average concentration of a pollutant is a good indicator when the concentration is roughly constant during that period of time. Ozone, however, shows a characteristic diurnal behaviour with maximum concentrations in the early afternoon hours and minimum values in the morning and evening hours. This variation is much more pronounced in urban than in rural sites. At high altitudes near the top of the boundary layer the variation tends to disappear.

Standard deviations would provide interesting additional information provided the original data are reasonably normally distributed which is rarely satisfied. It can be expected that at high altitudes where hardly any diurnal variations are observed the measured values will congregate much more closely to the mean value than at low altitude sites giving rise to small standard deviations. Urban centres with strong emission sources of primary pollutants have a high frequency of both low and high concentrations and will therefore show relatively large standard deviations.

Typical behaviour of ozone volume fractions during a photosmog episode involves very low, even zero values in absence of light owing to ozone consuming reactions with primary pollutants and very high values in the early afternoon hours. Such behaviour can best be characterized by the ratio of daily maximum and minimum values. The average of the daily maximum/minimum ratios for the whole period represents a simple characteristic of the type of monitoring site. When minimum values were found to be zero they were replaced by 0.4 in order to avoid division by zero. This criterion was applied previously in some instances (Cvitaš *et al.*, 1995).

Air quality standards are usually based on peak hourly or half-hourly values and the frequency of their incidence. We have tried to take this also into account. We calculated the maximum ozone volume fraction each day and calculated the average for the whole period.

Two more parameters were chosen on the basis of ozone volume fractions in excess of a frequently chosen air quality limit: an hourly average of 80 ppb. One gives the total volume fraction in excess of the chosen limit for the whole period, the other just the number of hours the limit was exceeded.

RESULTS

The described parameters were calculated for the 12 EMEP stations and the average values based on hourly average volume fractions calculated for four seasons are compared in Table 2.

By comparing the parameters some interesting features can be identified. As expected the average value in column 2 of Table 2 does not vary strongly. By far the highest value was found at the high-altitude station Krvavec where no low values occur. Low average values were measured in the western stations Bottesford and Vezin, while all the others lie within the range of 30 to 40 ppb.

Table 2. Statistical parameters obtained from hourly average volume fractions of ozone given as averages of four* summer periods of 1997 to 2000

Station No.	Average *A* / ppb	Standard deviation / ppb	Ratio max/min *R*	Average max *M* / ppb	Total excess / ppb h	Duration of excess *D* / h
1	25.5	13.0	14.3	40.5	80.0	9.8
2	26.8	16.8	18.5	46.8	165.3	19.0
3	32.8	15.8	8.5	49.8	180.8	23.3
4	33.8	14.0	6.8	48.0	0.3	0.3
5	31.8	14.5	4.8	47.5	3.5	0.8
6	40.3	13.0	3.0	53.3	49.5	7.8
7	44.3	16.8	4.0	64.5	442.3	69.3
8	39.8	14.5	3.8	57.3	176.8	24.3
9	55.7	9.7	1.3	64.0	333.3	63.7
10	33.5	17.0	21.0	54.3	68.5	13.0
11	34.3	11.0	2.0	45.3	3.7	1.0
12	30.3	22.8	59.0	65.8	1120.8	91.3

For stations Krvavec (9) and Peyrusse Vielle (11) only three seasons were taken into account. Data for 1998 at Krvavec and 1997 at Peyrusse Vielle were unavailable.

The standard deviations (column 3) are almost constant between 11 and 17 ppb, except for the high altitude station 9 where it is significantly lower and the obviously polluted site Montelibretti (12) where it is much higher.

The maximum to minimum ratios (column 4) which were used before for characterizing monitoring sites (Cvitaš *et al*, 1995) classify the stations in the range between 1 and 59. The high values are representative of sites with significant local photochemical production as well as ozone consumption. Stations Montelibretti (12), Payerne (10), Vezin (2) and Bottesford (1) appear to be leading in this respect.

The incidence of high ozone volume fractions can be represented in various ways. We have chosen three: (i) the average maximum value is obtained as the average of daily maximum values, (ii) the total excess is calculated as the sum of hourly volume fractions in excess of 80 ppb the so called accumulated ozone time (AOT80) (Wayne, 2000), and (iii) the duration of ozone volume fractions exceeding the limit of 80 ppb in hours. These values are given in columns 5, 6 and 7 of Table 2. Stations Montelibretti (12), K-puszta (7) and Krvavec (9) show the highest values irrespective of the parameter chosen. Parameters (ii) and (iii) show hardly any difference in classifying the stations and since (iii) is simpler we gave it preference.

The next step consists in the combination of two criteria: the one given by the maximum-to-minimum ratio and the other representing adequately the peak values.

Mathematical logic requires multiplication of the two contributions. The ratio is always a value greater than 1 and rarely exceeding 50. Multiplication by a factor of the order of one would be desirable to retain the same order of magnitude for the product. Therefore we chose the average maximum value (M) divided by the average volume fraction (A) – a factor in the range between 1 and 2.2. The product as an index characterizing a monitoring site with respect to photochemical pollution, $P_1 = R\,M/A$, varied between 1.5 and 128 for the examined twelve stations. The most polluted station in a class of its own is Montelibretti (12). The stations Payerne (10), Vezin (2), Bottesford (1) represent a medium class where photosmog episodes can occasionally occur but probably very rarely. The stations with indices $P_1 < 7$ represent clean sites with respect to photochemical pollution. Two of the EMEP sites (Diabla Gora (4) and Neuglobsow (3)) fall in between the clean and medium class.

The second index was calculated by a factor taking into account the number of hours when the air quality limit of 80 ppb was exceeded. In order to avoid multiplication by zero when 80 ppb was not exceeded at all, the chosen factor was $(1 + 7\,D / N_d)$ where D is the number of hours with ozone volume fractions in excess of 80 ppb and N_d is the number of monitoring days per season. The number of hours with such excessive ozone volume fractions in a season could well be above 100 which represents roughly 50 % of the days in a semi-annual season. If the air quality limit was exceeded once (one hour) per week on the average the formula would lead to a factor of 2 and it could drop down to 1 when the limit was never exceeded. Using this second index, $P_2 = R\,(1 + 7\,D / N_d)$, to classify the stations a very similar ranking of stations was obtained. This method however gives a clear grouping into three classes: clean ($P_2 < 10$), medium ($10 < P_2 < 40$), polluted ($P_2 > 100$). The ratio of maximum to minimum index within a class is less than 2.8 and between the mean values for the classes in our examples it is greater than 4.7.

Table 3. The ranking of twelve EMEP stations according to the devised indices

Station No.	Index P_1
9	1,5
11	3,1
6	3,7
8	4,9
7	5,9
5	6,8
4	9,8
3	12,9
1	22,7
2	34,2
10	32,5
12	128

Station No.	Index P_2
11	2,4
6	3,6
9	4,5
5	4,7
8	6,8
4	7,0
7	13,5
3	17,1
1	19,7
10	28,0
2	31,8
12	268

The calculated two indices as described above for the twelve stations are compared in Table 3. The first method is somewhat simpler than the second and does not alter the ranking of the stations from that on the basis of the average maximum-to-minimum ratio. The second method yielding P_2 gives a higher weight to the peak values but nonetheless the results *i.e.* the ranking of stations remains practically unchanged. The high altitude station Krvavec (9) changes from the first position when ranking according to P_1 to third position when ranking with respect to P_2. The ranking of the Hungarian station 7 changes drastically because of the incidence of peak values exceeding 80 ppb is very frequent. It is the second site in this respect as seen from Table 2.

DISCUSSION

Air pollution indices are usually defined in order to give an indication of air quality at a particular location and time and to inform the public whether the ambient air can be regarded as good or unhealthy (McNaught and Wilkinson, 1997). The present method was devised in order to classify sites according to the type of pollution that can be expected in a particular season at the given site. Twelve stations from the EMEP network were examined for their behaviour during the summer or growth season.

The parameters found most useful with respect to simplicity of how they can be calculated and the information they provide were the average daily maximum-to-minimum ratio and the average daily maximum ozone volume fraction. By multiplication of these factors an index is obtained according to which the stations can be classified into three or four groups. One group represents relatively clean air stations with little local photochemical production and scarce episodes exceeding the air quality standard for ozone given by an hourly average of 80 ppb. These stations are characterized by an index value of less than 15. The second group represents stations where there is local photochemical production of ozone and the hourly average ozone volume fraction exceeds the air quality limit occasionally. The corresponding value of the index lies in the range of 10 to 50. The third group represents stations with frequent photosmog episodes, a high local photochemical production and significant local primary pollutant sources. Among the investigated EMEP stations only the station Montelibretti in Italy falls into that class with an index greater than 100.

Based on the present study the second method yielding P_2 provides a clearer classification of stations with respect to most frequently encountered air pollution problems in the summer period. It gives greater weight to effect related ozone data *i.e.* to values exceeding standards.

The classifications were based on the average values for four seasons. However, in most stations no large changes are to be expected when applying the method for individual seasons. An exception is the Hungarian station K-puszta where the index P_2 is equal to 20,5 for the first two seasons (1997 and 1998) and 6,5 for the

last two seasons (1999 and 2000). It is up to the experts in charge of the station to give an explanation of such a difference which is not observed in the neighbouring stations.

CONCLUSIONS

After several attempts two indices based on monitoring data for ozone have been defined by trial and error in order to characterize ambient air monitoring stations. They both take into account contributions from the typical diurnal behaviour of ozone and from frequency of high values measured at a particular site. The diurnal behaviour is best represented by the average of daily maximum-to-minimum ratios for a season. The frequency of peak values was represented either by the average of daily maximum values or by the duration in hours when the air quality limit of 80 ppb was exceeded. The first method is simpler but gives less weight to peak values than the second. The second gave a better classification of the investigated sites.

The use of the indices is twofold: (i) they can be used to indicate what kind of photochemical pollution can be expected at a particular site and hence what effects can be expected in the neighbouring region and (ii) they can be used for checking the consistency of data at a monitoring site.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

ADVANCED AIR QUALITY MODELING ASSESSMENT IN TAIWAN

HG Leu[1], HC Chien[1], JS Fu[2,*] and CC Jang[3]

ABSTRACT

An economic incentive scheme was adopted in the second amendment of the APCA of Taiwan in 1992. Significant progress such as the monthly average concentrations of SO_2, NO_X, and PM_{10} has been decreased. However, cross-boundary transport of air pollutants is hindering the efforts to further improve Taiwan's air quality. A modeling effort has been undertaken to conduct a Taiwan air quality modeling assessment considered cross-boundary transport of air pollutants by applying an advanced modeling system, the Models-3/CMAQ, developed at USEPA. For this study we use the Taiwan Emission Database System (TEDS) that is a comprehensive emission database in Taiwan. Meteorological input fields for the CMAQ model simulations are provided by the Mesoscale Model Version 5 (MM5). 36- and 12-km grid resolutions set up by the MM5 meteorological processing model for episodes in 2001 used in USEPA's Regional Air Quality Modeling in East Asia are used as the boundary conditions for this study. The focus of this paper is to establish feasibly the Models-3/CMAQ application over the domain, i.e., covering the entire Taiwan. This Taiwan modeling application was aimed at studying the formation and regional transport of ozone, PM and acid deposition, for selected episode in 2001. This paper gives a description of the model configuration and setup and presents some preliminary model simulation results. This application provides an understanding on the formation of regional ozone and haze problems for the policy makers in Taiwan, but provides the experience for the Taiwan Environmental Protection Administration (TEPA) to refine the model and adapt it more thoroughly to conduct air quality management in Taiwan.

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INDEX TERMS

Models-3/CMAQ, Taiwan Emission Inventory System, Air Pollution Fee, Taiwan Air Quality Modeling

INTRODUCTION

The rapid economic development in Taiwan drives the growth of air polluting activities such as fuel burning, manufacturing, vehicle driving, and constructing. Therefore, air quality improvement is a big challenge in Taiwan. An economic incentive scheme was adopted in the second amendment of the APCA of Taiwan in 1992. Taiwan Environmental Protection Administration (TEPA) started to collect Air Pollution Fee (APF) since 1995. Significant progress such as the monthly average concentrations of SO_2, NO_X, and PM_{10} has been decreased. However, cross-boundary transport of air pollutants is hindering the efforts to further improve Taiwan's air quality. A modeling effort has been undertaken to conduct a Taiwan air quality modeling assessment considered cross-boundary transport of air pollutants by applying an advanced modeling system, the Models-3/CMAQ, developed at United States Environmental Protection Agency (USEPA). The "one-atmosphere" Models-3/CMAQ system was designed to approach air quality as a whole by including state-of-the-science capabilities for modeling multiple air quality issues, including ozone, particulate matter, visibility degradation, acid deposition, and air toxics, at multiple scale. For this study we use the Taiwan Emission Database System (TEDS) that is a comprehensive emission database in Taiwan. Meteorological input fields for the CMAQ model simulations are provided by the Mesoscale Model Version 5 (MM5). 36 km × 36 km and 12 km × 12 km grid resolutions set up by the MM5 meteorological processing model for episodes in 2001 used in USEPA's Regional Air Quality Modeling in East Asia are used as the boundary conditions for this study. The focus of this paper is the Models-3/CMAQ application to establish feasibility of model simulations over the domain, i.e., covering the entire Taiwan and running the model for episodes. This Taiwan modeling application was aimed at studying the formation and regional transport of ozone, PM and acid deposition, for selected episodes in 2001. This application provides an understanding on the formation of regional ozone and haze problems for the policy makers in Taiwan, but provides the experience for the TEPA to refine the model and adapt it more thoroughly to conduct air quality management in Taiwan.

USEPA'S MODELS-3/CMAQ MODELING SYSTEM

Over the past nine years, USEPA devoted major resources to developing an advanced modeling system with a "one-atmosphere" perspective, i.e., the U.S.EPA's Models 3/Community Multi-scale Air Quality (CMAQ) modeling system (Dennis, et. al., 1996; Byun, et. al., 1997; Byun and Ching, 1999; U.S.EPA, 1999). Models-3/CMAQ is a numerical modeling system that can simultaneously simulate the

transport, physical transformation, and chemical reactions of multiple pollutants across large geographic regions. The system is useful to states, other government and international agencies for making regulatory decisions on air quality management, as well as to research scientists for performing atmospheric research. It is a combination of Models-3, a flexible software framework, and the CMAQ modeling system for supporting air quality applications ranging from regulatory issues to scientific research on atmospheric processes. A modular science design of CMAQ allows the user to build different chemistry-transport models for various air quality problems. The "one-atmosphere" Models-3/CMAQ system was designed to approach air quality as a whole by including state-of-the-science capabilities for modeling multiple air quality issues, including ozone, particulate matter, visibility degradation, acid deposition, and air toxics, at multiple scales. The Models-3/CMAQ system was first released to the public in July 1998 and had a recent update release in May 2003 (U.S.EPA, 2003). Through the Taiwan-US bilateral collaboration, TEPA is engaged in uses of the advanced air quality modeling tool to assess the trans-boundary issue and its air pollution control strategies.

MODEL CONFIGURATION AND SETUP

Model Domain

In this Models-3/CMAQ application, the model domain covered the East Asia and in Figure 1. 36 km×36 km and 12 km×12 km grid resolutions set up by the MM5 meteorological processing model for episodes in 2001 used in USEPA's Regional Air Quality Modeling in East Asia are used as the boundary conditions for this study. The domains had 130 x 94 horizontal grid cells using a 36-km resolution, 135 x 198 horizontal grid cells using a 12-km resolution, and 56 x 108 horizontal grid cells using a 4-km (Figure 2.) resolution based on Lambert

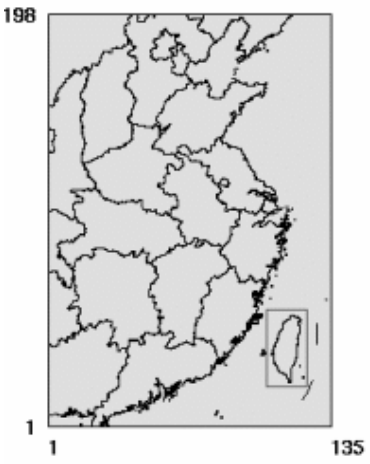

Figure 1. 12km Boundary Domain



Figure 2. 4km Taiwan Domain

Conformal map projection centered at (34^0N, 102^0E). Twelve vertical layers were configured initially following the Sigma (s) layer structure with denser grids at lower levels to better resolve the boundary layer. The s -layer interfaces occurred at: 0.995 (38 m), 0.988 (92 m), 0.97 (230 m), 0.938 (482 m), 0.893 (846 m), 0.839 (1300 m), 0.777 (1850 m), 0.702 (2557 m), 0.582 (3806 m), 0.400 (6083 m), 0.20 (9511 m), and 0.00 (16,262 m).

Model Configuration

The May 2003 release version of Models-3/CMAQ system was used in this modeling work. Further details of model configuration and science modules are given in Models-3/CMAQ science document (U.S.EPA 1999). The key science modules used in this modeling work are given below. Note that the selected science modules are the default options given in the May 2003 Models-3/CMAQ release version.

Model Inputs and Setup

The Mesoscale Model Version 5 (MM5) was used to provide meteorological input fields for the model simulations. The 36-, 12- and 4-km domains and their meteorological outputs simulated by MM5 in the USEPA's East Asia modeling effort were used in this work. The newest Meteorology/chemistry Interface Processor (MCIP) 2.2 that corrected layers collapsing released in June 2003 was used to process the raw MM5 output data into the format and structure required by the Models-3/CMAQ modeling. The Sparse Matrix Operator Kernel Emissions (SMOKE) Modeling System was used to prepare emission inputs based on the recently updated Taiwan Emission Data System (TEDS) (TEPA, 2001).

INITIAL RESULTS AND DISCUSSION

Figure 3. gives an example profile of several species (NO, PAR, and NH_3) prepared by SMOKE in January 2001. Initial results from the Models-3/CMAQ simulation are discussed below. The discussion first focused on fine PM 2.5 and visibility and major PM 2.5 constituents such as sulfate PM and nitrate PM. As part of a series of on-going modeling efforts, January 2001 episodes Models-3/CMAQ simulation over the Taiwan island was conducted. Initial tests showed that the Models-3/CMAQ system was capable of simulating key criteria pollutants reasonably well over a typical day and within an acceptable run time. The objective of this study was to conduct a preliminary model results on Taiwan's scenarios. The preliminary results were shown as Figure 4.

The air pollution fees (APF) fund finances TEPA in various air quality improving projects. These projects include: motor vehicles inspection and maintenance, promotion of low-polluting vehicles, compensating new cars to replace old cars, subsidizing public transportation, providing free consulting to major emission sources, subsidizing landfill gas power generation, and etc. These projects provide even more incentives for air quality improvement (Chen and Chiang, 2000).

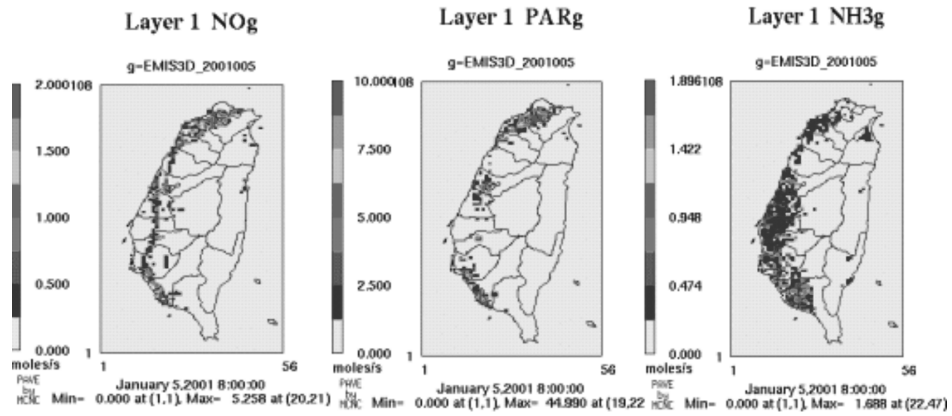

Figure 3. Preliminary results of NO, PAR and NH_3

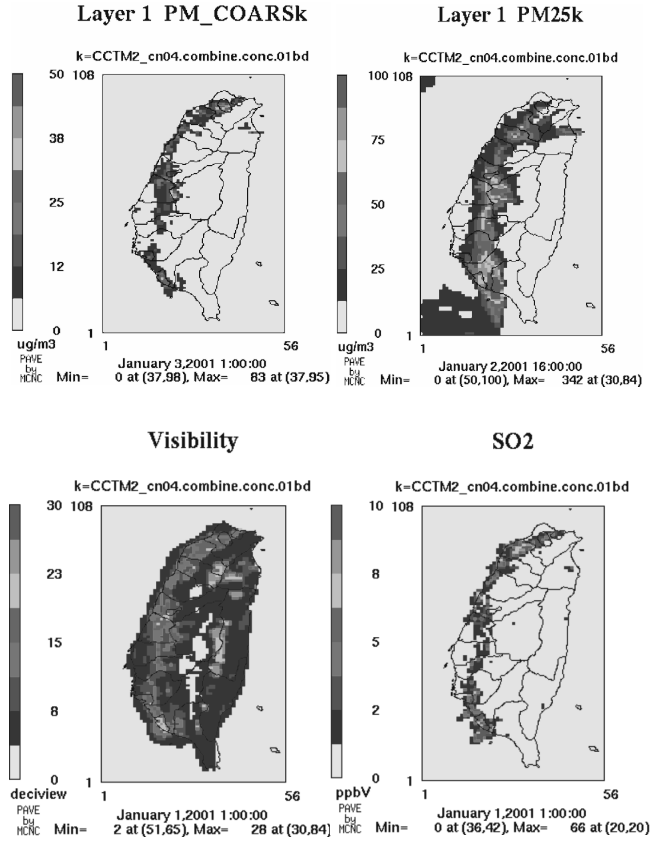

Figure 4. Preliminary results of PM, $PM_{2.5}$, Visibility and SO_2

However, cross-boundary transportation of air pollutants is hindering our efforts to further improve our air quality. For example, the dust storm from Mongolia caused the high PM_{10} levels in January, February, and April of 1999. Using an advanced air quality modeling system such as USEPA's Models3/CMAQ, the "One Atmosphere" model, we are able to assess multi-pollutants at once such as ozone, particulate matter, acid deposition, and visibility. The Models3/CMAQ is conducted with the air quality assessment applications in Asia countries (Fu, et al., 2003). The scientists from TEPA and USEPA and faculty from Taiwan and US are working on their bilateral air quality modeling assessment collaboration to investigate the cross-boundary and trans-pacific of air pollutants issues. In addition to emission reduction, the economic concerns are taken into account. Cost-effective control strategies will be developed by using Models3/CMAQ with ControlNET that is a pollutant cost database. These modeling system and control database provide a decision support system for TEPA's policymakers.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

PCBS AND PCDD/FS IN ZAGREB AMBIENT AIR SAMPLES BETWEEN 1997 AND 2001

S Herceg Romanić[1], B Krauthacker[1, *], Z Milanović[2]

ABSTRACT

Polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-para-dioxins and dibenzofurans (PCDD/Fs) belong to a large group of persistent organic pollutants. PCBs are commercial products while PCDD/Fs are undesirable by-products of industrial processes which include chlorine (chemical, paper industry) and waste incineration. Once emitted, they spread over all abiotic and biotic compartments of environment. In this study we summarise our findings of PCB and PCDD/F levels in ambient air samples collected in Zagreb between 1997 and 2001.
From October to December 1997, samples were collected at two sampling points: Jakuševec (10 samples) and Ksaver (14 samples) and analysed for the presence of six PCB indicator congeners (PCB-28, PCB-52, PCB-101, PCB-138, PCB-153, PCB-180). The highest level found at both locations was that of PCB-28. The levels of six indicator PCBs were measured again together with 14 more PCB congeners at Ksaver and Jakuševac between June 1999 and February 2001. PCB concentration ranges in air samples collected in 1997 and 2001 overlap. The comparison of respective periods in 1997 and 1999 shows a slight decrease at Ksaver.
The levels of PCDD/Fs were determined in 29 samples collected in May–June 1997, January–April 1998, November 1999 and January–March 2000 at five different locations in Zagreb. The calculated I-TEQ values were 9-47 fg/m^3 for samples collected in May/June 1997, 17-308 fg/m^3 for samples collected in January/April 1998, 21-29 fg/m^3 for samples collected in November 1999, and 15-90 fg/m^3 for samples collected in January–March 2000.

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INDEX TERMS

PCBs, PCDD/Fs, organochlorine pollutants

INTRODUCTION

Polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-para-dioxins and dibenzofurans (PCDD/Fs) belong to a large group of persistent organic pollutants. PCBs are commercial products and due to their excellent properties they had a worldwide industrial use. PCDD/Fs are undesirable by-products of industrial processes which include chlorine (chemical, paper industry) and waste incineration. Once emitted, they spread over all abiotic and biotic compartments of environment. In many countries, extensive studies were done on their presence in ambient air. Only limited data are available for ambient air in Croatia.
The measurements of PCDD/Fs levels in the ambient air in Croatia were initiated in 1993 by analysing PCDD/Fs in two ambient air samples collected in Zagreb (Ksaver) and Jastrebarsko, a town near Zagreb (Krauthacker et al. 1998). In this study, we summarise our findings on PCB and PCDD/F levels in ambient air samples collected in Zagreb between 1997 and 2001.

METHODS

Sampling: The samples were collected in Zagreb, the capital of Croatia situated inland, to the northwest of the country at the foot of the Medvednica (1035 m) to the north and on the banks of the river Sava to the south. All samples were collected on quartz fibre filters and polyurethane foam. The first round of PCB samples was collected at two locations: Jakuševec, a suburb to the south of Zagreb with a city dump (10 samples) and Ksaver, a residential area to the north (14 samples); from October to December 1997. The second round was collected at Ksaver (47 samples) from June 1999 to February 2000 and at Jakuševec (33 samples) from June 2000 to June 2001. PCDD/PCDFs samples were collected at five locations: Žitnjak, an industrial zone to the east of Zagreb, Jakuševec, PUTO, the waste incinerator located near Jakuševec, orđićeva, city centre with intense traffic, and Ksaver. Sampling dates and average temperatures are presented together with results in Table 2.

Analysis: Polyurethane foam and quartz fibre filters were extracted together and therefore all results refer to levels in particles and gas phase together. The methods used have been described earlier (Krauthacker et al. 1998; Herceg Romanić and Krauthacker 2000). PCBs were analysed at the Institute for Medical Research and Occupational Health in Zagreb, while PCDD/PCDFs were analysed by MWC UmweltConsulting, Berlin, Germany with MPU GmbH, Dep. Analytical Laboratory, Berlin, Germany.

RESULTS AND DISCUSSION

Table 1 shows the PCB and Table 2 PCDD/PCDF levels in ambient air collected in Zagreb in 1997 and 2001. In 1997, six indicator PCBs were measured: PCB-28, PCB-52, PCB-101, PCB-138, PCB-153 and PCB-180, and in 1999/2001 twenty PCBs (listed in Table 1) were measured. There is no marked difference between the two rounds

Table 1. Polychlorinated biphenyls (pg/m^3) in ambient air collected in Zagreb from 1997 to 2001

	Ksaver				Jakuševec			
	1997 (N=14)*		1999/2000(N=47)**		1997 (N=10)*		2000/2001(N=33)**	
Congener	range	median	range	median	range	median	range	median
PCB-28	17-57	29	3-312	36	15-92	36	5-204	81
PCB-52	9-36	19	2-65	13	10-44	21	2-173	14
PCB-60	NA	NA	0-23	8	NA	NA	1-33	10
PCB-74	NA	NA	0-19	2	NA	NA	0-23	8
PCB-77	NA	NA	/	0	NA	NA	0-8	0
PCB-101	4-28	10	2-223	14	5-36	14	1-163	27
PCB-105	NA	NA	0-36	2	NA	NA	0-30	6
PCB-114	NA	NA	0-14	0	NA	NA	0-13	3
PCB-118	NA	NA	0-24	3	NA	NA	0-24	8
PCB-123	NA	NA	0-12	3	NA	NA	0-17	7
PCB-126	NA	NA	0-4	0	NA	NA	0-10	0
PCB-138	2-21	8	12-128	6	4-24	10	1-72	13
PCB-153	3-16	7	1-92	4	9-20	12	1-55	9
PCB-156	NA	NA	0-1	0	NA	NA	0-3	0
PCB-157	NA	NA	/	0	NA	NA	0-1	0
PCB-167	NA	NA	0-4	0	NA	NA	0-3	0
PCB-169	NA	NA	0-3	0	NA	NA	/	0
PCB-170	NA	NA	0-2	0	NA	NA	0-6	0
PCB-180	1-13	5	0-7	2	10-51	13	0-23	2
PCB-189	NA	NA	0-2	0	NA	NA	/	0

N – number of analysed samples; NA- not analysed; 0 – below determination limit;
* Herceg Romanić and Krauthacker, 2000; ** Herceg Romanić and Krauthacker, 2003

for individual PCBs with respect to location and the year of sampling. The ranges overlap. Higher levels were determined at higher ambient temperatures in Ksaver (Herceg Romanić and Krauthacker, 2002; Herceg Romanić and Krauthacker, accepted for publication) what is in agreement with general observations that at locations where no PCBs sources are present, higher levels in warmer seasons are the

result of evaporation from the environmental sorbens. This was not the case at Jakuševec location. In our samples PCB-28 and PCB-52 showed the highest levels at both sampling sites in both rounds. It is evident from Table 1 that the medians of eight PCB congeners are below detection limit because they were present in less than 50% of samples. A comparison between rounds shows a slight decrease in six indicator PCBs at Ksaver (from 1997 to 1999) (Herceg Romanić and Krauthacker, 2003), but not at Jakuševec (from 1997 to 2000) with the exception of PCB-52 and PCB-180 (Herceg Romanić and Krauthacker, accepted for publication)

Table 2. PCDD/PCDF levels in ambient air samples collected in Zagreb from May 1997 to March 2000

SAMPLING LOCATION	SAMPLING TIME	AVERAGE TEMP. (^{o}C)	fg I-TEQ/m^3
PUTO-1	16.05.-19.05.1997	22.2	39
PUTO-2	11.06.-14.06.1997	23.2	12
ŽITNJAK-1	29.01.-02.02.1998	-2.5	83
ŽITNJAK-2	25.02.-27.02.1998	8.2	306
JAKUŠEVEC-1	16.05.-19.05.1997	22.2	47
JAKUŠEVEC-2	11.06.-14.06.1997	23.2	18
JAKUŠEVEC-3	16.01.-19.01.1998	3.1	94
JAKUŠEVEC-4	13.02.-16.02.1998	10.5	124
JAKUŠEVEC-5	16.03.-19.03.1998	4.9	49
JAKUŠEVEC-6	05.11.-08.11.1999	0.1	29
JAKUŠEVEC-7	10.01.-13.01.2000	-0.5	25
JAKUŠEVEC-8	06.03.-09.03.2000	9.8	15
ĐORĐIĆEVA-1	23.05.-26.05.1997	15.4	9
ĐORĐIĆEVA-2	06.06.-09.06.1997	20.1	41
ĐORĐIĆEVA-3	19.01.-22.01.1998	4.6	56
ĐORĐIĆEVA-4	13.02.-16.02.1998	13.7	169
ĐORĐIĆEVA-5	16.03.-19.03.1998	5.8	78
ĐORĐIĆEVA-6	05.11.-08.11.1999	0.1	26
ĐORĐIĆEVA-7	10.01.-13.01.2000	-0.5	50
ĐORĐIĆEVA-8	06.03.-09.03.2000	9.8	17
KSAVERSKA-1	23.05.-26.05.1997	15.4	10
KSAVERSKA-2	06.06.-09.06.1997	20.1	11
KSAVERSKA-3	02.02.-09.02.1998	1.4	72
KSAVERSKA-4	02.03.-04.03.1998	7.9	47
KSAVERSKA-5	31.03.-03.04.1998	14.6	17
KSAVERSKA-6	02.11.-05.11.1999	5.6	21
KSAVERSKA-7	17.01.-19.01.2000	0.3	39
KSAVERSKA-8	28.02.-03.03.2000	6.7	90

Table 2 shows PCDD/PCDF levels in ambient air samples collected in Zagreb, expressed as toxic equivalents (I-TEQ), which were calculated using the international toxic equivalence factors (I-TEFs). The levels of PCDD/PCDFs in samples collected in colder seasons are higher than in warmer seasons. The highest level was measured in the industrial zone Žitnjak, which suggests a source of PCDD/PCDFs in that area. The PCDD/PCDF level in that sample exceeded 150 fg I-TEQ/m^3 (Krauthacker et al., 1998)which is proposed the maximum acceptable level in ambient air in countries like Germany. In general, PCB and PCDD/PCDF levels in ambient air collected in Zagreb (with the exception of a single sample from Žitnjak) kept within the ambient air pollution limits adopted in most European countries.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
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GASEOUS MERCURY SPECIES IN THE POLLUTED PART OF THE KAŠTELA BAY (EASTERN ADRIATIC COAST)

Ž Kwokal[1] and M Branica

ABSTRACT

The concentrations of volatile mercury species, elemental (Hg^0) and dimethyl mercury (CH_3HgCH_3), were measured in the part of the Kaštela Bay polluted by mercury (in the vicinity of the former chlor- alkali plant). The concentrations of CH_3HgCH_3 obtained are in the range between 0.01 and 0.03% of the total mercury in the water column (200–400 ng L^{-1}). However, the Hg^0 concentrations are higher up to 15 times. The presence of these species in the water column leads to the assumption of the natural removal of Hg and the selpurification of the polluted part of the Bay. The total gaseous mercury (TGM) concentrations in the air above the sea surface are in the range between 0.2 and 0.3 μg m^{-3} at the same sampling stations. An abandoned cell house of the closeddown chlor-alkali plant is a hazardous source of the total gaseous mercury (3 - 4 μg m^{-3} in the air) as well as a nearby factory outlets (about 1 μg m^{-3}). A long atmospheric «lifetime» of an elemental gaseous mercury as well as its easy transport to remote areas, represent a serious problem which exceeds regional boundaries. All mercury species were mesaured using a Cold Vapour Atomic Absorption Spectrometry with the application of different methods for the separation of species from the samples.

INDEX TERMS

Gaseous mercury, Atmosphere, Water, Chlor-alkali, Kaštela Bay

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INTRODUCTION

Global cycling of mercury begins with the evaporation of mercury vapour from land and sea surface. Mercury exists in the atmosphere in three diferent forms: a dominant total gaseous mercury (TGM) (with more than 90% of an elemental gaseous mercury and a minority of other species, such as: $HgCl_2$, CH_3HgCl and CH_3HgCH_3), a reactive gaseous mercury (RGM) (a water soluble mercury species, mainly composed of $HgCl_2$) and a total particulate mercury (TPM) (mercury associated with an atmospheric particulate matter).
The elemental gaseous mercury, as a dominant form of mercury in the atmosphere, is unreactive and water insoluble, with an atmospheric «lifetime» of approximately one year, which leads to a global dispersion. Mercury is released into the atmosphere through many different natural processes and human activities. Natural sources of mercury in the atmosphere are: a degassing of the earths crust, volcanic activities and weathering processes. An anthropogenic emission sources or man-made emissions of mercury include a fosil fuel combustion (primarily coal in a coal-fired power plants), mining and smelting of mercury ores, the incineration of wastes and industrial processes using mercury (chlor-alkali, paper and pulp industry,etc). The anthropogenic mercury emissions to the global atmosphere are estimated to approximately 2000 t y^{-1} (Pacyna EG, and Pacyna JM, 2002). A metallic mercury is mainly utilized in a chlor-alkali industry for the production of chlorine. The chlor-alkali industry produced 14 % of the total anthropogenic mercury emission in Europe (Pacyna et al, 2001). The chlor-alkali plant situated in the Kaštela Bay released mercury into the bay for 40 years (1949 – 1989). By installing a new technology for the recycling of mercury, the factory reduced direct mercury emission with effluents into the bay during 1985. (Zvonarić T, 1991). There is no consumption of mercury in the production of chlorine, but in any plant there are some inevitable losses. Having an understanding of the technological process of the production, one can calculate the losses of mercury per ton of the chlorine produced. It has been estimated that about 200 tons of mercury was discharged into the Kaštela Bay until 1989 when the chlor-alkali plant was closed down (Zvonarić T, 1991) Once released into the air, seawater and soil, mercury is hard to control because it undergoes different chemical transformations (oxidation, reduction, methylation, dimethylation, demethylation, biomagnification). Via such processes, mercury enters the biological system, ultimately threatening mankind.

METHODS

Sampling site

The Kastela Bay is situated in the central part of the eastern Adriatic coast in the vicinity of the town of Split. It is the largest bay in the central Dalmatia (14.8 km in length and 6.6 km in width) heavily impacted by the industrial activities

concentrated in the area (chlor-alkali production, chemical and cement industries and shipyards). The bay is identified as an area highly polluted in part with mercury discharged from the PVC factory which was closed down in 1989.

Sampling and analyses

The method for the TGM mesaurments in the air is based on a gold trap amalgamation, thermal desorption and detection by a Cold Vapour Atomic Absorption Spectrometry (CVAAS) (Kwokal and Branica, 2000). The air samples are collected onto a gold wire (99.99, 0.2 g) inserted into a quartz tube. The air is sucked in by a pump at the flow rate of 20 L h^{-1} (1 to 2L of the sampled volume). The flow rate is measured and controlled by a flowmeter. After obtaining the selected sampling volume, the quartz tube with a gold wire is disconected from the pump system and stored in a tightly closed quartz storage vessel for the protection of the gold wire from the additional adsorption of the atmospheric mercury until analysis (Kwokal at al. 1994). All samples were collected in triplicate at 1.5 to 2.0 m above the ground. The mercury was thermally desorbed and detected in an Elemental Mercury Detector (a mercury MONITOR ™ 3200 by a Thermo Separation Products). The detection limit of such a CVAAS system is 5 pg with the linearity range from 5 to 10000 pg. The detection limit of the method for the mercury mesaurments in the air is found to be 0.0001 μg m^{-3} for 5 L of the air sample. For the calibration purposes, different amounts of the mercury standard solution (10 ng ml^{-1}) were added to a 20 % H_2SO_4 / 10% $SnCl_2$ solution. The formed mercury vapour was trapped onto a gold wire, thermally desorbed and mesaured as described elsewhere. The concentrations of the gaseous mercuy species Hg^0 and CH_3HgCH_3 in the water column were mesaured by the method described elsewhere (Kwokal Ž, and Branica M. 2001).

RESULTS AND DISCUSION

The TGM concentrations were measured in the air in the vicinity of the chlor-alkali plant several years prior to (1986-1987) as well as 14 years after the closedown of the factory (2003) (Fig.1).

Regrettably, prior to the closedown, it was impossible to measure the TGM concentrations both inside the factory and in the cell house (the chlor-alkali production using a liquid elemental mercury as a cathode). The factory outlet, only a few meters away from the cell house, was chosen as a «hot spot» for the measurements of the TGM concentrations. During the factory operations, the TGM concentrations in the air (about 2 m over the surface) were in the range between 25 and 35 μg m^{-3} while 13 years after the closedown, the TGM concentrations at the same location, were in the range between 0.9 and 1.1 μg m^{-3}, only. The TGM concentrations in the air diminished significantly a few hundred meters east and west from the chlor-alkali plant. The TGM concentrations measured at the distance of 400 m from the plant during the period 1986-1987,

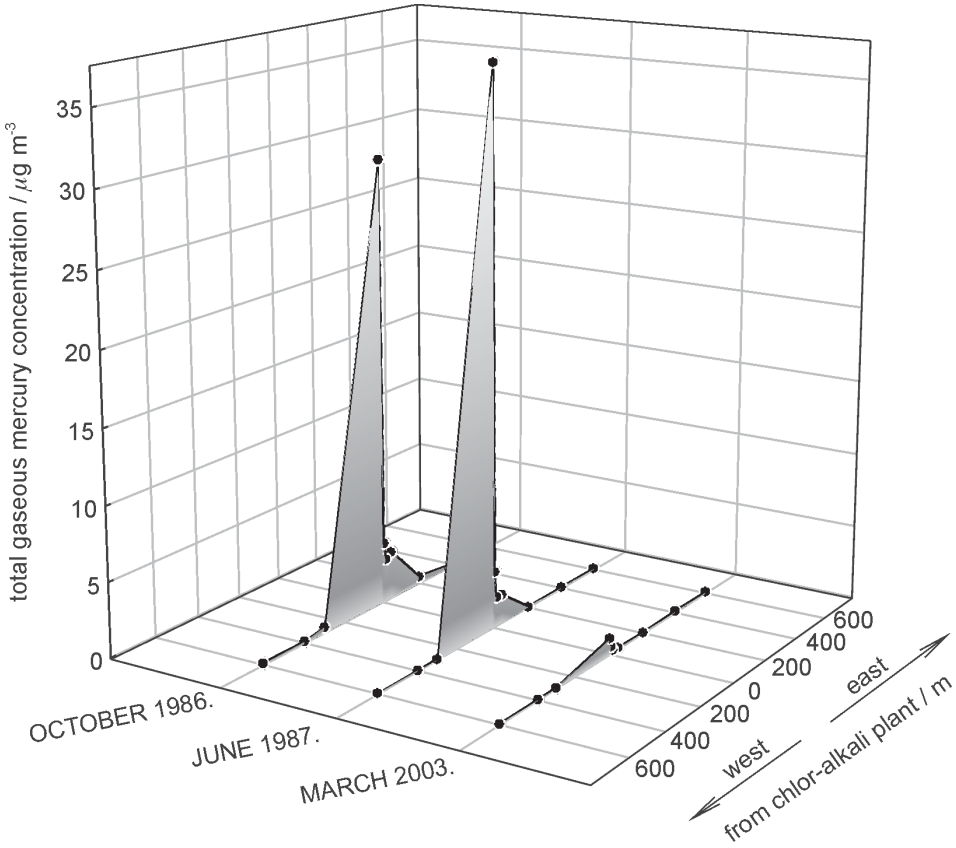

Figure 1. Total gaseous mercury concentrations (μg m^{-3}) in the air of the Kaštela Bay (East-West) from the chlor-alkali plant (closed down in 1990).

were in the range between 0.015 – 0.3 μg m^{-3}, while in 2003, the concentrations were in the range between 0.02 – 0.08 μg m^{-3}. However, the inhabitants of the nearby area (a few hundred meters away from the plant) were daily exposed to high TGM concentrations in the air. The TGM concentrations measured in 1987 in the house closest to the chlor-alkali plant, were in the range between 1 and 3 μg m^{-3}. As a consequence, the mercury concentrations in the hair of the 13 year-old girl living in the house, were found to be in the range between 1.4 and 1.6 μg g^{-1}. In 2003, the TGM concentrations were measured for the first time in the abandoned and empty former cell house. Even though the cell house is windowless, doorless, and exposed to various weather conditions, the TGM concentrations inside are still high (between 3 and 4 μg m^{-3}). Therefore, the dust on the floors still contains sufficient quantities of the elemental mercury which are a permanent source of the air contamination. Besides, the soil in the vicinity of the factory is also contaminated with mercury (up to 2 μg g^{-1}) which also pollutes the air. Since the

distance from the factory outlet to the sea is about 50 m, the mercury is also significantly present in that part of the Kaštela Bay. A long-term investigations carried out with respect to the impact of the discharged mercury upon the aquatorium, were based on the measurements of different mercury species in the water column, sediments and biological matter. Until recently, the concentrations of gaseous mercury species were not measured in the water column, sediments, and above the sea surface. The concentrations of dimethylmercury (CH_3HgCH_3) were detected in a very restricted area of the polluted part of the Kaštela Bay. These concentrations represented 0.01 – 0.03 % of the total mercury concentrations in the water column at the same location (200 – 400 ng L^{-1}) (Kwokal Ž, and Branica M, 2001). The concentrations of the gaseous elemental mercury (Hg^0) detected in the water column of a larger area, were from 1 to 15 times higher than the dimethilmercury concentrations. The Hg^0 concentrations were elevated at the surface, while the CH_3HgCH_3 concentrations were higher at the bottom of the water column. The Hg^0 concentrations in the seawater were the highest (up to 0.5 ng L^{-1}) in the shalow part, where the concentrations of the total mercury in sediments were also the highest (up to 85 mg kg^{-1} w.w.) (Kwokal at al, 2002). At the same location, the TGM concentrations in the air just above the sea surface, were about 0.2 μg m^{-3}, while the TGM concentrations in the vicinity were in the range between 0.03 and 0.05 μg m^{-3}.

CONCLUSION

The part of the Kaštela Bay is significantly polluted by mercury discharged for 40 years from the chlor-alkali plant into the aquatorium, the soil and the air in the vicinity of the plant. A long-term measurements of the concentrations of different mercury species, such as: total, reactive and monomethyl mercury, were carried out in the water column, sediments and biological matter. However, for the better understanding of the biogeochemical cycle of mercury and the fate of its species, it was necessary to measure the concentrations of the gaseous mercury species in the water column and sediments, as well as the TGM concentrations in the air of the area investigated. The presence of the the volatile Hg^0 and CH_3HgCH_3 species in the water column, and sediments, leads to the natural removal of the total mercury and consequentely selpurification of the polluted part of the Bay. Although the chlor-alkali plant was closed-down about 13 years ago, the area in the vicinity of the plant is still polluted by mercury, especially in the vicinity of an abandoned cell house and the neglected factory outlets, which results in the elevated TGM concentrations in the air and the sea. While the elevated concentrations of mercury in the water column and sediments represent a local problem, the TGM concentrations in the air, owing to its physicochemical characteristics and a long atmospheric «lifetime» (about 1 year) exceed regional boundaries. Therefore, a comprehensive restoration of the polluted area (soil and aquatoria) is strongly recommended.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

THE PRESENCE OF TOTAL GASEOUS MERCURY IN THE OPEN-AIR AND THE ATMOSPHERE OF SOME ELECTROCHEMICAL LABORATORIES

Ž Kwokal[1] and M Branica

ABSTRACT

The concentrations of the total gaseous mercury (TGM) were measured in the atmosphere of the electrochemical and reference laboratories at the «Ruđer Bošković» Institute in Zagreb and Šibenik, as well as outdoors. The TGM concentrations measured in the atmosphere of the laboratories in Zagreb and Šibenik were found to be in the range between 250 and 2000 ng m^{-3}, and between 40 and 250 ng m^{-3}, respectively.

Outside the laboratories in Zagreb and Šibenik, depending on the wind and temperature, the TGM concentrations were in the range between 30 and 200 ng m^{-3} and between 1 and 25 ng m^{-3}, respectively. During a long duration of a Bura wind (north-east) the TGM concentrations in Šibenik were comparable to the TGM concentrations in the polar region. It seems that the Bura wind purifies both the Šibenik aquatorium and the atmosphere. The TGM concentrations were measured using a Cold Vapour Atomic Absorption Spectrometry (CVAAS) technique based on the preconcentration of mercury onto a gold wire followed by its thermal desorption and the determination by an Atomic Absorption Spectrometry (AAS). The detection limit of this procedure is 0.1 ng m^{-3} for the 5L of the air sample.

INDEX TERMS

Gaseous mercury, Atmosphere, Electrochemical laboratories.

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INTRODUCTION

Mercury is the only metal existing at room temperature as a liquid. With the melting point at –38.9 °C, boiling point at 357 °C, density of 13.53 g cm^{-3} at 25 °C, vapour pressure of 0.180 Pa at 20 °C, ionisation potential higher than any other electropositive element (with the exception of hydrogen), chemically inert, mercury is quite different from other metals.

Mercury exists in the atmosphere in three main forms: elemental gaseous mercury, reactive gaseous mercury and total particulate mercury. All mercury species which pass through a 0.45 μm filter or some other simple filtration device (e.g., quartz wool), and are collected onto a gold wire, represent total gaseous mercury (TGM). The total gaseous mercury is mainly composed of the elemental mercury vapour including a small quantity of other species, such as $HgCl_2$, CH_3HgCl and $(CH_3)_2Hg$. The total particulate mercury (TPM) is a mercury adsorbed or bound to the atmospheric particulate matter (composed of Hg^o and RGM). The reactive gaseous mercury (RGM) is a water-solubile mercury species with a sufficient vapour pressure to exist in the gaseous phase as well (mainly as a $HgCl_2$) (Munthe, 1998). More than 90% of mercury exsts in the air as an elemental mercury vapour, with the exception of the unpolluted areas with a low particulate mercury concentrations, where the concentrations of the elemental mercury exceed 99%. In its liquid metallic form, mercury has found innumerable technical and medical applications. Based on the formation of amalgams with various metals, mercury is also applicable in the electrochemical research and analyses (polarography and voltammetry).

The determination of the low concentrations (below 10^{-9} mol dm^{-3}) of dissolved trace metals in natural waters, organic matter and chemical speciation, can be carried out using various electrochemical methods and techniques, such as an anodic stripping voltammetry (ASV) and a chatodic stripping voltammetry (CSV). A hanging mercury drop electrode or a static mercury drop electrode are frequently used. During the experiments, elemental (liquid) mercury evaporates into the laboratory atmosphere.

The elemental mercury mainly enters the body via inhalation (mercury vapour is a monatomic gas which evaporates from a liquid metallic mercury) because it is poorly absorbed in the digestive track. Depending on the length and intensity of the exposure, a severe damage to the human brain, kidneys and lungs may occur. Even though the toxicity of mercury is an irrefutable argument, opinions differ as to the extent to which mercury affects human health (e.g.,causing various lethal diseases). As far as its toxicity is concerned, mercury still remains «an element of mystery» (Clarkson, 2002.). Therefore, it is essential to strictly follow the recommendations of the health and environment protection organisations when working with mercury in laboratories. High concentrations of the elemental gaseous mercury often occur in the air of electrochemical laboratories. It is possible to diminish them for a several orders of magnitude, simply by aerating the laboratory for a certain period of time.

METHODS

The method for the TGM mesaurments in the air is based on a gold trap amalgamation, thermal desorption and detection by a Cold Vapour Atomic Absorption Spectrometry (CVAAS) (Kwokal and Branica, 2000). The air samples are collected onto a gold wire (99.99, 0.2 g) inserted into a quartz tube. The air is sucked in by a pump at the flow rate of 20 L h^{-1} (1 to 2L of the sampled volume). The flow rate is measured and controlled by a flowmeter. After obtaining the selected sampling volume, the quartz tube with a gold wire is disconected from the pump system and stored in a tightly closed quartz storage vessel for the protection of the gold wire from the additional adsorption of the atmospheric mercury until analysis (Kwokal at al. 1994). All samples were collected in triplicate at 1.5 to 2.0 m above the ground. The mercury is thermally desorbed and detected in an Elemental Mercury Detector (a mercury MONITOR ™ 3200 by a Thermo Separation Products). The detection limit of such a CVAAS system is 5 pg with the linearity range from 5 to 10000 pg. The detection limit of the method for the mercury mesaurments in the air is found to be 0.1 ng m^{-3} for 5 L of the air sample. For the calibration purposes, different amounts of the mercury standard solution (10 ng ml^{-1}) were added to a 20 % H_2SO_4 / 10% $SnCl_2$ solution. The formed mercury vapour was trapped onto a gold wire, thermally desorbed and mesaured as described elsewhere.

RESULTS AND DISCUSSION

The concentrations of total gaseous mercury (TGM) were measured in the atmosphere of the experimental electrochemical laboratories in Zagreb and Šibenik, of the Center for Marine and Environmental Research, «Ruđer Bošković» Institute. The TGM concentrations were also measured in the atmosphere of other laboratories as a referent ones: Laboratory V, Zagreb, Laboratory B, Šibenik where the elemental mercury was never used, as well as Laboratory I in Zagreb, where the elemental mercury is no longer in use. The measurements were also performed outdoors in the vicinity of these laboratories.

Even though the elemental mercury is stored in a tightly closed bottles in the electrochemical laboratories, the handling of mercury during various chores (decanting, filling the electrodes, analyses, etc.), enables its evaporation into the laboratory atmosphere. In the electrochemical laboratory A in Šibenik, there was about 300 ml of the elemental liquid mercury present (Table 1). The laboratory is situated about 10 m from the sea coast and exposed to winds which allow good aeration through the open windows.

During a long duration of the Bura wind (March 2003), the concentrations of TGM in the air in the vicinity of the laboratory were 1.2 ng m^{-3} which corresponds to a global background concentrations of approximately 1.5 to 2.0 ng m^{-3}. It also corresponds to the level concentrations of the unpolluted polar region (Canadian

Table 1. Total gaseous mercury outdoors and in the atmosphere in both electrochemical laboratory (A) and the laboratory for mercury measurements (B) -CMER-RBI, Šibenik .

DATE	LABORATORY	WEATHER CONDITIONS AND LABORATORY ATMOSPHERE		CONC. OF TOTAL GASEOUS MERCURY (ng m^{-3}) INDOORS	CONC. OF TOTAL GASEOUS MERCURY (ng m^{-3}) OUTDOORS
06.07.1997.	A	CALM, NO WIND 28 ^{0}C INDOOR 28 ^{0}C OUTDOOR	REGULARLY AERATED	250	20-24
	B			42	20-24
25.07.1997.	A	CALM, NO WIND 27 ^{0}C INDOOR 27 ^{0}C OUTDOOR	LABORATORY CLOSED FOR 12 HOURS	3219	18-19
			LABORATORY INTESIVELY AERATED 5 MIN.	167	17-19
	B		REGULARLY AERATED	55	17-19
15.12.2001.	A	DRY WEATHER "BURA WIND" 18 ^{0}C INDOOR 3 ^{0}C OUTDOOR	REGULARLY AERATED	110	2-5
	B		REGULARLY AERATED	7	2-5
23.02.2002.	A	DRY WEATHER "BURA WIND" 17 ^{0}C INDOOR 7 ^{0}C OUTDOOR	REGULARLY AERATED	200	3-4
24.02.2002.		DRY WEATHER "BURA WIND" 17 ^{0}C INDOOR 7 ^{0}C OUTDOOR	LABORATORY CLOSED FOR 10 HOURS	400	2
			LABORATORY INTESIVELY AERATED 30 MIN.	90	3
22.03.2003.	A	DRY WEATHER "BURA WIND" WERE BLOWING 1 MONTH 18 ^{0}C INDOOR 9 ^{0}C OUTDOOR	REGULARLY AIRATED	42	1.2-1.8
25.03.2003.	A		LABORATORY CLOSED FOR 15 HOURS	410	3-77
			LABORATORY INTESIVELY AERATED 10 MIN.	100	5-8
			LABORATORY CLOSED FOR 5 HOURS	290	4-8
	B		REGULARLY AERATED	8	7-8

Arctic), which are in the range between 0.6 and 1.8 ng m^{-3} (Ebinghaus at al., 2001). It seems that a northern wind Bura not only purifies a water column in the Šibenik aquatorium (Bilinski at al. 2000), but also an atmosphere.

At the same time, the TGM concentrations in the electrochemical laboratory (A) and the referent laboratory (B), were found to be 42 ng m^{-3} and 8 ng m^{-3}, respectively. During the summer months, the situation is different. The TGM concentrations in a completely shut laboratory (Table 1), were found to be 3219 ng m^{-3} (a maximal value). An intensive aeration of the laboratory for 5 minutes, diminished the TGM concentrations for about 20 times

The TGM concentrations in the atmosphere of the electrochemical laboratories in Zagreb are mostly higher than those in the Šibenik laboratories (Table 2). The presence of larger quantities of the elemental liquid mercury in the laboratory (up to 1 L) and a numerous staff, are the main reasons for the elevated TGM

concentrations. Even laboratory surfaces (especially floors) can be contaminated after a long-term exposure to gaseous mercury, especially if not thoroughly cleansed with powdered sulphur after various «accidents». As in Šibenik, an intensive aeration for a brief period of time enables diminishing of the TGM concentrations for several times. The ventilation systems in the Zagreb laboratories, should operate continuously and intensively. This is evident from the referent laboratories V and I (mercury not in use for more than twenty years), where the TGM concentrations are found to be 105 ng m^{-3} and 250 ng m^{-3}, respectively (Table 2).

Table 2. Total gaseous mercury outdoors and in the atmosphere of electrochemical laboratories (II-IV) and referent ones (I and V) of CMER-RBI, Zagreb.

LABORATORY	WEATHER CONDITIONS AND LABORATORY ATMOSPHERE	CONC. OF TOTAL GASEOUS MERCURY (ng m^{-3}) INDOORS	CONC. OF TOTAL GASEOUS MERCURY (ng m^{-3}) OUTDOORS
I	REGULARLY AERATED INDOOR 28 ^{0}C OUTDOOR 6 ^{0}C	250	30-60
II	LABORATORY CLOSED FOR 12 HOURS INDOOR 18 ^{0}C OUTDOOR 6 ^{0}C	1100	30-60
	INTESIVELY AERATED 10 MIN. INDOOR 16 ^{0}C OUTDOOR 6 ^{0}C	400	
	REGULARLY AERATED 5 HOURS INDOOR 18 ^{0}C OUTDOOR 6 ^{0}C	750	
III	LABORATORY CLOSED FOR 24 HOURS INDOOR 20 ^{0}C OUTDOOR 11 ^{0}C	1000	60-70
	INTENSIVELY AERATED 10 MIN. INDOOR 17 ^{0}C OUTDOOR 11 ^{0}C	350	
	REGULARLY AERATED 5 HOURS INDOOR 19 ^{0}C OUTDOOR 11 ^{0}C	500	
IV	LABORATORY CLOSED FOR 17 HOURS INDOOR 23 ^{0}C OUTDOOR 11 ^{0}C	4400	200-300
	INTENSIVELY AERATED 10 MIN. INDOOR 21 ^{0}C OUTDOOR 11 ^{0}C	1570	
	REGULARLY AERATED 7 HOURS INDOOR 22 ^{0}C OUTDOOR 11 ^{0}C	2200	
V	REGULARLY AERATED INDOOR 19 ^{0}C OUTDOOR 16 ^{0}C	105	45-80

A similar difference in the TGM concentrations occurrs in the open-air in the vicinity of the laboratories in Šibenik and Zagreb. The TGM concentrations in Šibenik and Zagreb are in the range between 1.1 and 25 ng m^{-3}, and between 30 and 200 ng m^{-3}, respectively, with the exception of the vicinity of the laboratory IV in Zagreb (near the window) where the TGM concentration is found to be 300 ng m^{-3}.

CONCLUSION

The TGM concentrations in the atmosphere of the electrochemical laboratories where the elemental (liquid) mercury is experimentaly used in various kinds of electrodes, are markedly higher than in the laboratories where mercury is not in

use at al. Tightly shut laboratories, showed that the TGM concentrations were higher than permissible concentrations. This can be avoided by an intensive aeration of the laboratory. Therefore, special attention must be paid to intensive daily aeration of laboratories. The measurements of the TGM concentrations in the open-air (outdoors) in the vicinity of the laboratories in Šibenik and Zagreb, show that the TGM concentrations in Šibenik are very low during a long duration of the Bura wind (north-east). These concentrations are as low as the concentrations in the polar region (Canadian Arctic), which are in the range between 0.6 and 1.8 ng m^{-3}.

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The 14th International Conference
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Dubrovnik, CROATIA 6-10 October 2003

SOURCE APPORTIONMENT OF COARSE AND FINE PARTICLES IN THE HADERA URBAN AREA ALONG THE EAST MEDITERRANEAN COAST

Y Mamane*, O Yossef and E Melamed

ABSTRACT

This study deals with receptor modeling of fine (<2.5 μm) and coarse (2.5 to 10 μm) particles in order to identify the main sources and their impact on ambient particle concentration in the Hadera urban area, a complex of small towns along the east coast of the Mediterranean Sea. The study consisted of the following: (1) Statistical and meteorological analyses of existing ambient air quality monitoring data collected by the Hadera District; (2) 24 hr sampling of fine and coarse particles and elemental analysis of each fraction using X-ray fluorescence (XRF); (3) Scanning electron microscopy (SEM) of selected samples collected also with a dichotomous sampler, and (4) receptor modeling of PM10 using several statistical tools.

Data from continuous monitoring station showed that PM-10 levels were largest in autumn and spring due to intrusion of dust storms in the region. XRF and SEM analyses of selected summer and autumn samples showed that S and elemental carbon dominated the fine fraction (<2.5 μm) and Ca dominated the coarse fraction (2.5 to 10 μm). Possibly, some of the sulfates are transported from Eastern Europe. Elements associated with alumino-silicate minerals were found in small quantities. Sea salt (Na, Cl) was found at both fractions. V and Ni are highly correlated, indicating the heavy use of crude oil in the area. SEM analyses of several thousand particles for different samples substantiate the XRF findings.

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Apportionment of ambient particles in Hadera using the Chemical Mass Balance Receptor Model yield inadequate source resolution. Apparently the use of source profiles from the published literature (mainly collected in the USA) may not be suitable for the Hadera Airshed. It is expected that more definitive answers on the impact of various sources in the area will be obtained when source profiles of the local point and fugitive sources are available.

INDEX TERMS

$PM_{2.5}$, PM_{10}, scanning electron microscopy, x-ray fluorescence, source apportionment.

INTRODUCTION

Particulate matter (PM) pollution has long been recognized to impact human health. Since the 1952 London episode (Wilkins, 1954), studies in various locations have reported that variations in airborne particles are associated with variations in daily mortality (Schwartz, 1994, and references therein). Epidemiological studies have demonstrated association not only between ambient particles and excess mortality, but also with excess morbidity. Only very few of these studies had a detailed characterization of the particles involved. In the study of Dockery et al. (1993), the air pollution data included total particle mass ($d < 10\,\mu m$ or PM_{-10}), fine particle ($d < 2.5\,\mu m$) mass, sulfate concentration, and aerosol acidity. They found that fine particles contributed to excess mortality in certain U.S. cities. The physical and chemical properties of particles are essential to the understanding of particle formation, transport, and impact on human health. They provide also the necessary information needed for source apportionment.

Particles are a mixture of solid particles and liquid droplets that vary in size, chemistry and origin. While larger particles ($d > 2.5\,\mu m$) comprised of crustal material (silicates, carbonates,...) and biological species (spores, pollen, plant and animal debris,...), fine particles are emitted from combustion sources (volatile and elemental carbon), and are also formed through oxidation of sulfur and nitrogen oxides to sulfates or nitrates particles. Nitrates may be found also in the coarse fraction (2.5 to 10 μm) (Mamane and Mehler, 1987).

It is the aim of this research to evaluate the applicability of scanning electron microscopy (SEM) and receptor modeling to inhaled particles that may be linked to health effects, and to identify the sources that contribute to particulate air quality in the Hadera region. This study will provide the chemical and physical properties of coarse, and fine ambient particulate data to transport meteorological models applied to Hadera urban region, a complex of small towns nearby an industrial area and a 2500 MW coal power plant.

METHODS

This research deals with the chemical and physical characterization of fine and coarse particles using scanning electron microscopy (SEM) and X-ray fluorescence (XRF) techniques.

Ambient particle samples were collected with dichotomous samplers in two sites in the Hadera area, one downwind of the 2500MW coal fired power plant, and one in a background rural location. Samples were taken in two seasons: summer and fall 2002. They included 24 hr samples of fine (0 to 2.5 μm) and coarse (2.5 to 10 μm) particles on Teflon filters for gravimetric and elemental analysis by XRF. In parallel to the dichotomous sampler continuous mass monitors provided the loadings, variability and general trends of PM_{-10}.

All Teflon filters collected by the dichotomous samplers were analyzed by XRF that provides the elemental concentration of the fine and coarse particles. Individual particles collected on Nuclepore filters were analyzed by SEM coupled with energy dispersive x-ray analyzer (EDX) (Mamane and Dzubay, 1988 and 1990; Mamane, 1990; Mamane et al, 1990; Hopke and Casuccio, 1991; Hunt et al, 1992; Mamane et al, 2001). Several thousand particles were analyzed. For each particle a digitized micrograph and EDX spectrum were stored, as well as information on particle size, shape, morphology, and surface texture; x-ray counts (elemental concentration) of 15 to 30 elements. Each particle was assigned to a pre defined category, such as minerals, biologicals (see Figure 4), spores, fly ash, incinerators, sulfates, sea salt, etc...

Source apportionment was performed on the coarse and fine fractions using chemical mass balance models and appropriate source signatures (Stevens and Pace, 1984; Dzubay et al., 1988; Watson et al., 1990). Other statistical tools such as cluster, factor analysis, and multiple linear regression analysis assisted in identifying the main particle sources. Combination of these tools enhance the source apportionment of particles (Dzubay and Mamane, 1989).

RESULTS

To this day, the following results have been obtained:

- PM-10 levels were largest in autumn and spring due to the occurrence of dust storms in the region. These findings were based on continuous monitoring of PM10.
- XRF and SEM analyses showed that S as sulfates (Figure1) and elemental carbon (Figure 2) dominated the fine fraction (<2.5 μm) and Ca as calcites dominated the coarse fraction (2.5 to 10 μm, Figure 3). Elements associated with Alumino-Silicate minerals were found in small quantities in natural sources and in coal fly ash.

- Based on summer air mass back-trajectories, showing that air is flowing from the northwest sector, it is concluded that a large fraction of the sulfates are transported from eastern Europe.
- Sea salt (Na, Cl) was found at both particle size fractions.
- V and Ni are highly correlated, indicating the use of crude oil in the area in large industrial boilers.
- SEM analyses of several thousand particles substantiate the above findings: sulfates and elemental carbon (diesel particles) dominate the fine fraction; sulfates are probably in the form of ammonium sulfates. Calcites and dolomites dominate the coarse size fraction; oil fly ash particles were quite abundant at both fractions (Figure 5); very few coal fly ash particles were identified; factor and cluster analyses pointed at the existence of this source.
- Apportionment of ambient particles using the Chemical Mass Balance Receptor Model yield inadequate source resolution. Apparently the use of USA source profiles may not be suitable to the Hadera Airshed. More definitive answers on the impact of various sources in the area will be obtained when local source profiles are available.

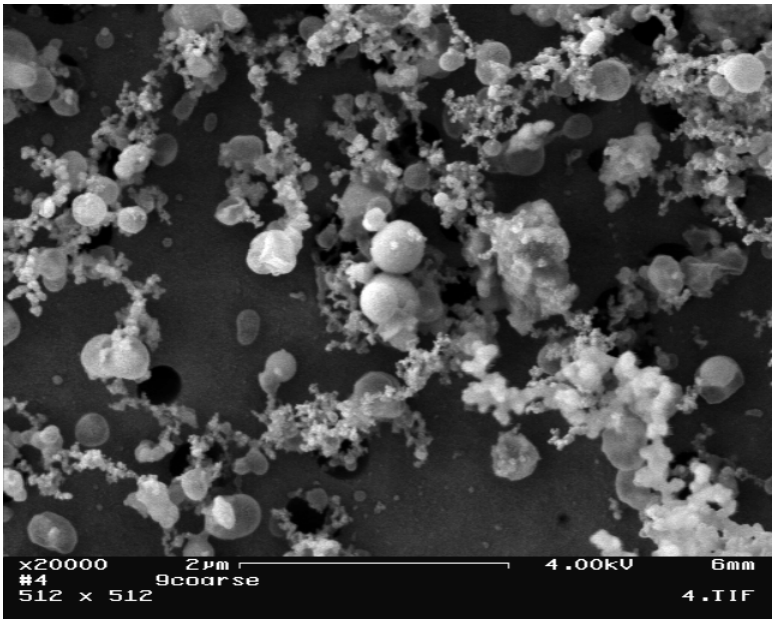

Figure 1. A close up of a field of view of the Fine Fraction. Most particles are either spherical sulphates (similar to ammonium sulphates in appearance) or short aggregates of diesel particles.

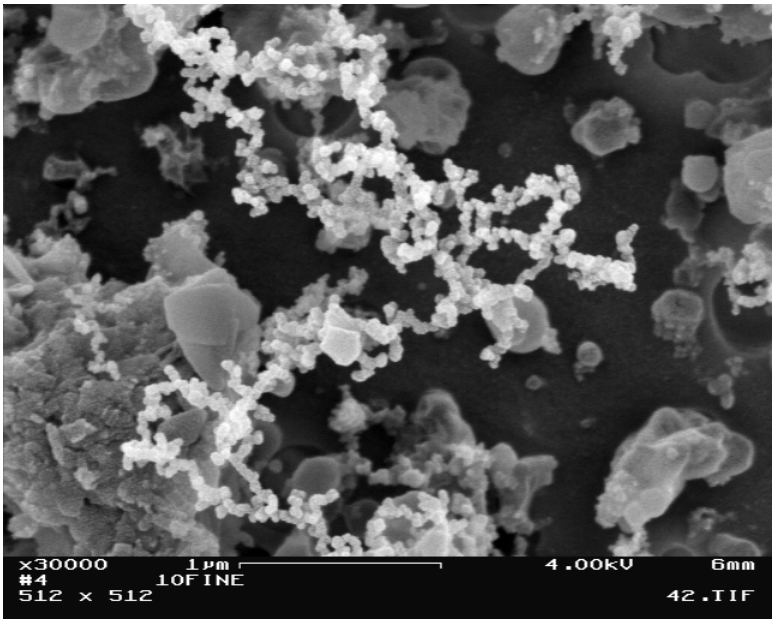

Figure 2. A close up of small diesel particles in the fine fraction. Spherules (nanoparticles) in the chain aggregate are very uniform in size, and are around 30-50 nm. Some irregular minerals are also seen.

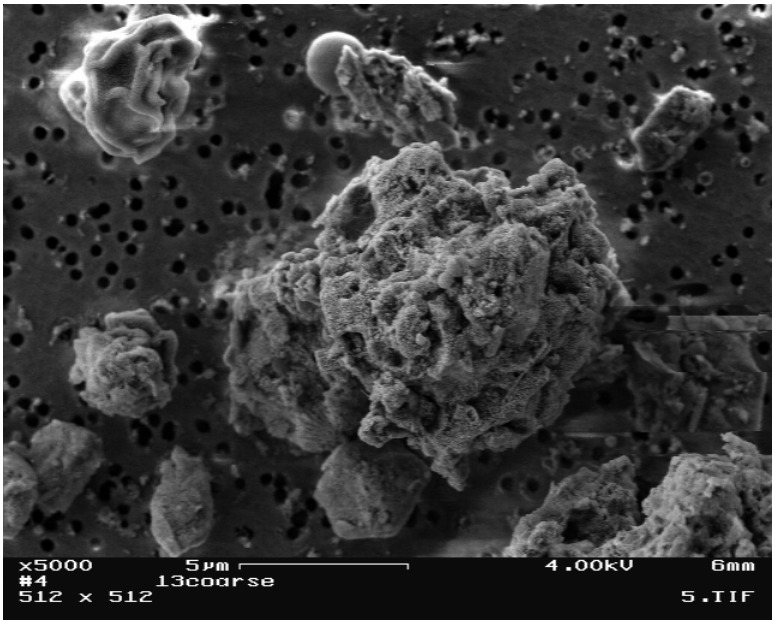

Figure 3. Typical Irregular Mineral with very rough pourous surfaces. A spherical 1.5 μm coal fly ash is seen at the top, and a "crushed" spore at the upper left corner.

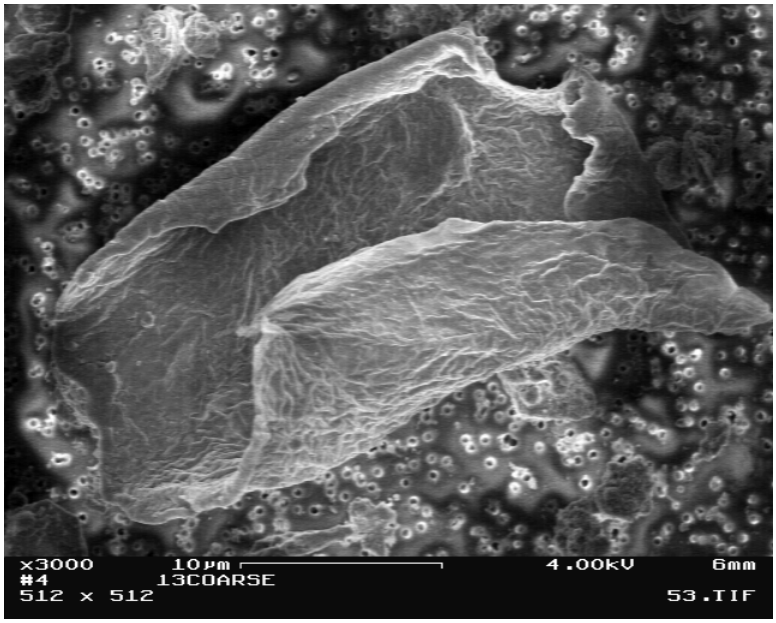

Figure 4. A flat 30 μm "skin" biological particle, very thin and irregular in shape, from the coarse fraction. Such unique particles were found in indoor samples in California.

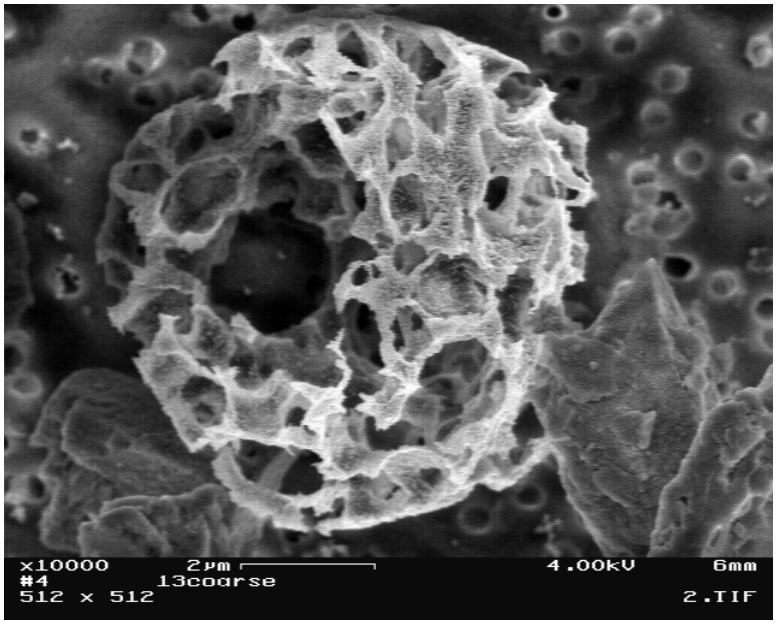

Figure 5. Oil Combustion Cenosphere rich in Ni and V collected in the coarse fraction. These are typical particles emitted from combustion of heavy oil (as oil no. 6).

ACKNOWLEDGEMENT

The authors acknowledge the assistance of the Hadera Town Association for the Environment. This research was funded by the Israeli Electric Company.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

OZONE ANALYSIS WITH DOMINANCE BASED ROUGH SET APPROACH IN A HIGH-RISK ENVIRONMENTAL AREA

A Matarazzo, MT Clasadonte*, A Zerbo

ABSTRACT

In this paper we consider the presence of ozone in a highly industrialized area, such as the province of Syracuse, Italy. The quantity of ozone, read every hour, is related to some meteorological variables, which have been registered simultaneously (such as temperature, humidity, speed and wind direction), so as to help us to interpret the different levels of pollution in relation to these meteorological factors.
In order to reach this goal, the data are analysed by using a new methodology, the Dominance Based Rough Set Analysis, which provides the results in terms of decisional rules "if…, then…". Afterwards, these rules are examined so as to verify their significance and, consequently, the possibility to use this approach as an effective operating tool for the management of air quality in a high-risk environmental area. The data analysed have been read in CIPA monitoring stations in Villasmundo and Melilli in the year 2000. The hourly readings of the pollutant in both stations reveal its marked seasonal incidence, with reference to emergency situations, which are mainly concentrated in the hottest months (June-September) and the hottest hours. This study shows a set of decisional rules, which can be used in an innovative way for the improvement of air quality; in this work we illustrate in some tables only the most important examples, where the different rules obtained have been used.

INDEX TERMS

Ozone, meteorogical variables, Rough Set Analysis, decisional rules, high-risk environmental area.

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INTRODUCTION

In the control of air quality, the monitoring of the principal pollutants, which aims at verifying the respect of the standards fixed by the laws in force, is no longer enough for a proper protection of public health and the environment. Therefore, the search for new operational instruments is nowadays particularly important in order to face the problem of pollution in a more effective and preventive way (1). That's why, in previous works (2 - 6), we embarked on a research concerning the management of air pollution and aiming at finding new strategies to prevent this phenomenon of air degradation. At first, the analysis was carried out by using the classical approach of the *rough sets* theory (3, 4). Later, we applied its more recent methodologies, which were meant for the analysis of "multi-criterial sorting" problems (7, 8), to the analysis of SO_2 and NO_2 in a high-risk area (5, 6). Such approach, which we experimented with in the study of air pollution, has some undeniable advantages if compared with other methodologies. Indeed, it allows to process both qualitative and quantitative data without the introduction of thresholds for the discretisation of the latter; it doesn't require the elimination of incoherent data, which are on the contrary taken into due consideration as elements of uncertainty; it doesn't require additional technical information, such as weighs – importance, *trade off*, appurtenance functions, parameters of distribution, etc.; the "importance" of the factors it takes into consideration is an output, not an input of the analysis; it provides the results in terms of "if…, then…" decisional rules, which are easy to understand, have a very rich syntax and are open to many interpretations and comparisons. This mathematical model allows you not only to estimate the levels of air pollution reached in a territory and to analyse the dispersion or the accumulation of the different pollutants with regard to some meteorological variables. It also allows you to predict air "quality levels" a few hours ahead, given the meteorological variables and the assessment of the emissions. The pollutant we take into consideration in this study is ozone (O_3); the data we analyse are those provided by some reading stations of the CIPA (Industrial Pool for the Protection of the Environment) monitoring net, which are placed in the industrial area of Priolo – Melilli (Syracuse) and take hourly readings of both pollutants and meteorological variables, in accordance with the D.P.C.M. n. 30 of 28/03/83. Such area is considered as a "high-environmental-risk" area for the density of industries there placed and is classified as zone "A" in accordance with the law 615/66 (9). The analysis of data is carried out using the *rough sets* approach in its recent methodological variant, which is based on the use of the dominance relation in order to build up approximations of suitable unions of pollution ordered classes.

ANALYSED DATA

The Italian law says that there are limit values of O_3 average hour-concentration, as well as for other air pollutants. If these limits are exceeded, we enter in the so-called "caution level" or "alarm level" (D.M. 15/04/94). In Sicily, the "Territory and Environment Council Decree 888/17" of 1993 (10) states that there are three

thresholds levels of O_3 pollution. If pollution is over these levels we are respectively in a situation of *pre-alarm* (over the 1st level: 100 μg/Nm^3), *alarm* (over the 2nd level: 200 μg/ Nm^3), and *emergency* (over the 3rd level: 300 μg/ Nm^3). These situations put on the alert all the responsible sources for this pollution which should reduce the emissions in order to avoid the exceeding of the permitted limits and protect the quality of air. (11) In the analysis we have carried out, the three pollution classes are studied in relation with some meteorological variables which, as we know, can be a big influence on the pollutant concentration. They are: *temperature, humidity, wind speed, and wind direction;* to these we added the *hour* of the data readings. Two reading plants have been selected for this study. Namely they are the station of Melilli and the station of Villasmundo, the only two stations, in the monitoring net taken into consideration, which analyse the hourly concentration of O_3. The station of Melilli, a small village in the middle of the industrialized area, reads both the quantity of pollutant and the conditions of the meteorological variables which are present at the moment of the reading. The station of Villasmundo, a hamlet of Melilli which has more or less the same number of inhabitants and is decentralised from the industrial pole, reads the quantity of O_3, but not the meteorological variables, provided by the station of the data gathering centre. The equipment used by the CIPA monitoring net in order to analyse ozone concentration is chemiluminescence type.

RESULTS OF OZONE ANALYSIS

The following tables show, for each reading station: a) the distributions of hourly readings relative frequency, concerning the ozone pollution classes; b) the distributions of the corresponding decisional rules relative frequency, which are obtained by applying the *rough sets* methodology to the gathered data. We only took into consideration the 100%-consistency rules, i.e. if the antecedent is true, the consequent (the assignation to pollution classes) will always be true.

These are the symbols used in the following tables and their respective meanings: **R** = rule number; **A1:** attribute **1** = hour of reading; **A2:** attribute 2 = air temperature (°C); **A3:** attribute 3 = index of air relative humidity (percentage); **A4:** attribute 4 = wind speed (m/sec); **A5:** attribute 5 = wind direction (N = North; E = East; S = South; O = West); D: decision = pollution class (A = EMERGENCY, 3RD LEVEL; B = ALARM, 2ND LEVEL; C = PRE-ALARM, 1ST LEVEL), C = 100 μg/Nm^1, B = 200 μg/Nm^1, A = ≥ 200 μg/Nm^1

VILLASMUNDO STATION

Table 1. Frequency in % of hourly readings for O_3 pollution classes (A, B, C)

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
C	95	60	41	33	28	27	25	17	37	82	97	99
B	5	39	58	62	67	54	47	49	51	17	3	1
A	0	1	1	5	5	18	27	34	12	0	0	0

Table 2. Frequency in % of the decisional rules concerning O_3, hourly readings

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
C	70	53	42	31	35	24	21	17	28	49	87	79
B;C	2	6	12	24	21	27	32	35	23	16	2	7
A	0	3	0	5	6	17	20	25	10	1	0	0
A;B	26	38	45	40	38	31	25	23	38	33	11	14

Tables 3-4. Results of ozone analysis in the months of May and June

R	A1	A2	A3	A4	A5	D
1				≤1,3		**B;C**
2	0-10;20;22;23					**B;C**
3	13;15		≤43,1	≥3,2		**A**
4	12		≤49,4	≥2,8	E	**A**
5	16	≤28	≤47,2	≥2,7		**A**
6	16	≤25,8	≤64,8	≥2,2		**A**

R	A1	A2	A3	A4	A5	D
1			≥85,5	≤1,5		**C**
2			≥44,4		S	**B;C**
3	0;2;4-8					**B;C**
4	13;14		≤40,2			**A**
5	11-13;16;17	≤33,6	≤47,6			**A**
6			≤38,7			**A;B**

Tables 5-6. Results of ozone analysis in the months of July and August

R	A1	A2	A3	A4	A5	D
1		≥23,3	≥72,1			**C**
2			≥42,7	≤1,2		**B;C**
3	15;16		≤39,3		E	**A**
4	10;11		≤48,2	≥1,9	E	**A**
5	13	≤34,3		≥3,5	E	**A**
6	14	≤41,8	≤29	≥1,3		**A**

R	A1	A2	A3	A4	A5	D
1			≥85,6			**C**
2	5	≥22,5	≥39,9		O	**B;C**
3	12-14	≤36,4	≤42,5			**A**
4	16		≤39,1		E	**A**
5	15		≤34			**A**
6	10-18					**A;B**

In order to clarify how to read the tables and point out at the completeness of the information they provide, we want to illustrate their semantics with two examples. Rule 1 in table 3 show that, "in the month of May, if the wind speed is less than 1.3 m/sec, then the pollutant concentration will surely be less than 200 μg/Nm^3"; rule 5 in table 3 show that "if in May the hours are 16, the air temperature is less than 28°C, humidity is less than 47.2 % and the wind speed is more than 2.7 m/sec, then the ozone concentration will surely be more than 200 μg/N m^3". As to O_3, the hourly readings in Villasmundo station show a prominent seasonal incidence of emergency situations, which are mainly concentrated in the hottest months (June – September); while we can notice an almost total lack of these situations during the periods from January to March and from October to December. This can be explained with the geographical position of Villasmundo, (low hills area, peculiar orographic configuration, good exposure, a bit far from the industrialized area) which certainly plays a very important role. In particular, from Table 1 we can notice that, in the period March-September, the quantities of pollutant that were measured, fall into class B (alarm) with a frequency higher than 50%. In the months of July and August there is a stronger incidence of class A (emergency) with a frequency of 27% and 34% respectively (Table 2).

From the rules obtained, we can deduce that it is possible to establish the different pollution classes according to the air temperature and the humidity rate, and also we can deduce that the latter's thresholds-values form a negative trade off

with temperature, compensating each other. The humidity rate plays an important role, often even by itself: during many months, its values are thresholds which allow you to outline the different pollution classes.
As to temperature, which should play a fundamental role for the explanation of the phenomenon we are analysing, the rules calculus algorithm used in the software and the syntactic structure of the rules themselves show this criterion to be among the direct descriptors of the rules in exam only a few times. Moreover, the influence of temperature can be indirectly seen by considering the frequent presence of the "time" conditional attribute in many rules; the "fresh" and "hot" hours pointed out by such descriptor. More precisely, time provides a relative explanation of air temperature, that is the temperatures of the month taken into consideration. Moreover, the phenomenon could be explained by the fact that in the "fresh" hours there could be a decrease in production in the industrial area. Very often, intervals of "fresh" hours themselves assign actions to classes C or B, while "hot" hours intervals, together with other factors, characterise the assignation to class A (emergency). For instance, one can see rules 2, 4, 5 and 6 in Table 3, rules 3, 4, and 5 in Table 4, rules 3, 4, 5, and 6 in Table 5, rule 6 in Table 6.
The technical consequence of such syntactic structure is that, in general, the temperature descriptor is used only a few times, especially in the hot months, which results in a higher descriptive complexity of the rules. This is particularly true of the class C assignation rules, which are therefore manifold but not very "strong", i.e. supported by a few concrete observations. Obviously, even in the rules obtained in this station we can find some interesting *trade offs* of various nature and chain rules, which the reader can easily analyse and understand.

MELILLI STATION

Table 7. Frequency in % of hourly readings for O_3 pollution classes (A, B, C)

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
C	81	35	5	20	20	12	6	1	16	52	62	91
B	19	62	81	73	74	63	36	29	57	47	37	9
A	0	3	14	6	7	25	58	70	26	1	1	0

Table 8. Frequency in % of the decisional rules concerning O_3, hourly readings

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
C	65	39	11	29	27	21	11	1	17	47	51	70
B;C	8	16	49	24	25	32	35	47	32	5	14	4
A	1	3	13	4	9	19	33	34	21	2	0	1
A;B	25	43	27	43	39	27	21	6	30	45	34	35

Tables 9-10. Results of ozone analysis in the months of March and April

R	A1	A2	A3	A4	A5	D
1		≥11,2	≥59,9		O	**B;C**
2	1;5			≤2,2		**B;C**
3	14		≤58		E	**A**
4	0;9;17;22;23		≤67,4	≥2,6		**A**
5	15		≤51,5		S	**A**
6	13			≥3,6	S	**A**
7			≤63,2	≥1,7		**A;B**
8		≤13,2	≤80,1		O	**A;B**
9		≤1,1	≤89,1		E	**A;B**
10				≥1,3	N	**A;B**

R	A1	A2	A3	A4	A5	D
1		≥11,8	≥90,8	≤2,4		**C**
2			≥65,4			**B;C**
3			≥44,5	≤1,7		**B;C**
4			≤23,8		O	**A**
5	11;14;19		≤39		E	**A**
6	12;18		≤32,5		S	**A**
7			≤32,5			**A;B**
8		≤11,8	≤64,8			**A;B**
9		≤9,7		≤1,1		**A;B**
10		≤13,9	≤44,9			**A;B**

Tables 11-12. Results of ozone analysis in the months of May and June

R	A1	A2	A3	A4	A5	D
1			≥66,7			**B;C**
2				≤1,1		**B;C**
3			≥52,3		E	**B;C**
4		≥16,1	≥42,4		O	**B;C**
5	5-9;12;15;18;20					**B;C**
6	11;13		≤42		E	**A**
7		≤25.6	≤24.6			**A**

R	A1	A2	A3	A4	A5	D
1			≥41,3		O	**B;C**
2	2;3;6-9;20;21;23		≥33,6			**B;C**
3	2;3			≤1,8		**B;C**
4	11		≤26,8		E	**A**
5		≤21,1	≤45,6	≥2,4		**A**
6	2;6	≤23,3	≤45,6	≥1,7		**A**
7		≤31,2	≤38,9		E	**A;B**

Tables 13-14. Results of ozone analysis in the months of August and December

R	A1	A2	A3	A4	A5	D
1			≥82,5	≤1,5		**B;C**
2	16;17					**A**
3	13		≤67,7			**A**
4	14;18		≤56,1			**A**
5	12		≤39			**A**
6	12		≤43,6	≥2,2		**A**

R	A1	A2	A3	A4	A5	D
1			≥ 87,6			**C**
2				≤0,8		**C**
3	2;8;20			≤3		**C**
4			≥ 60,7			**B;C**
5					O	**B;C**
6				≤2,4		**B;C**

As to Melilli station, the data concerning air pollution are very worrying. This can be immediately deduced from Table 7, which is about the class distribution of the hourly readings. Indeed, we can observe a clear concentration of emergency cases in the hot months, as we have already noticed in Villasmundo station; although the frequency of such events in Melilli station in the period June-September is almost twice as high as the one observed in Villasmundo, and is nil in January and December only. In the months of July and August, most of the data fall into class A (emergency), with values of 58% and 70%, respectively. It's also important not to underestimate the frequencies of the observations falling into class B: these, indeed, in the period February – June and in the month of September oscillate between 57% and 81% of the total observations.

If we compare this distribution with the decisional rules one (Tab. 8), we can observe that the assignation rules frequency to class A follow, more or less, the same trend as the one concerning the hourly readings falling into class A. However, in the period June – September, the frequency of these rules is less than the

corresponding classes ones. This clearly indicates that in the hottest periods the phenomenon we are analysing is particularly intense. However, its explanation in terms of decisional rules doesn't become more articulated, as the phenomenon is a rather homogeneous one.

Moreover, we can observe that, in general, by analysing the decisional rules here obtained (Tab. 8), the software has generated a big number of assignation rules to class C, and that these are very weak, i.e. each supported by a small number of positive actions. On the other hand, in the hot months, the frequencies of decisional rules concerning classes (B or C) and (A or B) are relatively higher. Such phenomenon is probably due both to a greater difficulty in explaining the assignations to class C, and to a "technical" reason: the software algorithm builds the classes approximations (and, therefore, the rules) using information about probable inequality signs of each considered criterion's value, which are assigned to the ordered classes (A, B, C). The syntax of the decisional rules calculated according to the given parameters for the data processing, considers low thresholds (that is, of the $\geq$ kind) and high thresholds (that is, of the $\leq$ kind) for the temperature and humidity criteria in the assignation to classes C and (B or C) on one side, and A and (A or B) on the other, respectively.

As the level of the pollutant is strongly related to the air temperature, it's relatively more difficult to describe C and A situations in terms of decisional rules which have the above mentioned syntax, also because we can't frequently use the "temperature" criterion. Obviously, the rules obtained for such cases are totally correct though they are consequently a bit more complex and less strong.

These simple observations allow us to understand the particular role played by the reading time in the obtained rules: indeed, we often obtained rules that have only time as their conditional attribute (thus enough in itself to classify the actions). This attribute consists of a series of consecutive hours, which can, for convenience sake, be described as "hot hours" and "fresh hours". These are particularly important for the phenomenon we are studying as they also show relatively higher or lower temperatures, i.e. in relation to each of the months examined. See, for example, the following assignation rules to classes C or B and, more frequently, to class A, on the basis of hot hours and fresh hours, alone or together with other meteorological factors: Tab. 12, rules 2 and 3; Tab. 13, rules 2, 3, 4, 5 and 6. In particular, we can observe that rule 2 in tab. 13 states that, in August, the time of the day in itself (4:00 or 5:00 pm) determines an emergency situation concerning the pollutant in exam.

The humidity degree as well has a fundamental role, as it often represents in itself the discrimination thresholds among the different pollution classes. Thus, for example, the lower thresholds of classes C and (B or C) are shown by the rules 1 and 4 of tab. 14 as 87.6% and 60.7%, respectively; the lower threshold of class (B or C) and the higher one of class (A or B) are shown by the rules 2 and 7 of tab. 10 as 65.4% and 32.5%, and by the rules 1 and 7 of tab. 12 as 66.7% and 41.6%, associated with wind direction East. Clearly, the humidity degree plays

an important role in many assignation rules to the emergency class; for example, in rule 4 of tab. 10 (at the maximum level of 23.8% together with wind direction West) and in rule 7 of tab. 11 (at the maximum level of 24.6%, together with the temperature maximum level of 25.6° C). Obviously, in other rules, it is associated also with the wind speed and direction.
As to this last factor, we can observe that it has often a remarkable influence, together with other attributes and conditional criteria, especially in the assignation to class A (emergency), which is a consequence of the geographical localisation of the two stations in relation to the industrial area.
Lastly, we just want to hint at the fact that in the rules here considered we can notice different trade-offs and chain rules, which show the complex interactions among the factors taken into consideration. For example, we can mention rules 3 and 5 of tab. 9, where we can see a trade-off resulting from values, attributes' values, and criteria at once (time, humidity degree and wind direction) for assignation to class A, and rules 8 and 10 of tab. 10, which show an interesting negative trade-off between the higher thresholds of class (A or B) in terms of temperature and humidity degree. Moreover, if we also consider rule 9, we can observe a relevant qualitative trade-off resulting from the humidity degree and the wind speed (not higher than 1.1 m/s). Lastly, in the same tab. 10, we can notice two typical chain rules (rules 2 and 3), which show how the lower threshold of class (B or C) in terms of humidity degree (from 65.4% to 44.5%) can weaken consistently, also considering wind speed at a level not higher than 1.7 m/s.

CONCLUSIONS

As we have already pointed out, even for ozone, the data analysis through the rough sets approach, apart from remarkable methodological aspects, provides important information concerning the phenomenon in exam. It also shows the more or less important role played by each of the meteorological variables in the pollutant assignation to the different classes of the intervention actions. The fundamental working mechanisms of the relations between antecedent (attributes and conditional criteria) and consequent (assignation class) are remarkable, as they provide interesting information on the semantic importance of chain rules and quantitative and qualitative trade-offs showing the interaction among several atmospheric factors.
In carrying out the analysis, every meteorological variable taken into consideration has proved fundamental for an accurate description of the phenomenon; in other words, none of the ones considered has proved useless and redundant. Therefore, it's impossible to eliminate one of them without diminishing the quality of the approximations.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

TRACE GAS DETECTION BY CAVITY RING-DOWN SPECTROSCOPY

I Labazan[1], N Krstulović[1] and S Milošević[1, *]

ABSTRACT
Cavity ring-down spectroscopy (CRDS) is a novel direct laser absorption technique. It has been applied in many environments from open air, human breath, static gas cells, supersonic expansions, flames to discharges and plasma jets. The basic principle of CRDS is quite simple: a short laser pulse is coupled into a stable cavity consisting of two highly reflecting curved mirrors. The quantity measured is the decay rate of photons in the cavity. It contains information about cavity losses and absorption or reflection of particles within the cavity. The short overview of this, by many considered as a disruptive technology, will be given with special attention to trace gas and aerosol detection in the atmosphere. Detection of species such as NO, N_2O, NO_3 etc, have been demonstrated with ppb and in some cases ppt sensitivity. We shell present development of our universal device based on CRDS and several of its applications.

INDEX TERMS

Trace gas detection, cavity ring-down spectroscopy, atmospheric molecules

INTRODUCTION

Molecular gases in the atmosphere influence the climate and the life quality in different ways. Still not all contributions to the absorption are known, even of the well known atmospheric molecules, needed to understand the Earth's radiation budget. The other need is for in-situ monitoring of various trace constituents, from radicals to aerosols. Cavity Ring-Down Spectroscopy (CRDS) is a direct absorption technique that gives important contribution solving both tasks. CRDS technique provides minimum detectable levels of species in ppb and ppt range and it has been applied in many environments and in many variants. There are several reviews

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of this rapidly evolving topic of a general scope (Berden et al 2000, Peeters et al 2001, Wheeler et al 1998) and several addressing specifically the trace gas detection and solving environmental problems (Atkinson 2003, Sigrist 2003, Shorten et al 2003, Ashworth 2002, Czyzewski et al 2002, Gagliard and Gianfrani 2002, Kleine et al 2001, Tao et al 2000, Vasudev et al 1999, Steinfeld 1999, Jongma et al 1995). Particularly great attention is given to the detection of nitrate radicals (Mazurenka et al 2003, Brown et al 2002a,b, 2001, Evertsen et al 2002, Ball et al 2001, Lauterbach et al 2000, Wang et al 2000, King et al 2000) and aerosols (Thompson et al 2003, 2002, Bulatov et al 2002, Sappey 1998, Ramponi et al 1988). It has been shown that technique is suitable for a real-time quantitative analysis of polluted air without any preprocessing of the air sample (Dahnke et al 2002, Fawcett 2002). Several groups are developing devices based on CRDS for various applications (Awtry and Miller 2002, Spuler et al 2000). Here we list only most recent papers not included in general reviews mentioned above. Number of publications has reached more then two per week that proves as CRDS is a very expanding technique. Development of CRDS goes together with rapid advances of tunable lasers, but recently also using non-coherent light has been demonstrated (Hamers et al 2002), making hopes for a robust easy to operate and cheap detectors even more real.

METHODS

Typical experimental set-up, illustrated in Figure 1, consists of a tunable laser, optical cavity, and a fast optical detection system. The principle of conventional pulsed CRDS is quite simple. A short laser pulse is coupled into a stable high finesse optical cavity. A small amount of intensity leaks out of the cavity and is detected as a function of time (so called ringdown curve). A ringdown curve is described by single-exponential decay function in the ideal case of linear absorption and validation of the Beer-Lambert law. It is characterized by a lifetime τ of photons in the cavity. Usually, one measures total cavity loss $\beta / c = 1/ (\tau c)$ expressed in units of cm^{-1}. Total loss, is given by

$$\frac{\beta(\lambda)}{c} = \frac{1}{L}(|\ln(R)| + \kappa(\lambda) l_{abs}) \qquad (1)$$

where L is the cavity length, λ is the wavelength, l_{abs} is the single pass absorption length, R mirror reflectivity, $\kappa(\lambda)$ is the extinction coefficient which includes contributions from absorption and Rayleigh scattering. If losses are only due to absorption one can determine then density of absorbing molecules or atoms from measured losses, provided that relevant absorption cross sections are known. The main advantage of CRDS over conventional absorption techniques arrises from the fact that measured quantity is time, and not the intensity ratio. However, one has to take care about bandwidth problems (Yalin and Zare 2002) and various saturation effects (Labazan et al 2000) as in conventional absorption.

In the case when number density of absorbing species changes rapidly during the ringdown which are from few to few tents of microseconds the other expression for extinction applies:

$$\kappa(\lambda,t) = -\frac{L}{c \cdot l_{abs}} \left\{ \frac{d}{dt} \left[\ln \frac{S(t)}{S_0} \right] - (1-R) \right\} \tag{2}$$

where S(t) is the ringdown signal and S_0 the ringdown signal at t = 0. 1-R is the effective mirror loss. Such a case appears for example during chemical reactions, pulsed discharges or laser ablation process (Labazan and Milošević 2002).

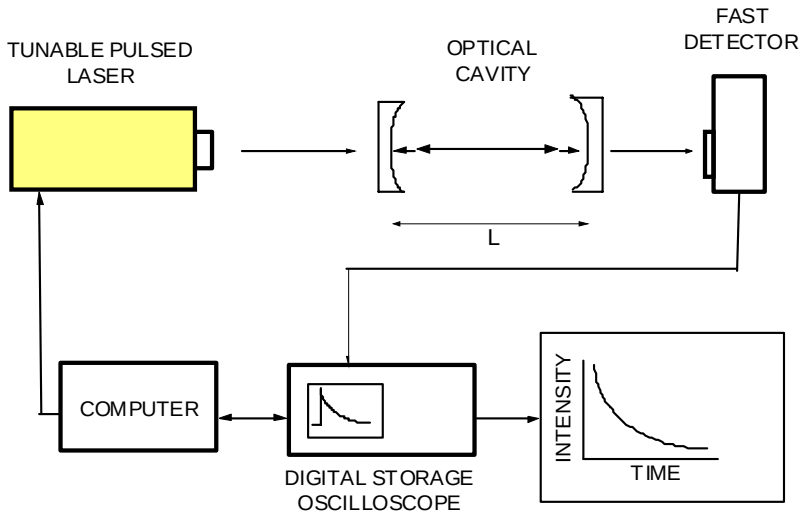

Figure 1. Schematic diagram of cavity ring-down setup.

RESULTS AND DISCUSSION

Figure 2 shows typical ringdown curves in a semi-log plot for the case of constant absorption during the ringdown time (left) and for the case of rapidly changing absorption – laser ablation (right). In the later case we apply special analyses of ringdown curves over time segments. Within the first time segment particles did not reach the cavity axis. Following are several time segments as a plume is passing through the cavity axis. As all particles are gone, cavity is empty, and slope of the curve again equals that of empty cavity (or equivalent to laser off the resonance). Appropriate sampling allows time resolution of the CRDS signal down to 200 ns. The ringdown curves are measured at given laser wavelength and slope of each curve represents one point in the wavelength resolved spectrum.

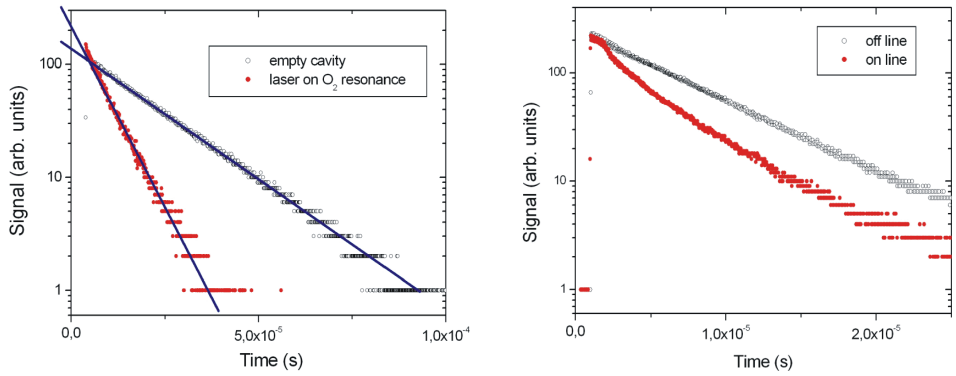

Figure 2. Typical ring-down curves for constant absorption (left) and rapidly changing (right).

The example shown in Figure 3 represents absorption of oxygen in the region of the b – X (1,0) electronic transition (Atmospheric system). This result was obtained with mirrors of 99.991 % reflectivity and resonator length 0.851 m. The oxygen is well studied by CRDS, usually considered as a benchmark system (Berden et al 2002).

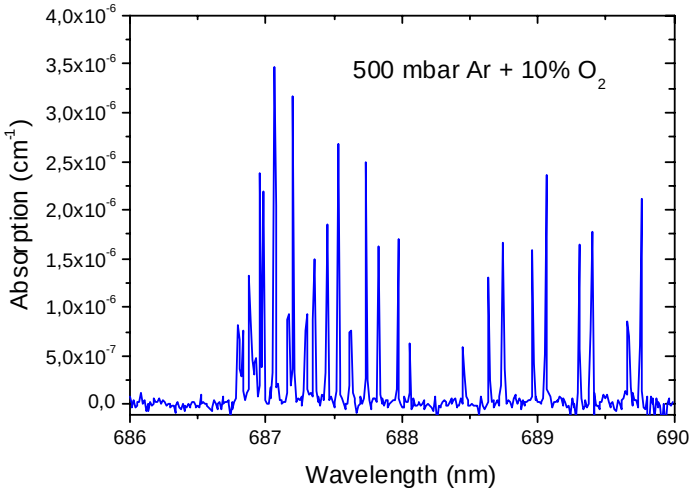

Figure 3. Absorption spectrum of argon-oxygen mixture contained in the cell.

In our laboratory we have so far implemented CRDS to measurements at high densities within the heat-pipe ovens (Labazan et al 2000), studies of laser induced plumes (Labazan and Milošević 2002) in vacuum and background pressure and inductively coupled RF plasma discharges at low pressures. Various atoms and molecules have been observed, both with classical CRDS and time-resolved CRDS, some of them being also of importance in air pollution monitoring. We are currently developing a CRDS based device which performances will allow also air pollution monitoring.

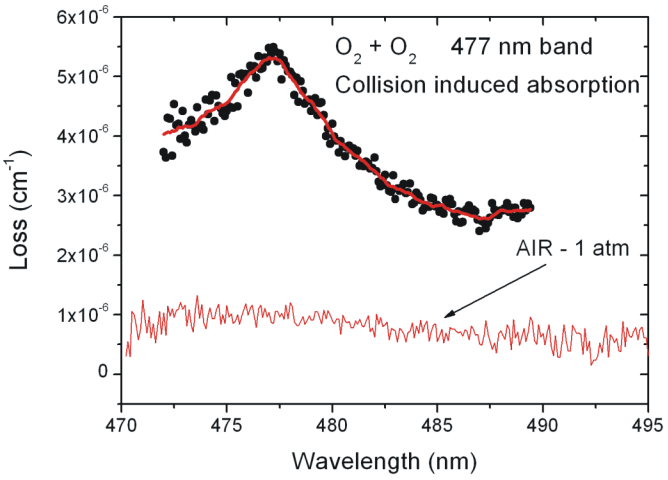

Figure 4. Total cavity loss in the spectral region of oxygen collision-induced absorption band in pure oxygen and in ambient air.

With commercially available mirrors of high reflectivity and typical cavity lengths of 0.5 to 1.5 m, characteristic lifetimes of 50-100 μs and more could be easily achieved allowing measurements of extinctions of 10^{-8} cm^{-1} to 10^{-10} cm^{-1}. For example, in the case of air pollution monitoring the detection limit of 0.5 ppt for Hg was measured (Spuler et al 2000), while in detection of aerosols the ultimate theoretical detection capability of about 100 water particulates per m^3 is expected (Bulatov et al 2002).

CONCLUSION AND IMPLICATIONS

We believe that using CRDS technique as comparative and in addition to for example gas chromatography, laser induced breakdown spectroscopy (LIBS) and inductively coupled RF plasma (ICP) technology, could bring fundamental innovations to the trace elemental analysis of ambient air and other environments.

ACKNOWLEDGEMENTS

This work was financially supported by the Ministry of Science and Technology of the Republic of Croatia under contract #0035003.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

CHLORINATED HYDROCARBONS IN THE ATMOSPHERE AND SURFACE SOIL IN THE AREAS OF THE CITY OF ZADAR AND MT. VELEBIT – CROATIA

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ABSTRACT

The results of the analysis of the polychlorinated biphenyls in the soil from a number of points at the 110/35 kV Electrical Transformer Station in Zadar indicate significant contamination. Because there is some speculation about the possibilities of the inflow of spilled contaminants from the karstic soil of the city of Zadar to the coastal sea from other sources inside the city of Zadar, investigations of the chlorinated hydrocarbons in the atmosphere and soil of several parts of the city of Zadar were performed and are presented in this paper. Air sampling and analysis were performed by RECETOX - TOCOEN & Associates, Brno, CZ, May 13 to 23, 2003. Four samplers were in the city of Zadar and one was 150 km north on Mt. Velebit. Two phases were collected - particles using quartz filter Whatmann (fraction $d_{ae} < 50\ \mu m$), and gas phase which was collected by the solid adsorbent trap - polyurethane foam (Gumotex Břeclav, density 0.03 $g.m^{-3}$). All field samples and field blanks were extracted with dichloromethane in Büchi System B-811 automatic extractor. Volume of extracts was reduced and fractionation achieved on sulphuric acid modified silica gel column. Samples were analysed on GC-ECD HP 5890. Soil samples were air dried at the Rudjer Boskovic Institute, CMER and extracted at 24 hours with n-hexane by Soxhlet extraction The analytical method used for the analysis of extracts included filtration through a column of Na_2SO_4 anh., cleaning on an alumina column and the separation of the PCB's from organochlorine

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insecticides on a miniature silica gel column. Results of determination include 7 PCB congeners (PCB 28, PCB 52, PCB 101, PCB 118, PCB 153, PCB 138, PCB 180) and the sum of 7 congeners. The highest values were observed at ETS Zadar with the range from 1.111 to 5.147 ngm^{-3} of air. At the same position ranges of PCBs in the dried soil are from 30.8 to 17780 ngg^{-1} Levels of PCBs determined in the air and soil samples in the Zadar area were compared with the same from other European countries. Distribution of investigated pollutants between particulate phase and aerosol are also discussed. Positive correlations statistically significant for the sum of 7 PCB congeners-were observed when comparing levels of PCBs in the soil and air of investigated locations.

INDEX TERMS

Croatia, war wastes, polychlorinated biphenyls, atmosphere, soil

INTRODUCTION

During the recent war, the karstic area of Croatia was jeopardized by hazardous waste and warrants particular attention because of its exceptional ecological sensitivity and the unfortunate unscrupulous destruction of its natural resources, infrastructure, homes and enterprises. Results of the analysis of polychlorinated biphenyls in the soil from the four locations (at two depths in some locations), indicate significant contamination of the investigated area of the 110/35 kV Zadar Electrical Transformer Station.

This was the reason for the through investigation of this site for the PCB levels in the soil samples around the damaged capacitor. Investigation of the PCB levels in the sediment and biota samples of the coastal water of Zadar showed relatively high values. Because there has been some speculation about the possible inflow of spilled contaminants from the karstic soil of the city Zadar to the coastal sea from other sources inside the city, the chlorinated hydrocarbons in the atmosphere and soil of several parts of city Zadar were investigated and the results are presented in this paper. As an air background area, the meteorological station Zavižan was selected. The Zavižan Meteorological Station is located beneath Vučjak Hill of Mt. Velebit, at the altitude of 1,594 m above sea level, which makes it the highest meteorological station in Croatia. Measurements of the chlorinated hydrocarbons in the atmosphere and surface soil at this station were also performed.

METHODOLOGY

Air sampling and analysis were performed by RECETOX - TOCOEN & Associates, Brno, CZ on May 13 to 23, 2003. Four samplers were in the city of Zadar and one was 150 km north on Mt. Velebit at the Zavižan location. In Zadar, the four locations were as follows: the Zadar historical center; the Zadar

industrial zone; the Zadar Electrical Transformer Station between the industrial and residential zones; and the Zadar meteorological station.
Four high volume ambient air samplers PS-1 (Graseby-Andersen, USA) were used (flow and volume: 20-25 m^3h^{-1} , 250-400 m^3 per 24 h, resp.).
Two sorbents were used for collection of particles (quartz filter Whatmann, fraction $d_{ae} < 50\,\mu m$) and gas phase (polyurethane foam, Gumotex Břeclav, density 0.03 $g.m^{-3}$). Frequency of sampling was 24 hours. Ten samples of the ambient air from every sampling site were collected during the 10 days sampling campaign (24 hours, about 300 m^3 each). There was one field blank quartz filter and one field blank PUF taken in each location. All filters were cleaned before the campaign. PUF filters were extracted with acetone in Soxtec extractor, quartz filters were heated to 450°C.
All the field air samples and field blanks were extracted with dichloromethane in Büchi System B-811 automatic extractor (quartz and PUF filters separately). One laboratory blank, one field blank and one reference material were analysed with each ten samples. PCB 121 was used as an internal standard, PCB 30, and PCB 185 were used as a recovery standards.
Volume of extracts was reduced and fractionation achieved on sulfuric acid modified silica gel column. Samples were analysed for PCB 28, PCB 52, PCB 101, PCB 118, PCB 153, PCB 138, PCB 180, alpha-HCH, beta-HCH, gamma-HCH, delta-HCH, p,p´-DDE, p,p´-DDD, p,p´-DDT using GC-ECD HP 5890. All results were confirmed on GC HP 6890 equipped with a mass selective detector HP 5972. Recoveries varied from 72 to 98 %.
Soil samples air dried at the Rudjer Boskovic Institute, CMER, were extracted for 24 hours with n-hexane by Soxhlet extraction. The analytical method used for the analysis of the extracts included filtration through a column of Na_2SO_4 anh. cleaning on an alumina column and the separation of the PCBs from organochlorine insecticides on a miniature silica gel column. The elutes were analyzed by EC gas chromatography after concentration down to 1 cm^{-3}. During all the analytical procedures, the Mirex standard was used as the internal standard. More specific details of the methods have been described in numerous published papers (Picer, 2000; Holoubek, 2001).

RESULTS

The results of the measurement of the concentrations of PCB congeners in the air samples in the vapor and particulate phases collected in May 2003 from the four locations in the city of Zadar and Mt. Velebit (Zavižan) are presented in Table 1. The concentrations presented are the median values of the 10 daily samples. At the same time (with the exception of the Zadar Electrical Transformer Station), samples of surface soil were collected close to the site of the atmospheric sample collectors. The results of these analyses are presented in Table 2.

Table 1. The concentration of the PCB congeners in the air samples in the gaseous phase (g) and the particulate phase (s) [ng m^{-3}] - the median values of the 10 daily samples).

Location	ZD-Centre		ZD-Industrial		ZD-Trafostation		ZD-Meteorolog.stat.		VELEBIT - Zavižan	
PCB cong.	(g)	(s)	(g)	(s)	(g)	(s)	(g)	(s)	(g)	(s)
PCB 28	0.023	0.002	0.028	0.001	1.943	0.017	0.016	0.001	0.011	0.002
PCB 52	0.011	0.001	0.005	0.001	0.580	0.017	0.013	0.002	0.007	0.001
PCB 101	0.022	0.002	0.024	-	0.040	0.001	0.007	0.001	0.007	0.001
PCB 118	0.006	0.001	0.009	0.001	0.031	0.001	0.007	0.001	0.004	0.001
PCB 153	0.025	0.002	0.027	0.002	0.036	0.002	0.020	0.001	0.014	0.002
PCB 138	0.017	0.002	0.023	0.002	0.031	0.002	0.017	0.001	0.009	0.001
PCB 180	0.009	0.001	0.009	0.002	0.018	0.001	0.013	0.001	0.008	0.001
Σ7 cong.	**0.112**	**0.009**	**0.127**	**0,010**	**2.666**	**0.041**	**0.096**	**0.008**	**0.061**	**0.009**

Table 2. Levels of PCB congeners in the soil samples [ng g^{-1}] collected by the Rudjer Boskovic Institute, Zagreb (C) and RECETOX-TOCOEN, Brno (T)

Location	ZD-Centre		ZD-Industrial		ZD-Trafostation		ZD-Meteorol. station		VELEBIT - Zavižan	
Institution	T	C	T	C	T	C*	T	C	T	C
PCB cong.										
PCB 28	0.2	0.2	0.4	0.2	3.2	68.0	0.3	3.0	0.7	0.7
PCB 52	0.3	0.3	0.4	0.3	2.4	54.0	0.8	1.4	0.5	1.4
PCB 101	0.3	0.2	0.8	0.3	3.5	23.0	0.7	0.3	0.3	1.0
PCB 118	0.3	0.6	0.6	0.6	5.4	-	0.2	0.2	0.1	1.1
PCB 153	1.3	0.8	3.1	0.6	5.6	10.0	1.9	0.1	0.5	0.8
PCB 138	1.5	1.0	4.1	0.7	6.6	14.0	1.7	0.1	0.4	1.3
PCB 180	0.9	0.7	2.6	0.5	4.1	5.9	1.5	0.1	0.3	0.2
Σ7 cong.	**4.9**	**3.8**	**12.1**	**3.2**	**30.8**	**174.9**	**7.1**	**5.1**	**2.9**	**6.5**

* Median level of 10 surface soil samples (depth 0-10 cm) collected in November 2002;
- No data

DISCUSSION

Due to present data in Table 1, it is obvious that the PCB levels in the atmosphere of the Zadar Electrical Transformer Station are significantly higher in comparison to the other localities.

Comparison of the PCB data from various studies is complicated because of the different quantification techniques and reporting conventions used by laboratories. To assess to some extent how the concentrations at the Zadar Electrical Transformer Station compare with those taken from other locations, congener-specific concentration data and other PCB data reported for various European locations in the late 1980s and 1990s are compiled in Table 3 (Váňa et al., 2001; Albaiges et al., 2002; Picer, 2003).

Table 3. Levels of PCBs in ambient air of several locations in Europe region [ng m^{-3}]

Locality	PCB species	Minimum	Maximum	Arithmetic mean	Geometric mean	Median
ETS, Zadar,2003	Σ 7PCBs	1.1110	5.1470	2.7010	2.4590	1.9470
CR, Kosetice (1996-2001)#	Σ 7PCBs	0.0045	0.4670	0.1442	0.125	0.1358
CR Praha, first half of 90	**Σ PCBs**	0.10	1.4			
France, Paris area, 1990	Σ 7PCBs	0.6	2			
Mediterranean Sea, 1989-90	Σ PCBs			0.49		
Slovenia, Semič, near residences, 1987	Σ PCBs	4	7	5		
Serbia, 1999	Σ PCBs		25.5			
Croatia, Zagreb, 1997	PCB 28	0,001	0,092			

every week collected samples, EMEP Middle European background station

From the comparison of the PCB concentrations in the air of the Zadar ETS as vapor and particulate phases (Figure 1), it is obvious that most of the investigated PCB congeners existed in the vapor phase. The same is observed at the other investigated sites. In Figure 3, the daily variations of the PCB levels in the vapor phase of the air sampled from the Zadar ETS are presented. Because PCBs 28 and 52 are the most abundant in the investigated samples, they are presented separately. Comparison of the PCB levels in the soil samples collected and measured by RECETOX - TOCOEN & Associates, Brno, CZ (TOCO) and Rudjer Boskovic Institute, Zagreb, Croatia (CMER) shows relatively good agreement except at the Zadar ETS. RECETOX performed analysis at this location on only one sample in May 2003, but CMER performed analysis on 10 samples in November 2002.
The regression lines between the natural logarithmic levels of the PCBs in the soil and atmosphere (median values of ten days of measurement) at all the investigated sites are presented in Figure 4. The PCB levels in the soil are taken from both institutions except for the PCB level in the soil at the Zadar ETS, which was sampled by CMER in November 2002. As seen, there is relatively good correlation ($p < 0.01$) between the sum of all the congeners in the soil and air of the investigated localities.

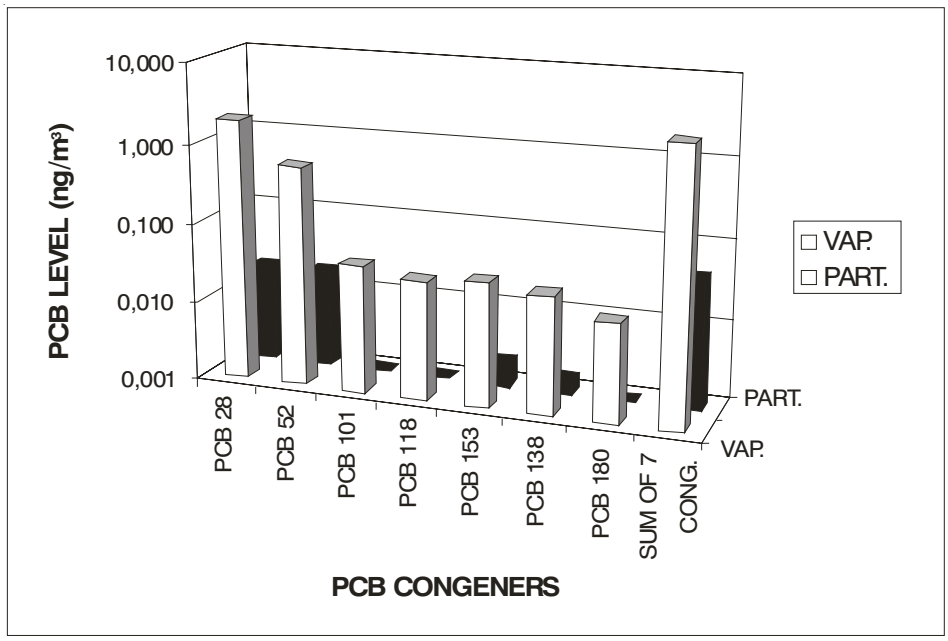

Figure 1. Comparison of PCB concentrations in the air of the Zadar Electrical Transformer Station as vapor and particulate phases

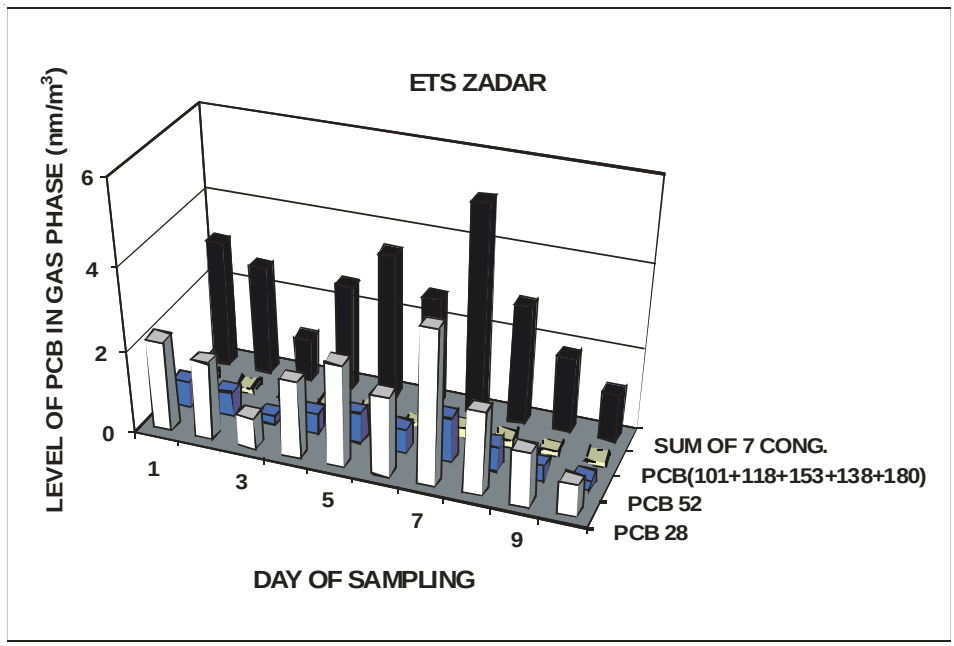

Figure 2. Daily variations of PCB level in vapour phase of air sampled from ETS Zadar

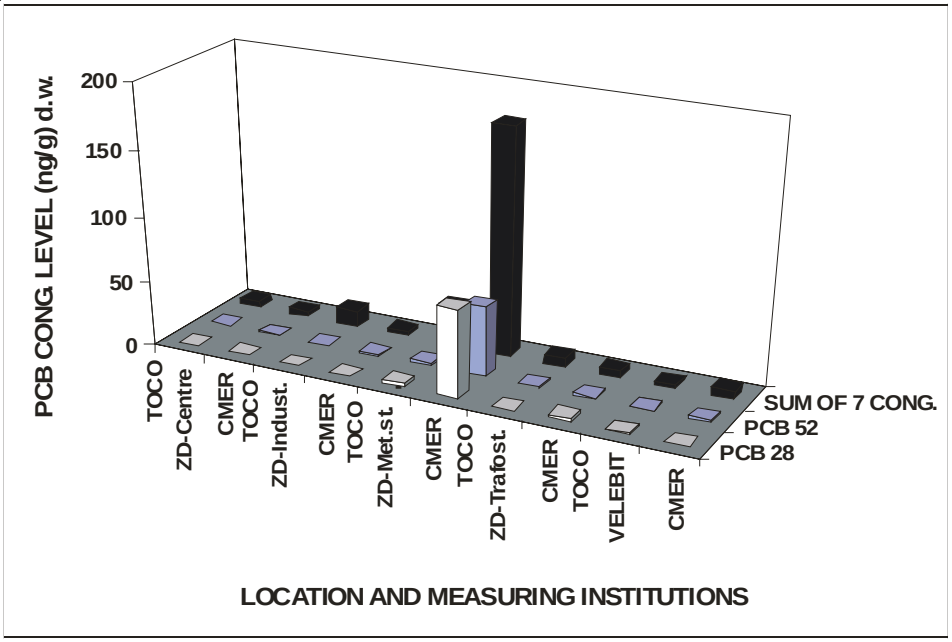

Figure 3. Comparison of PCB level in soil samples collected and measured by RECETOX - TOCOEN & Associates, Brno, CZ (TOCO) and Rudjer Boskovic Institute, Zagreb, HR (CMER)

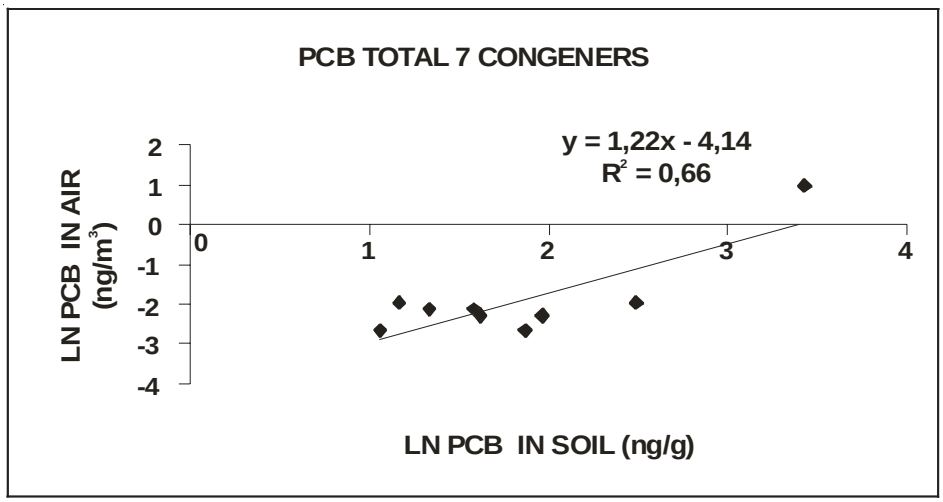

Figure 4. Comparison of the levels of 7 PCB congeners in the soil and air at the investigated locations

CONCLUSIONS

1) The levels of PCBs in the atmosphere at the Zadar Electrical Transformer Station were significantly higher in comparison to the other investigated localities during this investigation. In comparison to similar data from various European countries, the PCB levels in the atmosphere of the Zadar ETS are higher.
2) From a comparison of the PCB concentrations in air of the Zadar ETS as vapor and particulate phases, it is obvious that most of the investigated PCB congeners exist as the vapor phase. The same is observed from the other investigated sites.
3) There is relatively good correlation between the level of the sum of all the congeners in the soil and air at the investigated localities.

ACKNOWLEDGEMENT

The authors express their gratitude to the Ministry for Science and technology of Republic Croatia for financial support. This work has been carried out as part of the Contract ICA2- CT-2002-10007 (APOPSBAL) between the European Community and Rudjer Boskovic Institute, Zagreb, Croatia, and RECETOX, Masaryk University, Brno, Czech Republic.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

THE IMPACT OF ACID DEPOSITIONS WITH SANDSTONE AND GRANITE BODIES

P Primerano, P Catalfamo, F Corigliano*, S Di Pasquale and I Arrigo

ABSTRACT

It is known that acid depositions from heavy oil ash emissions combine with atmospheric humidity to cause serious damage to the surfaces of calcareous bodies. This paper describes the effects of these deposits on different types of stone, such as sandstone and granite. The data were obtained by contacting heavy oil ash with samples of these materials for 1-30 days at controlled humidity values and by spectroscopic and microscopic examination of the surface changes observed.

INDEX TERMS

Acid depositions, Oil fly ash, Stone decay, Granite sulphation, Sandstone sulphation.

INTRODUCTION

The accelerated decay of stone buildings observed over the last century has become the object of intense research activity. Stone sulphation has attracted a great deal of interest as its causes are little understood. The slow absorption of the atmosphere's sulphur dioxide and its oxidation to sulphuric acid has been indicated as the cause by some authors (Camuffo, Del Monte, Sabbioni et al., 1982; Cheng, Hwu, Kim et al., 1987; Del Monte, Sabbioni and Vittori, 1981; Gauri and Holdren, 1981; Tambe, Gauri, Li et al., 1991), but, in our opinion, it would only explain slow decay and not the acceleration recently observed.
Fly ash particles from oil combustion have been observed as components of black crusts adhering to damaged surfaces (Del Monte, Sabbioni and Vittori, 1984). This has induced these scientists to investigate their role. While research efforts

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aiming to demonstrate their catalytic effect on the absorption and oxidation of SO_2 have produced somewhat inconclusive results (Ausset, Croivisier, Del Monte et al., 1996; Ausset, Del Monte and Lefevre, 1999; Cheng, Hwu, Kim et al., 1987; Hutchinson, Johnson, Thompson et al., 1992; Sabbioni, Zappia and Gobbi, 1996), the assumption that strong primary acidity (SPA) carried by oil fly ash (OFA) might be responsible for damages to calcareous stone has been confirmed by findings (Primerano, Corigliano, Di Pasquale et al., 2003; Primerano, Marino, Di Pasquale et al., 2000). In the absence of SO_2 and in the presence of a relative humidity (RH) > 40% OFA depositions on marble and calcarenite very quickly (over a matter of days) give rise to gypsum crystals and coloured spots on the underlying surfaces (Primerano, Marino, Di Pasquale et al., 2000), respectively due to sulphuric acidity released by the OFA (Primerano, Campisi, Di Pasquale et al., 1999; Primerano, Di Pasquale, Mavilia et al., 1998).
As sulphation damage has also been observed on sandstone and even on slightly porous stones such as granite (Smith and Magee, 1990; Smith, Magee and Whalley, 1993), we thought it would be interesting to extend our studies of the effects of OFA on these materials since they are in common worldwide use in the artistic buildings.

EXPERIMENTAL

Samples of oil fly ashes and stone. We used 5 samples of ash taken at different times from three Sicilian ENEL (Italian Electricity Board) oil-fired power stations: San Filippo del Mela (SFM), Messina; Termini Imerese (TI), Palermo and Priolo Gargallo (PG), Siracusa; depending on the year in which the samples were taken, they were labelled SFM-83, SFM-85, TI-81, TI-94 and PG-94.
The ashes we studied were sampled from the electrofilters, sieved through 100 μm mesh and considered representative of the aliquot emitted with fumes, at least as far as SPA content is concerned.
As regards the stones, we used commercial samples of serena stone and granite, labelled SER and GRA respectively, as representative of silicate stones; the first is a sandstone (Camuffo, 1991), the other is an intrusive igneous rock (Raguin, 1977).
Treatment of the samples and analytical methodologies. The analytical procedures employed to quantify the main constituents and the extractable acidity content of the OFA samples are reported in refs. Primerano, Di Pasquale, Mavilia et al., 1998 and Primerano, Marino, Di Pasquale et al., 2000.
For our tests we used test pieces (1-5 cm x1-5cm x1-2cm) of SER and GRA. 0.5-2 mm layers of predried ash were deposited manually on the surface of the stone samples; for periods ranging from 1 day to 1 month the samples were kept in controlled humidity chambers at relative humidity (RH) values in the 0-94% range. The effects of deposits were evaluated after brushing off the ash layer at pre-established times; the surface of the material was examined by reflecting optical microscopy (ROM, Zeiss stereomicroscope), scanning electron microscopy (SEM, Jeol mod. T300), WDS microprobe and X-ray diffraction (XRD, Siemens mod. GDS diffractometer).

RESULTS AND DISCUSSION

A deposition of up to 2 mm of the most acid (TI-94 and PG-94) OFA samples on the surfaces of SER and GRA test pieces kept in environments at RH in the range 0-50% for 1 month did not show any alteration; both optical images of the surfaces after contact with OFA and XRD and SEM analyses remain unchanged. The same was observed when less acid (SFM-83; SFM-85 and TI-81) ash samples were deposited.

Test pieces covered with 1 mm of TI-94 and PG-94 kept in environments at RH=58% for periods of up to 1 month, showed incipient surface alterations after 15 days; on those contacted with less acid samples SFM-83, SFM-85 and TI-81, the first signs of alteration were observed after 30 days.

On test pieces contacted with the most acid samples at RH values = 80% significant alteration was observed after only two days; optical microscope photographs (Figs. 1,2) show the appearance of colouration (ranging from green to reddish-brown and yellow) similar to that obtained by contacting marble and calcarenite with the same ash; colouration intensifies the longer contact is maintained. Samples with lower free acidity such as SFM-85 and SFM-83 are also capable of causing major alteration if 94% relative humidity is maintained for at least three days.

Figures 3 and 4 show SEM images of the surfaces of SER and GRA samples before and after 8 days' contact at 94% relative humidity with 0.5 mm layers of TI-94 and PG-94. The images 3b and 4b, when compared to 3a and 4a, are extraordinarily clear and show prismatic bihydrate calcium sulphate crystals (gypsum) formed on the exposed surfaces of the test pieces. WDS microprobe analysis (data not reported) confirmed the presence of sulphur only where there were prismatic gypsum crystals and revealed the presence of vanadium, iron and nickel on the damaged surface. XRD not reported analysis also confirmed the presence of typical gypsum patterns on the altered surfaces of both SER and GRA samples.

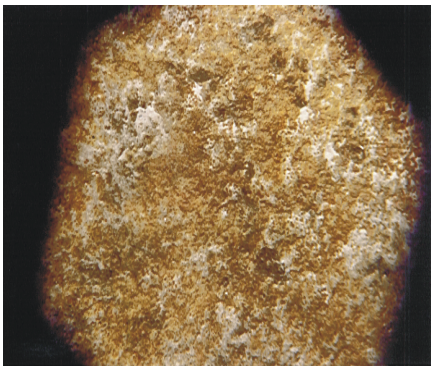


Figure 1. Optical microscope photograph of SER, after contact with SFM-83 at RH=94% for 3 days.

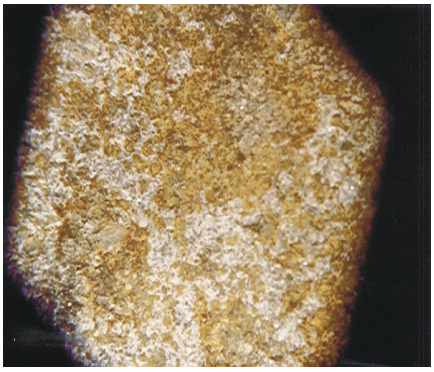
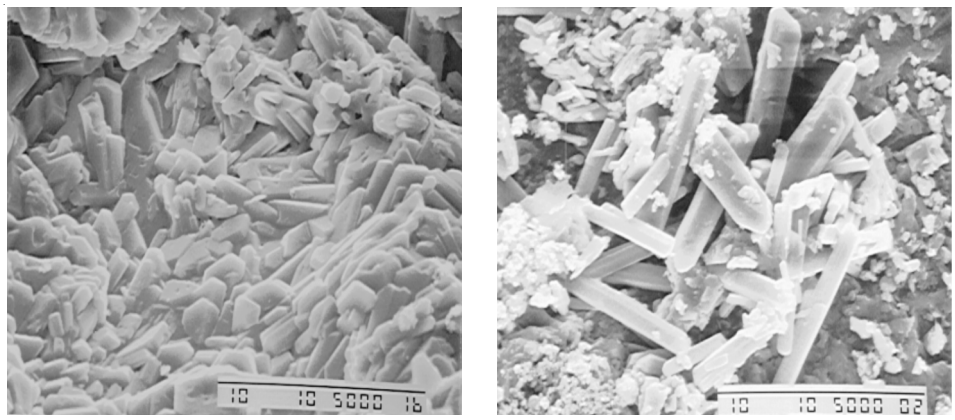


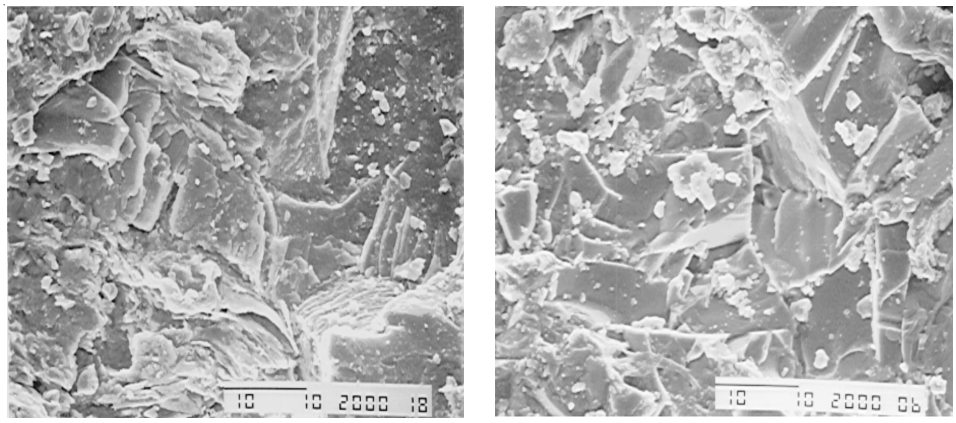
Figure 2. Optical microscope photograph of GRA, after contact with SFM-85 at RH=94% for 3 days .



(a) (b)

Figure 3. SEM images of the SER test pieces before (a) and after (b) 8 day's contact with TI-94 at RH=94%

Thus, the above results show that contact with OFA causes no alteration of stone surfaces only in an environment with low relative humidity. Where there is absence or lack of humidity, no release of aggressive or reactive material is observed, but OFA nevertheless maintain all their polluting potential. The pollutant transfer mechanism undoubtedly operates *via* absorption of humidity from the atmosphere, which is made possible by the hygroscopic nature of the ashes. The humidity absorbed from the air environment triggers the reaction of bisulphates and/or hydrolysable metallic ions contained in the ashes:



(a) (b)

Figure 4. SEM images of the GRA test pieces before (a) and after 8 day's contact with PG-94 at RH=94%.

[1] $VOSO_4 + H_2O \Leftrightarrow VO(OH)HSO_4$;
[2] $VOSO_4 + 2\ H_2O \Leftrightarrow VO(OH)_2 + H_2SO_4$
[3] $Fe_2(SO_4)_3 + 2\ H_2O \Leftrightarrow 2\ Fe(OH)SO_4 + H_2SO_4$;
[4] $Fe_2(SO_4)_3 + 4\ H_2O \Leftrightarrow 2\ Fe(OH)_2HSO_4 + H_2SO_4$;
[5] $Fe_2(SO_4)_3 + 6\ H_2O \Leftrightarrow 2\ Fe(OH)_3 + 3\ H_2SO_4$.

where [2] and [5] are total and [1], [3] and [4] step hydrolytic reactions.
The basic nature of solid bodies in contact tends to neutralise this acidity with consequent changes. This is not surprising in limestone and sandstone, because both stones contain calcite: the first as a main and the second as a secondary component (i.e., as the ligand of the main components, quartz and silicate) (Camuffo, 1991). Therefore the gypsum formation observed in the SER sample may be explained by the reaction between the calcite present as a silicate binder and OFA sulphuric acidity:

[6] $2\ HSO_4^- + CaCO_3 \rightarrow CaSO_4 + SO_4^{2-} + H_2O + CO_2$;
[7] $H_2SO_4 + CaCO_3 \rightarrow CaSO_4 + H_2O + CO_2$

The formation of vanadium and iron hydroxides and/or calcium vanadates, is responsible for the appearance of colouration on the attacked surfaces.
The above reactions cannot explain gypsum formation in the GRA sample, where calcite is absent and quartz and feldspar (a mixture of orthoclase, albite and anorthite) are the predominant and mica the secondary components (Raguin, 1977). It is likely that feldspar plays a significant role here. Indeed it is possible that feldspar hydrolyzes according to the reactions:

[8] $CaAl_2Si_2O_8 + 2H_2O \Leftrightarrow H_2Al_2Si_2O_8 + Ca(OH)_2$;
[9] $2(K,Na)AlSi_3O_8 + 6H_2O \Leftrightarrow H_2Al_2Si_2O_8 + 4H_2SiO_3 + 2(K,Na)OH$;

and that these reactions are favoured by high acidity values. When the stone is contacted with OFA and humidity is sufficient to activate the hydrolytic reactions [1]-[5], the sulphuric acidity produced by OFA tends to neutralize the basic environment produced by hydrolysis of the feldspar with the consequent formation of gypsum (e.g., from anorthite, reaction [8]) or of potassium and sodium sulphates (e.g., from orthoclase and albite, reaction [9]). These reactions may explain the sulphation observed on granite surfaces and may, ultimately, lead to the formation of kaolinite. They can be also present and make some contribution in sandstone sulphation.

CONCLUSION

The enviromental dangerousness of oil fly ash (OFA) emitted into the atmosphere by industrial activities, which we have already warned of in relation to calcareous materials, has in this paper also been confirmed for silicate materials, such as sandstone and granite. The deposition of OFA on the surfaces of these stones produces serious alterations within a few days except at humidity values below

50%. The formation of gypsum and coloured spots is the result of reactions between the strong primary acidity (SPA) released by OFA and the basic components (calcite and/or feldspar) of sandstone and granite in conditions of humidity. In the lack of humidity, the OFA deposited on the stone surfaces retains all its polluting potential and is thus ready to become reactive when suitable conditions of humidity return.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

AUTOMATED MICROSCOPIC RECOGNITION OF ATMOSPHERIC PARTICLES IN AMBIENT AIR SAMPLES

E Schultz[1, *], O Ronneberger[2] and H Burkhardt[2]

ABSTRACT

Digital microscopy in combination with specific imaging methods and pattern recognition techniques provides a new approach to particle analysis, possibly even for routine purposes. The feasibility of this approach was demonstrated by the automated recognition of airborne pollen grains. A recognition rate of 97% was achieved for pure pollen samples of the six allergic most relevant pollen species in Central Europe. This result based on (1) the excitation of primary fluorescence of pollen, (2) 3D volume image data from confocal microscopy, (3) the extraction of grey scale invariants and (4) the employment of so-called Support Vector Machines (SVM) for classification. The classification was based on a reference data base containing all pollen species of interest. No object specific codes were required. For routine applications the applicability to real-world samples was tested. These samples are characterised by a mixture of various particles. Additionally, it was assumed that only conventional microscopy will be available providing 2D images instead of 3D information. Under these conditions preliminary recognition rates of about 90 % were achieved, but not before enlarging the reference data base, considerably. A further improvement is expected not only by extending the reference data base but also by employing additional microscopic or spectroscopic techniques providing more optical information. On this basis, automated recognition may be suitable even for a classification of ambient particles in general. But it has to be considered that optical resolution is limiting a particle recognition to the coarse fraction >2.5 microns in diameter. However, even these particles may cause serious health

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effects due to a first peak in alveolar deposition at about 5 microns and the occurrence of airborne pollen and fungal spores in this size range.

INDEX TERMS

Airborne pollen, Optical microscopy, Image analysis, Particle recognition, Classification

INTRODUCTION

Health effects of airborne particles mainly depend on their composition and size distribution. This information is typically not provided by routine particle measurement due to high costs of size fractionated measurement and chemical analysis. Available particle data, therefore, are mostly restricted to the information on particle mass. Health related information in respect to particle size distribution and occurring particle phases, on the other hand, are quite easily accessible by optical analysis and subsequent image processing in combination with pattern recognition techniques. It has to be considered that optical microscopy has basic limitations due to optical resolution restricting particle analysis to the super micron particle range, but a greater number of health effective particles are occurring in this range, for example allergens like pollen and fungal spores. Data on the concentration of these components are still derived by eye from microscopic analysis of ambient air samples. These data suffer from considerably varying quality and limited reproducibility of particle analysis by visual inspection. Therefore it was felt that it may be meaningful to study the capability of novel techniques in optical microscopy, image processing and pattern recognition in order to improve the quality of pollen data and possibly provide valuable information about other health effective particles in the super micron range, too.

METHODS

Sampling

Optical analysis of ambient air samples requires particle sampling onto transparent media with low optical noise. For the present study, transparent collection plates and transparent collection tapes were used. For passive sampling, collection plates were weekly exposed in the sedimentation sampler Sigma-2 (VDI 2119, part 4). For pumped sampling, the collection tapes were fixed on a rotating drum in a Burkard pollen trap. Collection plates and collection tapes were coated with an highly transparent adhesive.

Additionally, untreated glass fibre filters were used. The filters were exposed in a low volume sampler. After sampling the glass filters were embedded in an immersion liquid of same refractive index as the filter material. By this, the filters became transparent and made them suitable for microscopic analysis (Ballach et al., 2001).

Microscopy

For microscopic imaging a 10- to 40-fold magnification was chosen. The used microscopes were the motorised ZEISS "Axioplan", for 2D imaging and the confocal Laser Scan Microscope ZEISS LSM 510 for 3D imaging.
Traditionally, translucent microscopy is used for optical analysis. However, the recognition of atmospheric particles in transmitted light is complicated by the huge variety of particles occurring in ambient air samples. Primary fluorescence of most biological particles provides an easily accessible feature in order to distinguish this particle component. Especially pollen grains are characterised by a strong primary fluorescence. The best signal to noise ration was found for blue light of about 450 nm wavelength for excitation. The corresponding green to yellow emission was used for the detection of pollen grains.

3D Volume Imaging

In order to identify an unknown object in an ambient air sample an experienced microscopist focuses into different planes of the object. Following this approach, a stack of images was recorded in z-direction and piled up to a 3D volume image. Fluorescence supports the 3D reconstruction due to the fact that the optical information can be understood as the measurement of locally occurring fluorescence activity. The intensity is largely independent of the direction of the exiting light and the direction of viewing. In order to avoid interfering light from other parts of the objects out of focus, confocal microscopy was used.

Feature extraction

Grey scale invariants were used to extract individual particle features for recognition. A detailed description of this technique is given by Siggelkow and Schael (1999). No object specific knowledge is needed for this technique. The grey scale invariants do not require any a prior knowledge about the morphology of the particle of interest, but use the grey value distribution of the particle. The extracted feature vector is invariant to rotation and translation of the particle, but is sensitive to only slight changes already, in particles morphology.
Therefore feature vectors of objects belonging to the same class could be expected to form individual clusters in the feature space.

Classification

So-called Support Vector Machines (SVM) were employed to classify the unknown objects (Vapnik, 1995). For this purpose, the classifier was trained by a reference data base consisting of known objects. The reference was extracted from an image data base comprising all objects of interest which were labelled by experienced microscopists. The main task of the SVM is to find the largest margins between the several clusters. For recognition of an unknown object, its feature vector is extracted and classified using these margins. This gives an estimate on the affinity to certain object class. A detailed description of the feature extraction and the classification is given by Ronneberger et al. (2002).

RESULTS

The described methods were employed to identify and distinguish airborne pollen as an example of a highly health effective component of the atmospheric aerosol. It was the aim to recognise those pollen which are known as the most allergic species. In Central Europe this group comprises pollen of hazel, yaw, birch, sweet grasses, rye and mugwort.
The achieved recognition rate was 92 % for a number of 32 pollen species, most frequent in Central Europe. Putting together the 26 allergic less relevant species in one class and trying to recognise the remaining six most allergic species, a recognition rate of even 97 % was achieved (Ronneberger et al., 2002).
This promising results were achieved by using pure pollen samples, directly taken on collection plates from the corresponding plants and by using 3D volume data from confocal imaging. Routine measurements make different demands. Therefore it was decided to

(1) use real-world samples on collection tapes from the Burkard pollen trap,
(2) employ conventional light microscopy with a 10-fold magnification and
(3) process 2D image data both from translucent and fluorescence microscopy.

This approach required a stepwise segmentation and selection of pollen-like particles prior to individual particle recognition. Furthermore, a greater number of about 150 pollen individuals from each species and about 1000 ordinary aerosol particles were recorded to establish a reference data base as a training set of sufficient size. The extension of the data base should compensate the loss of information due to 2D imaging instead of recording 3D volume data. The reference was additionally enlarged by including both fluorescence and translucent image data. For this purpose, the capability of the classifier was improved in order to simultaneously process multi-channel data.
This proceeding was tested with a set of images of about 1400 atmospheric particles. This operational data set was different from the above mentioned training set. The images were recorded from typical springtime samples containing the pollen species Alnus (alder), Corylus (hazel) and Taxus (yew). The automated recognition led to recognition rate between 87 and 92 % depending on the pollen species.

CONCLUSIONS

(1) The basic feasibility of an automated recognition of atmospheric particles could be demonstrated by example of airborne pollen.
(2) The extraction of “finger prints” by grey scale invariants and the use of support vector machines as a new type of classifier can be interpreted as a breakthrough in particle recognition.

(3) However, the achieved recognition rate of 97 % for allergic pollen species required unsuitable conditions for routine purposes, e.g. pure pollen samples and 3D confocal microscopy.

(4) Analysing field samples and employing conventional 2D microscopy complicates automated microscopic recognition, but arising problems are soluble by an extension of the reference data base.

(5) The reference has to be extended both in a quantitative and a qualitative aspect by enlarging the number of reference objects and the quantity of optical information, as well.

(6) The classification does not need any a prior knowledge about particle structure or morphology, the self-learning classifier basically is suited for the identification of any other particle component.

(7) Finally, it has clearly to be stated that the method is restricted to the supermicron particle range > 2.5 microns due to optical resolution. However, even these particles may severely effect health due to a first peak in alveolar deposition at about 5 microns and important allergens in this size range such as pollen and fungal spores.

OUTLOOK

On July 1, 2003 a corresponding research project has been started, funded by the German Federal Ministry for Education and Research. Within the scope of a three year study it is planned to develop an automatic microscope based particle monitor basing on the presented results. The main goals in this project are to develop the automatic collection and preparation of samples for microscopic imaging, to implement of an automatic self-learning selection of system parameters, to improve a particle pre-selection and segmentation, and adapt the system to the recognition of further particle phases such as hazardous asbestos fibres, latex containing tire wear, therapeutic sea salt etc.
In order to cover this range of applications the amount of optical information processed by the system must be extended. Valuable information can be expected from polarisation and IR microscopy and Raman spectroscopy.

ACKNOWLEDGEMENTS

The authors would like to thank U. Heimann for setting-up the work place for automated optical analysis, development of the image acquisition, and establishing the reference data base. Furthermore this work considerably profited from the previous work of V. Dietze and his experience in image analysis of airborne particle. Finally, we grateful acknowledge the financial and personal support of the Swiss Meteorological Service MeteoSwiss, Zürich.

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The 14th International Conference
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Dubrovnik, CROATIA 6-10 October 2003

ASSESSMENT OF AIR QUALITY AT WASTE MANAGEMENT ACTIVITIES: STRATEGIES OF SAMPLING

E Senante*, C Békaert, V Decottignies and L Galtier

ABSTRACT

Waste management activities are regulated by international and local regulations about releases of pollutants in the atmosphere. These requirements, such as the European Incineration Directive (2000/76/CE) or, more recently, the EPER European Decision (2000/479/CE), are the guarantees of a global air quality of the earth in agreement with the Sustainable Development commitment. These requirements ask waste management companies to control their own releases. This control relies on the capacity to analyse atmosphere releases in accordance with international standards from sampling to analysis.
The aim of this article is to give an overview of existing sampling techniques to make a sample in agreement with the objective of the measurement campaign (health impact, environment impact, process assessment, …).
As an illustration, a case study on surface sources is presented and described. Sampling was achieved with flux chamber and the objective was the assessment of VOC emissions from surface sources. Sampling strategy will be presented and discussed in this article.

INDEX TERMS

Sampling strategy, diffusive source, flux chamber.

INTRODUCTION

The measurement chain consists in four steps linked together: sampling, preservation, lab sample preparation and analysis. Each step has an influence on

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the results and needs to be well defined (establishment of specific method) in accordance with the objective to achieve.
Among analytical steps, sampling is certainly the most critical one as the quality and the representativity of the analysis relies on the quality and the representativity of the sampling step. Hence, sampling techniques (on-site materials such as bags, tubes and surface sampling) will be listed and discussed regarding the objectives of the measurement, the type of source (canalised, surface, diffuse…) and the sampling feasibility.

STRATEGIES OF AIR SAMPLING

Sampling strategy and equipment must be in accordance with the objective of the measurement and needs (precision, cost, reactivity of response). The choice of the sampling techniques depends on several criteria but mainly the measurement objective, the type of source and the analytical parameters.

– Measurement objective: worker exposure assessment, regulatory requirements, etc…
– Type or source: canalised, surface…
– Analytical parameters: VOC (Volatile Organic Compounds), PAH (Polycyclic Aromatic Hydrocarbons), dust, etc…

Type of sources

It is highly recommended, when discussing about different types of sampling, to spend some minutes to clearly explain what kind of emissions and processes are concerned. A classification has been done to understand the different types of sources.

Table 1. Definition of the different types of sources

Source	Definition	Example
Canalised (Bouscaren, 2002).	Injection into the atmosphere by using any kind of pipe whatever the shape of the cross section.	Chimneys, landfill gas wells.
Surface source (Bouscaren, 2002).	A type of diffusive source which can be defined in a concrete surface.	Polluted soils biological treatment surface, landfill site cells.
Ambient air	All the places where the air quality can be assess.	A forest, an industrial workshop, an industry, a school…
Worker exposure	Concentration relating to all the worker's activities during the day (working ambiances, maintenance, etc…)	A worker exposure that changes of workshop at a sorting plant.

SYNTHESIS OF AIR SAMPLING

Regarding these variables, Table 2 presents a synthesis which includes sampling types, sample container for different researched compounds.

SURFACE SAMPLING WITH FLUX CHAMBER : A CASE STUDY

In some cases, as the EPER Directive requirements, emission data must be declared in term of specific flux (kg per year of a list of compounds). For this reason, sampling methods must be able to meet this regulatory demand to take into account not only compounds concentration (for example mg/m), but also the flow rate emission (mg/h).

Sampling from surface sources is not standardized; a Work Group of the European Standardisation Committee (TC 264 Air Quality, WG 17) works about the standardisation of sampling from this type of sources.

The study case was the assessment of VOC emissions in a polluted soils biological treatment site due to a regulatory demand. VOC emissions had to be assess in concentration and flow rate for different stages of treatment, and among these techniques there were some surface sources. As there is no standard method to assess the diffusive emissions, we have adapted the existing technology to the researched objective.

Figure 1 presents the arrangement of all the system in a polluted soil biological treatment site.

Sampling in surface sources was carried out using a flux chamber and Tenax adsorbent cartridges. Flux Chamber from surface sources is a sampling device that allows to measure emission flow rates from various diffusing surfaces (water, soil, wastes), which are usually difficult to characterize with traditional means. The flux chamber used was ODOFLUX (see Figure 1) : it consists in a cylindrical enclosure with a spherical top. The flux chamber was supplied with a controlled flow of pure air coming from a compressor and a filtration system of active carbon. The air is sucked from the chamber at a controlled flow rate using a Gerstel pump that includes the cartridges support.

It is important to work under isokinetic conditions between the gas introduced into the chamber and the gas withdrawn. These isokinetic conditions insure that the gas is emitted at the surface as if there was no flux chamber (Odotech, 2003). This working condition is essential to obtain a good measurement of the real flux emitted from the surface. In this case, as the emission flow rate from the surface was very small, the isokinetic conditions were assured with inlet and outlet flow rate at the same value. A rotameter was used to control inlet air and outlet air rate from the flux chamber was controlled by a Gerstel pump.

Flow rate used in this campaign was 6,5 l/min: inlet air was supplied with a compressor at 6,5 l/min and outlet air was withdrawn with the Gerstel pump 1,5 l/min and a pump at 5 l/min was used to equal the inlet and oulet flow rate. The choice of this flow rate was a compromise to have a good mix in the chamber and

Table 2. Sampling strategies

Source	Sampling line or sampling type	Sample container	Researched parameters	Standard or reference	Comments and practical recommendations
Canalised	Transfer line with pump (isokinetic system): - thermostated and insulated cane (specially for chimney) - PTFE or stainless steel tubes (sampling from conducts at temperature below 80°C)	Filter followed by impinger with absorption solutions	Mercury Metals	ISO 9096 EN 13284-1	Difficult to respect isokinetism. For impingers, the preparation takes long time
		Impinger with absorption solutions	HF HCl	EN 1911-1	
		Filters (in quartz or PTFE)	Dust	EN 13284	
		Filters followed by adsorbents cartridges (XAD 2)	PAH Dioxins	ISO 9096 EN 13284-1	Preservation of cartridges sheltered from light and below 4°C.
		Cartridges	VOC	EN ISO 16017-1	Tedlar bags and cartridges are sensitive to high temperatures. For olfactometry analysis Tedlar bags are necessary.
		Tedlar bags			
Surface	Transfer line with pump and flux chamber	Tedlar bags	VOC, nitrogenous and sulphurous compounds	Flux chamber sampling non standardised.	Necessary to respect isokinetic conditions. Possibilities of condensation. It is not advised to reuse Tedlar bags
		Adsorbent cartridges (Tenax, charcoal or carbotrap, XAD 2)			
Ambient air	Transfer line with pump	Tedlar bags	VOC, nitrogenous and sulphurous compounds		It is not advised to reuse Tedlar bags
		Adsorbent cartridges			
		Filters	Dust		
		Analysers (optical system, FID and portable GC)	Dust Total VOC Specific compounds		
Worker exposure	Passive sampling	Diffusive badges with adsorbents (charcoal, carbotrap)	VOC	EN 689	Well position of the badges on workers.
	Transfer line with pumps	Fliters	Dust		

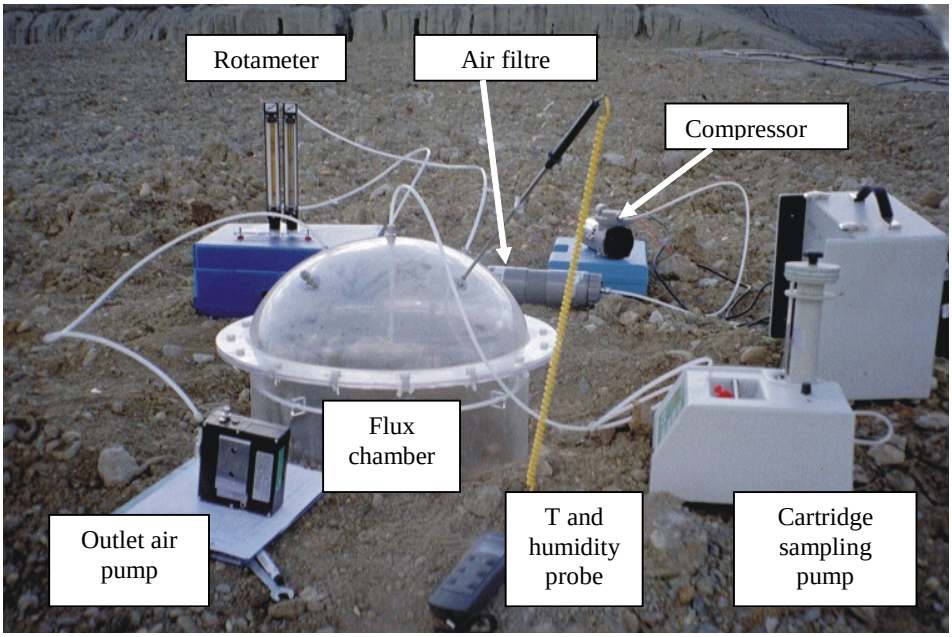

Figure 1. Flux chamber equipment

not too high to avoid cartridges saturation. Tenax cartridges were chosen according to the researched compounds : aromatic VOC, halogens, etc… The flow passed through the cartridges was calculated from the results of the total VOC estimated concentrations obtained with a portable PID (Photo Ionisation Detector).
Temperature and humidity were measured in continue with a probe, as shown in Figure 1. VOC sampling with adsorption cartridges, thermal desorption and CPG analyses were realised in accordance with the international standard EN ISO 16017-1.
With the results of concentration (from Tenax cartridges) and flow rate in the flux chamber we were able to answer the regulatory requirements of VOC flow rate emissions given in kg/day.

CONCLUSIONS

As it has been described in this article it is important to measure gaseous emissions to assess the impact of waste activities in order to reduce them. In this context the equipment and the sampling strategy have to be adapted in accordance with the objectives and needs.
In waste activities, we often find surface sources. The assessment of emissions in this kind of sources is asked in new regulatory texts (at local, national and european level). So, a protocol for sampling with a flux chamber has been developed with the objective of the assessment VOC flow rate emissions. This method seems to

be adequate to respond to a problematic which is not yet standardized : isokinetic and environmental conditions are important factors to take into account when using this kind of device.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

MONITORING AND CHARACTERISATION OF INDOOR PARTICULATE MATTER

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ABSTRACT

Indoor air quality is a major determinant of personal exposure to pollutants because people spend a substantial part of their time indoors. Particulate matter (PM), which has been involved in a number of health effects, is very important indoor air pollutant. One of the major sources of indoor air particulate pollution is the ambient air. Therefore we studied the relationship between outdoor and indoor particle concentrations as an important factor to determine the actual dose of the general population. The indoor concentration values resulting from our monitoring vary from 17.4 μg.m^{-3} to 194 μg.m^{-3}. The most of indoor particulate matters represent the particulates with diameter less than 10 μm. It was found that the indoor aerosol particle concentrations could achieve higher values than outdoor particle concentrations and the indoor to outdoor PM_{10} ratios were higher than 1.0. It is characteristic for buildings without a ventilation system or with an ineffective ventilation system and/or with dominant indoor sources. The dust particles are dangerous not only because of their high concentrations in dependence on their particle size but also because of their nature. We investigated the dust reactivity and their pathological potential determined by distribution of surface active centres and by presence of heavy metals in the finest fraction of the aerosols. Concentration of spins was obtained from ESR spectra. The determined surface spin concentrations were high. The surface activity is probably related to the presence of the metal ions in low oxidation number, especially in the presence of iron. Elemental analysis was carried out by energy-dispersion x-ray spectroscopy and the mass concentrations of metals (Fe, Pb, Cr, Cd, Zn, Hg, Cu, Co, Sb, As, Ni) were determined by Atomic Absorption Spectroscopy. The mass concentrations of metals were compared to the Slovak hygienic limits or to the WHO recommended concentrations. High indoor concentrations of heavy metals were found. The presence of metals in finest fractions bellow 10 μm was confirmed.

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INDEX TERMS

Indoor, particulate matters, PM_{10}, surface radicals, heavy metals.

INTRODUCTION

Interest in the effects of air pollutants upon health has been growing in recent years. Recently, attention has focused on the air quality issues in buildings. Dust particles suspended in air are generally considered to be one of the principal indoor risk factors. Other contaminants such as gaseous substances or biological components adsorbed on the surface of particles can cause dangerous effects on the human organism.

The indoor particle concentrations without indoor sources reach 65 % of outdoor concentrations (Wallace, 1996). However, if indoor sources exist, the indoor particles contribute to the effects of outdoor particle concentrations (Marconi 2000, Asmi 2000). According to literature data (Rezáčová et al., 2001), dust concentrations in buildings range from 10 to 200 $\mu g.m^{-3}$ depending on the indoor sources of particles and air ventilation rate. These indoor particulate matter contaminants originate from the building materials, cooking, heating and all activities related to combustion processes, smoking, cleaning and moving of occupants. The importance of indoor sources depends on the number and habits of the occupants too.

The occurrence of particulate matters in the air is undesirable both because of their health effect and their surface properties resulting in possible synergistic effect of various pollutants. Particles cause negative health effect, when they are inhaled and deposited in the respiratory tract. The location of deposition of particles in the respiratory tract depends on their particle size. Where indoor sources are dominant, it follows that exposure occurs principally indoors.

The purpose of this work was to investigate the relationship between indoor and outdoor levels of particulate concentrations. The determination of this relationship is very important for the actual dose estimation of general population to particulate matter. In addition, the distribution of toxic metals concentrations and surface reactive spots occurrence has been also investigated.

METHODS

Indoor particulate matter monitoring was carried out from January 2001 to December 2001 in various flats and residential buildings at different places in the urban area of the Slovakian city of Košice. All homes were naturally ventilated, the kitchen were equipped with gas-cooking stoves. The outdoor measurements were carried out near the indoor sampling places.

Dust measurement included total dust particles sampling onto a collection material (membrane filter Synpor 0,8 μm pore size, 35 mm in diameter) by

sampling equipment VPS 2000 (Envitech, Trenčín) at air flow rate of 960 litres/ hour during sampling period of approximately 24 hours. The sampling equipment was placed in the middle of the room 1500 mm above the floor. The windows and the door were closed during the monitoring period.
The particulate mass concentrations were determined gravimetrically. In order to minimize the humidity interference, the filters were dried at 80°C for 8 h before and after sampling and than were equilibrated at a constant temperature and humidity (e.g. 20°C and 50% RH) for 24 h before and after sampling.
The collected dust samples were analyzed by scanning electron microscopy/energy-dispersive X-ray analysis (SEM/EDX), atomic absorption spectroscopy (AAS), and electron resonance spectroscopy (ESR) as the main techniques. Particle size and morphology of collected dust particles were determined by SEM with the equipment Tesla BS 340. The elemental EDX analysis was carried out on the micro-analytical system LINK ISIS 300 (Oxford Instruments) operating in secondary mode at a potential 20 kV and at extension 600-30 000. The chemical analysis of the toxic metals content in dust samples was performed by SpectrAA-30 (Varian). The surface reactive spots concentrations were detected on the spectrometer ERS 220 (GAS, Berlin) with a resonator RSX 216 at room temperature under following conditions: the microwave power 10 mW, modulation amplitude 0,02 mT, time constant 0,5 s. The relative intensity of the was determined by comparing them with those of Cr^{3+}/MgO as standard samples. The ESR spectrum was recorded as the first derivation of the absorption spectrum at the speed record 14,3 mT/min.

RESULTS AND DISCUSSION

The indoor concentration values resulting from our monitoring vary from 17.4 $\mu g.m^{-3}$ to 194 $\mu g.m^{-3}$, the average outdoor concentrations being in the range 32 - 163 $\mu g.m^{-3}$. An indication of the average difference between indoor and outdoor PM_{10} is computed as the indoor-to-outdoor ratios of the average concentrations I/O. The PM_{10} I/O ratios ranged from 1,23 - 2,5 and confirm the previous finding (Števulová et al. 2001), that people in closed rooms are exposed to higher concentrations of pollutants than outdoors. New buildings provide better thermal comfort for the occupants, but using of the tight windows and doors and insufficient ventilation treatment causes bad air circulation indoors, which leads to accumulation of pollutants.
The individual particles of irregular shape of various particle sizes, as well as aggregates of ultra-dispersion particles were observed on the SEM micrographs of the dust samples collected at different locations in buildings. The majority of dust particles were non-spherical in shape with rough surface. The occurrence of spherical particles, as well as fibrous particles was not obvious. The evaluation of SEM micrographs of the collected dust samples showed (Eštoková 2002) that 80-90% of the particles were smaller than 10 μm. In the case of some samples, the particle size distribution was shifted in the range of particle size under 5 μm.

Scanning electron microscopy/energy dispersive x-ray analysis (SEM/EDX) provides preliminary information on the elemental composition of the samples. Figure 1 represents EDX spectrum of a selected solid aerosol sample.

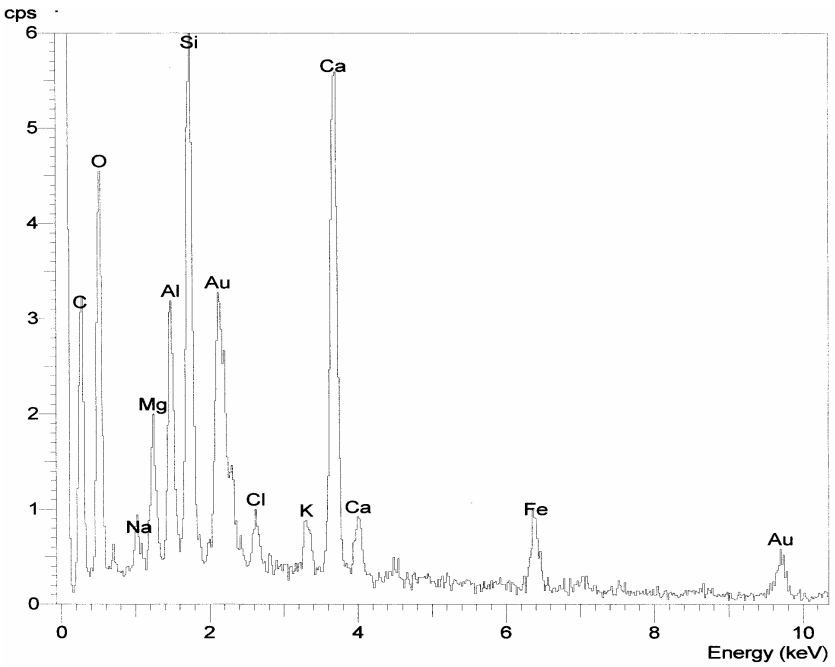

Figure 1. EDX spectrum of elemental chemical analysis of dust sample.

The EDX spectra of the majority of collected dust samples were very similar. The principal inorganic elements constituting the dust particles in order of decreasing peak intensity were Ca ≈ Si> O > Al > C > Mg > Fe > Cl > Na ≈ K. The presence of the carbon and oxygen, which can originate from organic compounds as well as from inorganic oxides, acids and/or salts, was confirmed. The presence of aurum peak on the spectrum is caused by the preparation of the particulate sample, where the aurum suspension was laid on the sample to ensure the sample conductivity. As shown in Figure 2, the spherical particle in shape having diameter 0.8 μm consists of copper.

The mass concentrations of heavy metals (Fe, Pb, Cr, Cd, Zn, Cu, Sb, As, Ni) determined by AAS are summarised in Table 1. The mercury content was not detected because of its low concentrations. Because of the absence of indoor heavy metal limits in the Slovak Republic, the measured weight percentage values were compared with Slovak hygienic limits for ambient air (Pb) or to the WHO recommended values for ambient air (Cd, Ni, Cr, As). The contents of zinc, copper, iron and antimony were not evaluated because of the absence of both indoor and ambient limits. The determined mass concentration values were high in analysed samples. In the case of

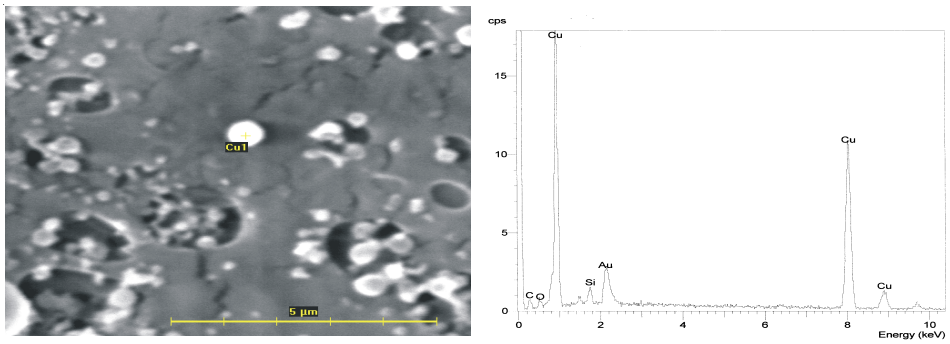

Figure 2. SEM micrographs and EDX spectrum of elemental chemical analysis of a dust sample.

cadmium and chromium, the mean mass concentration values were higher than limits, whereas the mean concentrations of other heavy metals were lower than limits but many concentrations above or near limit value were found.

Table 1. Mass concentrations of heavy metals [μg.m^{-3}]

element	***Cu***	***Pb***	***Cd***	***Ni***	***Cr***	***Zn***	***As***	***Fe***	***Sb***
mean	0,704	0,094	**0,094**	0,050	**0,058**	0,408	0,007	1,818	0,115
minimum	0,03	0,007	0,002	0,007	0,002	0,08	0,0001	0,36	0,0001
maximum	3,38	0,666	0,625	0,29	0,35	2,01	0,019	9,23	1,47
limit	**-**	**0,5**	**0,01**	**0,125**	**0,00125**	**-**	**0,0125**	**-**	**-**

The mass concentrations of lead in indoor air were lower than limit concentration 0,5 μg.m^{-3} (Notice of SR No. 705/2002). The decrease of lead concentrations in air is likely related to the extended use of petrol without lead compounds. In case of cadmium, the portion of 89% measurements exceeds the WHO recommended limit 0,01 μg.m^{-3}. The presence of cadmium in indoor air results probably from outdoor sources, e.g. from industry. The chromium content was also very high; 95% of measurements exceed the limit concentration. However, in comparison with those the mass concentrations of nickel and arsenic were lower; 13% and 20% portions of nickel and arsenic measurements in dust particles were higher than limit concentrations, respectively.

The surface of the inhaled particles, which determines the biological response, is large. The surface reactivity of particles depends on the number of reactive spots on the dust particles surface and on the distribution of various sites (free radicals and paramagnetic species) at the surface. It determines the pathogenic potential

of inhaled particles. The total surface spin concentrations of collected dust samples were determined in the range from 3.68×10^{20} to 3.84×10^{21} spin.g^{-1} (10^2 - 10^4 times higher values than the spin concentrations of mechanically activated quartz and silicon powders, Tkáčová, Števulová, 1995). The signals on ESR spectra recorded on some dust samples were identified as a superposition of signals arising from various paramagnetic species. It is mainly the presence of transition metal ions in a low oxidation state, typically iron, that have to be regarded as a possible cause of toxicity. According to Volante and Giamello (1994), the appearance of Fe^{2+} on the surface of the dust particles and its subsequent oxidation to Fe^{3+}, followed by ESR, leads to production of free radicals at solid-liquid interphase by direct reduction of atmospheric molecular oxygen. These sites may be implicated in the formation of dangerous active oxygen species in vivo.

CONCLUSION

Changing air conditions in buildings have tended to reduce ventilation and increase the opportunity for accumulation of undesirable levels of indoor air pollutants. The particulate matter is one of important indoor air pollutants which needs to be monitored and controlled. The risk of respiratory illness is connected with high dust particle concentrations in the indoor environment. The determination of the relationship between indoor and outdoor particles concentrations is very important for the actual exposure estimation of general population to particulate matter. The behaviour of the dust particles inhaled in respiratory tract depends on particle size distribution. Our results have been shown that the chemical nature of particles and their surface activity contribute to the risk factors of exposure to solid aerosols. The possible way to assess the risk of dust toxicity is the dust activity testing by high-reactive radicals formation (in vitro) on solid particle-water surface in presence of atmospheric oxygen. The aim of our future study will be oriented to these specific chemical processes.

ACKNOWLEDGEMENTS

The authors are grateful to the Grant Agency of Slovak Republic (project No. 1/0352/03).

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

A FEASIBILITY STUDY ON USING ATMOSPHERIC VISIBILITY AS AN ALTERNATIVE AMBIENT AIR QUALITY INDICATOR FOR METRO KAOHSIUNG, TAIWAN

CS Yuan*, YC Lin and CG Lee

ABSTRACT

The objective of this study was to investigate the feasibility of using atmospheric visibility as an alternative ambient air quality indicator for metropolitan area. Field observation of atmospheric visibility was conducted in metro Kaohsiung. Both regular and intensive observations of atmospheric visibility were conducted since November 1998. Regular observations of atmospheric visibilities were observed at 11:00 and 14:00 daily by unaided eyes. Two intensive observations of atmospheric visibilities were conducted from 8:00 am to 5:00 pm on January 8-16 and March 24-30, 2000. PM_{10} was measured at Cheng-tzung ambient air quality monitoring station with a hi-vol sampler during the intensive observation periods. Furthermore, atmospheric visibilities were then compared with pollutant standards index (PSI) and PM_{10} by statistical analysis. Regular observation of atmospheric visibility indicated that the most frequent atmospheric visibility ranged from 2.0 to 4.0 km, which were much lower than most mega cities over the world. Approximately 71.28% of these days, mainly from late fall to early spring, had atmospheric visibilities less than 8.0 km. Moreover, seasonal and diurnal variations of atmospheric visibility were also studied. Atmospheric visibility was usually lower in wintertime than in summer time, which was consistent with the variation of ambient air quality (i.e. PSI) in metro Kaohsiung. Moderate correlations between atmospheric visibility and PSI as well as PM_{10} were observed. Two ranking systems, the three-level and the five-level, was proposed based on field measured atmospheric visibility for metro Kaohsiung.

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INDEX TERMS

air quality indicator, atmospheric visibility, pollutants standard index (PSI), PM_{10} concentration, and statistical analysis

INTRODUCTION

Air quality index or indicator (AQI) is commonly applied to describe the status of ambient air quality since 1970's. More than fifty-five AQI had been defined and developed for many cities or areas in USA and Canada (USEPA, 1999). One of the most popular AQI is Pollutants Standard Index (PSI) that was originally developed by USEPA in 1976. PSI is defined as the maximum sub-index of five air pollutants including PM_{10}, SO_2, NO_2, CO, and O_3. Another approach for describing ambient air quality is atmospheric visibility, or characterized as visual air quality (VAQ), in Australia and New Zealand (Woun, 2001). In fact, atmospheric visibility can be directly visualized and more sensitive than PSI for general publics. Consequently, developing visual air quality as an alternative air quality index might be crucial for characterizing ambient air quality in urban areas.

Previous investigations reported that the year-round atmospheric visibility decreased gradually from 10.3 to 4.8 kilometers for the past two decades (Chang, 1999). Atmospheric visibility ranges from 6 to 12 kilometers in summer time, while the atmospheric visibility ranges from 3 to 5 kilometers in wintertime, in metro Kaohsiung (Liu, 2000; Yuan et al., 2000). According to the historical air quality measurements from Taiwan Environmental Protection Administration (TEPA), metro Kaohsiung demonstrates the worst air quality in Taiwan since more than 60% of Taiwan's heavy industrial plants (e.g. petrochemical plants, oil refinery plants, steel and non-metal plants, utility power plants, and cement plants) are located at metro Kaohsiung itself and its suburban. More than 8.7% of ambient air quality stations with PSI>100 were reported on a daily basis in the year of 2001, which is approximately 2.5 times higher than the nationwide average of 3.7% (Kaohsiung Environmental Protection Department (KEPD), 2002). In order to improve the ambient air quality of metro Kaohsiung, a two-year project was sponsored by KEPD to develope strategies for improving ambient air quality using atmospheric visibility as an alternative air quality indicator. This study attempted to investigate the feasibility of using atmospheric visibility as an alternative ambient air quality indicator for metro Kaohsiung.

METHODOLOGIES

Experimental Methods

In this study, field observation of atmospheric visibility was conducted to characterize the atmospheric visibility in metro Kaohsiung. Both regular and intensive observations of atmospheric visibility were conducted. Regular observation was

conducted twice daily at 11:00 am and 2:00 pm for almost three years since November 1998. Two intensive observations were conducted on January 8-16 and March 24-30, 2000, and observations were taken every hour from 8:00 am to 5:00 pm during these periods. The atmospheric visibility was visually observed by unaided eyes at two sites, Kaohsiung Meteorology Station and Farshing Temple. While, PM_{10} was measured with a hi-vol sampler at Cheng-tserng ambient air quality monitoring station during the intensive observation periods.

Statistical Analysis

The historical atmospheric visibilities observed on a daily basis at Kaohsiung Meteorology Station were reviewed to clarify the trend of variation for past two decades. Temporal and spatial variations of atmospheric visibility were further investigated. Seasonal and diurnal variations of atmospheric visibility were observed at two sites in this study. The average atmospheric visibility in wintertime was then compared to that in summer time. Moreover, the influence of pollutants standard index (PSI) and particulate matter (i.e. PM_{10}) on atmospheric visibility was also investigated. Atmospheric visibilities were then correlated with pollutant standards index (PSI) and PM_{10} through statistical analysis.

RESULTS AND DISCUSSION

Field Observed Atmospheric Visibility

The temporal and spatial variation of atmospheric visibility observed in metro Kaohsiung was discussed in this section. Results obtained from regular observation indicated that the atmospheric visibility observed in metro Kaohsiung ranged from 0.7 to 20.6 km. A bi-modal distribution of atmospheric visibility (0-8 km and 8-16 km) was observed in metro Kaohsiung. The most frequently observed atmospheric visibility ranged from 2.0-4.0 km. Approximately 71.28% of these days, mainly from late fall to early spring, had atmospheric visibilities less than 8.0 km. However, the atmospheric visibility observed in this study was lower than the previously reported monthly average of 9.2 km, with a range of 2.3-23.1 km, during the period of 1979-1998 (Yuan et al., 1999). Generally, the atmospheric visibility observed at Kaohsiung Meteorology Station (along a north-south axis) was approximately 0.2-1.0 km higher than that at Farshing Temple (along an east-west axis).

The monthly variation of atmospheric visibility during the regular observation period (November 1998 - August 2001) is illustrated in Figure 1. A seasonal variation of atmospheric visibility was observed in metro Kaohsiung, which concurred with previously reported trend. The atmospheric visibility was best in summer and worst in late autumn and winter. The seasonal average atmospheric visibility in spring (March-May), summer (June-August), autumn (September-November), and winter (December-February) were 5.4, 9.1, 8.2 and 3.4 km, respectively. The results indicated that the ambient air quality, measured in terms

of atmospheric visibility, was significantly worse in metro Kaohsiung than in most mega cities in the world. A diurnal variation of atmospheric visibility was also observed in metro Kaohsiung. The atmospheric visibility increased consistently from 8:00 am to about 1:00-2:00 pm and then leveled off after 1:00-2:00 pm.

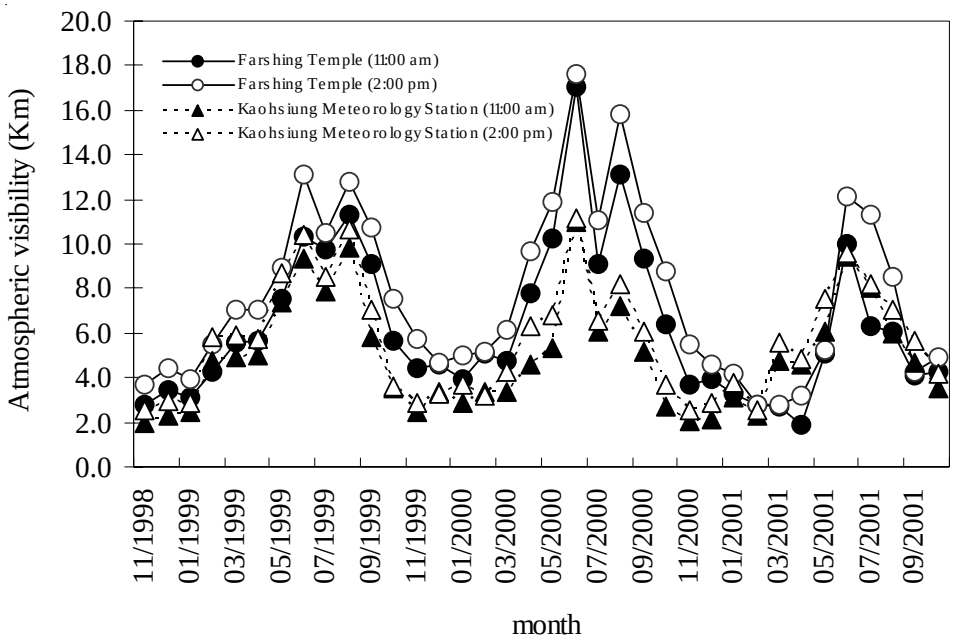
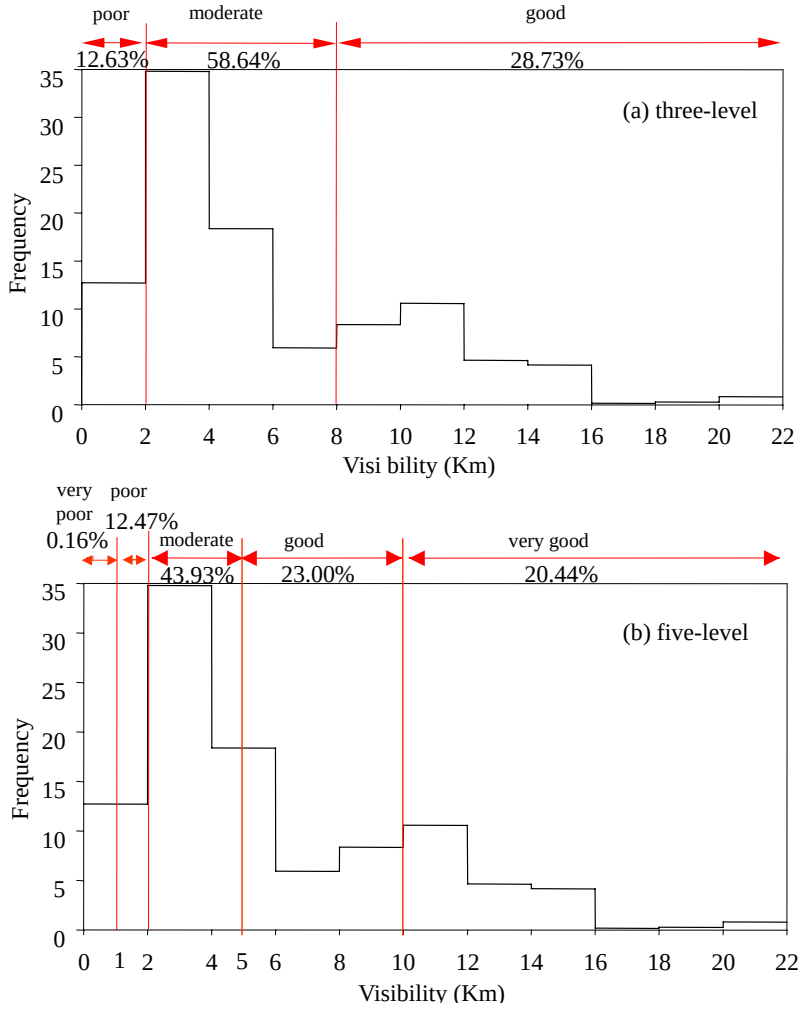


Figure 1. Seasonal variation of atmosphere visibility in metro Kaohsiung

Establishment of Visual Air Quality Index

An alternative air quality index was established in this study on the basis of atmospheric visibility. The alternative index also characterized as visual air quality index (VAQI) was then compared with the traditional PSI of ambient air quality in metro Kaohsiung. A moderate correlation between field observed VAQI and traditional PSI was revealed. Ambient air quality with a PSI value of 100 was equivalent to atmospheric visibility of approximately 3.0-4.0 km in metro Kaohsiung. Two ranking systems, the three-level and the five-level, were proposed for metro Kaohsiung. For three-level system, atmospheric visibility levels ranges of <2 km, 2-8 km, and >8 km were characterized as poor, moderate, and good visual air quality, respectively. For five-level system, atmospheric visibility levels ranges of <1 km, 1-2 km, 2-5 km, 5-10 km, and >10 km were characterized as very poor, poor, moderate, good, and very good visual air quality, respectively. The cumulative percentage frequencies of atmospheric visibility being less than 1.0 km, 2.0 km, 5.0 km, 8.0 km, and 10.0 km were approximately 0.16%, 14.63%, 56.56%, 71.28%, and 79.56%, respectively (Figure 2). This distribution agreed with the suggestions of previous investigator that atmospheric visibility could be

used as a tentative indicator of ambient air quality in urban areas (Jeng, 1996), although atmospheric visibility was not solely dependent upon ambient air quality but also dependent upon meteorological factors such humidity.



Correlation of Atmospheric Visibility with PSI and PM_{10}

Figure 2. Proposed levels of visual air quality index.

Based on the regular and intensive observation of atmospheric visibility, atmospheric visibility could be correlated with PM_{10} concentration in metro Kaohsiung. Two regression models were obtained as follows,

$$\mathrm{Log}(L_v \times PM_{10}) = A \quad \text{(regular observation period)} \tag{1}$$

$$L_v = B \times \mathrm{Ln}(PM_{10}) + C \quad \text{(intensive observation period)} \tag{2}$$

The regression constants of the above regression models at Kaohsiung Meteorology Station and Farshing Temple are listed in Table 1. The atmospheric visibilities correlated to PSI and PM_{10} concentration at two observation sites are also summarized in Table 1. As shown in Figure 3, the regression models between atmospheric visibility and PSI as well as PM_{10} varied with the observation periods and locations.

Table 1. Correlation of atmospheric visibility with sub-indexes of PM_{10}.

PSI (-)	PM_{10} ($\mu g/m^3$)	Vis-reg-F (km)	Vis-reg-M (km)	Vis-int-F (km)	Vis-int-M (km)			
20	20	21.7	17.2	14.9	14.9		30	30
14.5	11.5	12.7	12.8		40	40	10.8	8.6
11.1	11.3		50	50	8.7	6.9	10.0	10.2
	75	100	4.3	3.4	6.1	6.6		100
150	2.9	2.3	3.9	4.4		150	200	1.7
1.4	1.2	1.8		300	350	1.2	1.0	0.2
0.4								
Constants for Regression Models		A = 5.637	A = 5.537	B = -5.442 C = 31.205	B = -5.206 C = 30.543			

Vis-reg-F and Vis-reg-M represent atmospheric visibility and the regression models established for regular observation period at Farshing Temple and Kaohsiung Meteorology Station, respectively.
Vis-int-F and Vis-int-M represent atmospheric visibility and the regression models established for intensive observation period at Farshing Temple and Kaohsiung Meteorology Station, respectively.

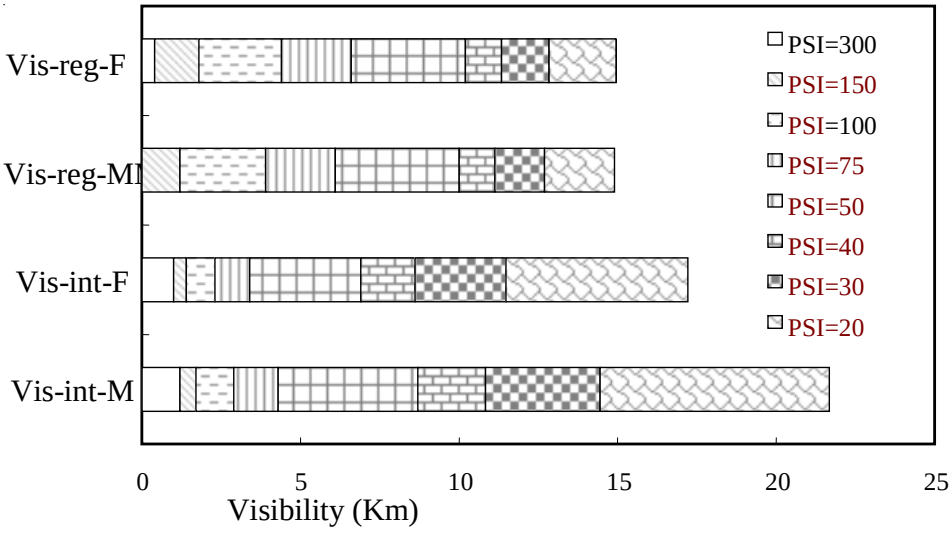


Figure 3. Correlation of atmosphere visibility with PSI.

CONCLUSIONS

This study successfully developed a visual air quality using atmospheric visibility as an alternative ambient air quality indicator for metro Kaohsiung. Regular observation of atmospheric visibility indicated that the atmospheric visibilities were much lower than most mega cities over the world. Approximately 71.28% of these days, mainly from late fall to early spring, had atmospheric visibilities less than 8.0 km. A diurnal variation of atmospheric visibility was also observed that the atmospheric visibility increased consistently from 8:00 am to about 1:00-2:00 pm and then leveled off after 1:00-2:00 pm. Moderate correlations between atmospheric visibility and PSI as well as PM_{10} were observed. Ambient air quality with a PSI value of 100 was equivalent to atmospheric visibility of approximately 3.0-4.0 km in metro Kaohsiung. Two ranking systems, the three-level and the five-level, were proposed for metro Kaohsiung. Atmospheric visibility was usually lower in wintertime than in summer time, which was quite consistent with the variation of ambient air quality (i.e. PSI) in metro Kaohsiung.

ACKNOWLEDGEMENTS

This study was performed under the auspices of Department of Environmental Department of Kaohsiung City Government. The authors would like to express their appreciation for their financial supports to accomplish this investigation.
Results obtained from the intensive measurements of atmospheric visibility and scattering coefficient indicated that atmospheric visibility had an opposite correlation with scattering coefficients for relative humidity less than 70%. The field measured scattering coefficients were 0.0928-0.5744 km^{-1} and 0.0852-0.6727 km^{-1}, respectively, for aforementioned separate intensive observation periods. This study concluded that a visual air quality index based on field observed atmospheric visibility was successfully developed as an alternative air quality index for metro Kaohsiung.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

QUALITY CONTROL IN PRECIPITATION ANALYSIS

D Borovečki[*, 1], Z Gliha[1], V Šojat[1]

ABSTRACT

Chemical laboratories involved in the international assessment of air pollution monitoring procedures have introduced a quality control system to ensure analytical results of adequate accuracy. One of the elements of quality control are interlaboratory comparisons. Synthetic precipitation samples are used to monitor accuracy in defining air quality indicators. In the Croatian Meteorological and Hydrological Institute (CMHI) chemical laboratory, 31 control samples have been analysed in the period 2000 - 2003.
Relative errors in the analysis of anions and cations and in the measurement of specific conductivity and pH value met the acceptance criteria (± 10% for ions, ± 0.10 for pH value). The application of recommended analytical methods and equipment (instruments) in the analysis of synthetic precipitation samples resulted in satisfactory accuracy.

INDEX TERMS

Quality assessment, Quality control, Interlaboratory comparisons

INTRODUCTION

The quality control system provides the base for comparisons of monitoring data generated in different laboratories from different countries. Participation in interlabo- ratory comparisons is extremely important step to identify level of quality control and assessment.
Since 1994, the CMHI chemical laboratory has been involved in international interlaboratory comparisons organised by the World Meteorological Organization

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(WMO) reference laboratories for the Co – operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe (EMEP) and the Global Atmosphere Watch (GAW) Programme and the International School of Ion Chromatography (ISIC).
For the EMEP Programme the reference laboratory is Norwegian Institute for Air Research. The Quality Assurance / Science Activity Center for the Americas (QA/SAC) co-ordinates the GAW Programme and control samples have been pre-peared by Precipitation Chemistry Reference Laboratory at the Illinois State Water Survey.
Under ISIC, control samples have been prepared by the National Chemical Laboratory of Slovenia and the Faculty of Engineering and Technology of Zagreb University.
There are between sixty and eighty laboratories involved in interlaboratory comparisons under the GAW Programme, about fifty under the EMEP Programme, and about an additional twenty under ISIC.
Laboratory skill is assessed as "very good" if the analysis results deviate from the expected value by less than 5% and as "good" if they deviate by 5% to 10%. If the deviation is between 10% and 20%, the laboratory is in the "improvement required" range, while deviations exceeding 20% are not acceptable. When measuring pH values, the acceptable deviation is ± 0.10 pH.

SAMPLES AND METHODS

Each year, the CMHI chemical laboratory analysed four synthetic samples prepared by the EMEP Programme reference laboratory, six samples from the GAW Programme reference laboratory and one sample prepared by the ISIC reference laboratory. In the period 2000 - 2003, the CMHI analysed 31 synthetic samples.
The concentration of ions in the EMEP and GAW Programme samples were at the levels usually found in precipitation. In the ISIC control samples, the concentrations were slightly higher. Chlorides were between 0.5 and 7.2 mg/L, nitrates between 0.1 and 10.9 mg/L, sulphates between 0.6 and 11.6 mg/L, sodium between 3.0 and 5.0 mg/L, potassium about 1.5 mg/L, magnesium between 1.7 and 20 mg/L and calcium between 5.7 and 66 mg/L.
For stability reasons, the samples were analysed within thirty days of receipt. The samples did not require any preparation for analysis. Their pH values and specific conductivity were measured and the following ions were analysed:

Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}.

The ion analysis was performed by ion chromatography (equipment: DIONEX-DX 500); the pH value was measured by pH-meter (equipment: RADOMETAR PHM 93.) and specific conductivity was measured by conductivity meter (RADIOMETAR CDM210).

RESULTS

Table 1 presents the deviation from reference values of the results of anion analysis and pH and specific conductivity measurements of control samples.

Table 1. Relative errors (%) in the analysis of anions, specific conductivity and pH value

year	number of samples	Cl^-	NO_3^-	SO_4^{2-}	specific conductivity	pH
2000	6	6,2	5	2,2	8,9	0,05
2001	14	6,7	3,5	2,7	6	0,09
2002	11	1,9	1,8	3	2,6	0,08

The results of the anion analysis and the specific conductivity measurements were within acceptable limits (± 10% deviation from reference values). The errors in the NO_3^- and SO_4^{2-} analysis were under 5% and in the chloride analysis between 5% and 10%. The deviations in pH values met the acceptance criteria.
A comparison of the results of the anion analysis of samples with high ion concentration (ISIC test) and those with low ion concentration (EMEP, GAW test) shows that the errors are comparable, irrespective of concentration, i.e. that the application of ion chromatography has provided the analytical measurements with a high level of accuracy.

Table 2. Relative errors (%) in the cation analysis

year	number of samples	Na^+	K^+	Mg^{2+}	Ca^{2+}	NH_4^+
2000	4		11,8	1,7	3,3	3,6
2001	14	3,9	5,3	2,7	4,5	3,9
2002	11	4,3	7,6	5,3	7,9	3,3

The cation analysis results met the acceptance criteria for deviations from reference values (± 10%). The errors in the K^+ ion analysis in 2000 somewhat exceeded acceptable limits (11.8%). The deviations in the results of the Na^+, NH_4^+ and Mg^{2+} ion analysis were under 5% and between 5% and 10% for the K^+ and Ca^{2+} ions.
Errors in the analysis of cations in high ion concentration samples (ISIC test) were under 5% while in lower ion concentration samples (EMEP, GWA test) they were in the range of 5% to 10%.
Figure 1 presents the mean values of relative errors in the analysis of anions and cations in control samples in the period 2000 - 2003.
The results of the Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+ and Mg^{2+} ion analysis of control samples deviated from exact values by less than 5% while the results of the Ca^{2+} and K^+ ion analysis deviated in the range of 5% to 10%.

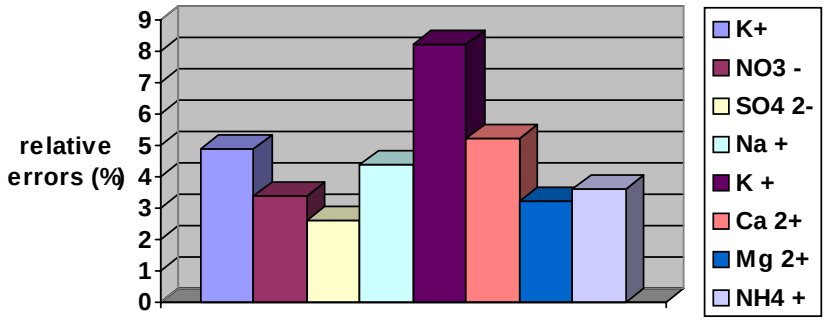

Figure 1. Mean values of relative errors in the analysis of ions in control samples

CONCLUSION

The international interlaboratory comparisons performed by the chemical laboratory of the Croatian Meteorological and Hydrological Institute in the period 2000 to 2003, resulted in adequately accurate analytical results. Higher accuracy was achieved in anion analysis.

With the application of recommended analytical methods and adequate instrument equipment, satisfactory results were achieved in analytical data testing and quality assessment .

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
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METALLIC AND ACIDIC COMPONENTS IN HIGH-RISK PARTICLE FRACTION IN ZAGREB AIR

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ABSTRACT

This paper presents the results of measurements of metallic (lead, manganese, cadmium) and acidic (chloride, nitrate, sulphate) components in high-risk particle fraction ($PM_{2.5}$ particles with equivalent aerodynamic diameter less than 2.5 μm) in the city of Zagreb, Croatia. Sampling was carried out continuously for one year (21 March 2001 – 20 March 2002). Twenty-four-hour samples of $PM_{2.5}$ were collected on cellulose membrane filters from approximately 100 m^3 of ambient air. The coarser particle fraction was removed from air stream using inertial impactor. Particle mass concentration was determined by gravimetry. Acidic anions (chloride, nitrate and sulphate) were analysed using ion chromatography. Metallic components (lead, manganese, and cadmium) were determined by atomic absorption spectrometry. Medians of mass concentrations of pollutants for the entire year were: $PM_{2.5}$ 31.1 $\mu g\ m^{-3}$, chlorides 0.32 $\mu g\ m^{-3}$, nitrates 1.77 $\mu g\ m^{-3}$, sulphates 3.37 $\mu g\ m^{-3}$, lead 0.05 $\mu g\ m^{-3}$, manganese 0.0071 $\mu g\ m^{-3}$, cadmium 0.00058 $\mu g\ m^{-3}$. A significant correlation ($P<0.05$) was found between the measured pollutants, except between cadmium with chlorides, sulphates and lead. The overall median anion content in the high-risk particle fraction was 19%, and the overall median metal content was 0.22 %.

INDEX TERMS

$PM_{2.5}$, chlorides, nitrates, sulphates, lead, manganese, cadmium

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INTRODUCTION

Chemical analysis of aerosol particles has gained increasing importance because of the effects of these particles on the environment (Schwartz, 1994, Gamble and Lewis, 1996, Lippmann and Thurston, 1996, Harisson, Smith, Pio and et.al., 1997). Epidemiological studies have shown that the exposure to urban particles is associated with an increase in mortality and morbidity, mainly of cardiopulmonary origin (Levy, Hammit and Spengler, 1999). Particle size and chemical composition play a major role in defining the relative toxicity of particles (Lippmann and Thurston, 1996, Magari, Schwartz, Williams and et. al., 2002).
This paper presents the results of measurements of metallic (lead, manganese, cadmium) and acidic (chloride, nitrate, sulphate) components in high-risk particle fraction ($PM_{2.5}$ particles with equivalent aerodynamic diameter less than 2.5 μm) in the city of Zagreb, Croatia.

MATERIALS AND METHODS

Twenty-four hour samples of PM2.5 particle fraction were collected in the northern, residential part of Zagreb, at the distance of approximately 20 m from the road with moderate to high traffic density. The sampling was carried out continuously over the one-year period (21 March 2001 - 20 March 2002). Samples of $PM_{2.5}$ were collected on cellulose membrane filters from approximately 100 m^3 of ambient air. The coarser particle fraction was removed from air stream using inertial impactor (Šega, 1999). Particle mass concentration was determined by gravimetry (SDČVJ, 1987.). Acidic anions (chloride, nitrate and sulphate) were analysed using ion chromatography (Weiss, 1995). Metallic components (lead, manganese, and cadmium) were determined by atomic absorption spectrometry (Christian and Feldman, 1970).

RESULTS

Table 1 summarises the descriptive statistic elements (number of samples, average values and standard deviations), and distribution parameters (minimum, maximum, median and inter quartile range) of mass concentrations for $PM_{2.5}$ particle fraction and acidic (chloride, nitrate, sulphate) components for overall measuring period, as well as for each season. The same parameters for metallic (lead, manganese and cadmium) components for overall measuring period, as well as for each season are shown in Table 2.
Number of samples, average values, standard deviations, minimum, maximum, median and inter quartile range of chloride, nitrate and sulphate content (%) in $PM_{2.5}$ particle fraction for overall measuring period, as well as for each season are shown in Table 3.

Table 1. Mass concentration of $PM_{2.5}$ particle fraction and acidic components ($\mu g\ m^{-3}$)

Measuring period	Pollutant	N	C_{avg}	SD	C_{min}	C_{25}	C_{50}	C_{75}	C_{max}
Spring	$PM_{2.5}$	81	42.2	21.1	4.7	26.2	39.0	51.9	100.3
	Cl^-	81	0.28	0.27	0	0.09	0.20	0.42	1.15
	NO_3^-	81	1.62	1.11	0.44	0.81	1.30	2.05	6.09
	SO_4^{2-}	81	3.33	2.07	0.67	2.01	2.81	4.11	13.53
Summer	$PM_{2.5}$	85	27.9	17.3	3.2	14.7	24.1	38.0	83.0
	Cl^-	93	0.30	0.19	0	0.19	0.24	0.35	1.20
	NO_3^-	93	0.95	0.44	0.07	0.65	0.87	1.18	2.22
	SO_4^{2-}	93	3.30	2.15	0.36	1.81	2.72	4.32	9.47
Autumn	$PM_{2.5}$	88	27.2	17.3	2.1	14.2	21.5	37.6	92.2
	Cl^-	89	0.39	0.25	0.08	0.24	0.34	0.49	1.73
	NO_3^-	89	3.69	2.50	0.57	1.62	3.33	5.13	11.40
	SO_4^{2-}	88	4.22	2.52	0.83	2.33	3.50	5.99	11.48
Winter	$PM_{2.5}$	90	42.8	21.1	4.9	25.1	38.6	55.8	101.6
	Cl^-	90	0.57	0.49	0.08	0.37	0.50	0.66	4.53
	NO_3^-	90	6.10	3.69	0.74	3.20	5.19	7.59	19.08
	SO_4^{2-}	90	6.05	4.15	0.67	3.20	4.80	8.43	20.76
Overall	$PM_{2.5}$	345	34.6	20.5	2.1	18.8	31.1	46.6	101.6
	Cl^-	363	0.39	0.34	0	0.20	0.32	0.52	4.53
	NO_3^-	363	3.04	3.05	0.07	0.91	1.77	4.47	19.08
	SO_4^{2-}	362	4.16	3.06	0.31	2.04	3.37	5.49	20.76

N – number of samples C_{min} – minimum values C_{25} – 25 percentile C_{75} – 75 percentile
SD – standard deviation C_{avg} - average values C_{max} – maximum values C_{50} - median

Table 2. Mass concentration of metallic component ($\mu g\ m^{-3}$)

Measuring period	Pollutant	N	C_{avg}	SD	C_{min}	C_{25}	C_{50}	C_{75}	C_{max}
Spring	Pb	81	0.05	0.02	0.01	0.04	0.05	0.07	0.14
	Mn	81	0.0055	0.004	0	0.0028	0.0048	0.0063	0.0214
	Cd	81	0.00059	0.0004	0	0.0003	0.00051	0.00079	0.00226
Summer	Pb	93	0.04	0.02	0	0.03	0.04	0.05	0.10
	Mn	93	0.0069	0.004	0	0.0041	0.0064	0.0084	0.0231
	Cd	93	0.00079	0.0006	0	0.0004	0.0008	0.00105	0.00427
Autumn	Pb	89	0.08	0.04	0.01	0.05	0.08	0.10	0.16
	Mn	89	0.0083	0.006	0	0.0045	0.008	0.0115	0.0281
	Cd	89	0.00053	0.0005	0	0	0.00043	0.0008	0.00211
Winter	Pb	90	0.10	0.06	0.01	0.06	0.10	0.14	0.32
	Mn	90	0.0126	0.007	0.0021	0.007	0.0114	0.0164	0.0344
	Cd	90	0.00066	0.0005	0	0.00032	0.00061	0.00095	0.00198
Overall	Pb	364	0.07	0.04	0	0.04	0.05	0.09	0.32
	Mn	364	0.0083	0.006	0	0.0041	0.0071	0.0113	0.0344
	Cd	364	0.00064	0.0005	0	0.00029	0.00058	0.00093	0.00427

N – number of samples C_{min} – minimum values C_{25} – 25 percentile C_{75} – 75 percentile
SD – standard deviation C_{avg} - average values C_{max} – maximum values C_{50} - median

Table 3. Relative content (%) of acidic components in overall particle mass

Measuring period	Component	N	w_{avg}	SD	w_{min}	w_{25}	w_{50}	w_{75}	w_{max}
Spring	Cl^-	81	1.02	1.29	0	0.16	0.45	1.58	6.90
	NO_3^-	81	4.87	3.69	0.82	1.78	4.07	6.81	21.69
	SO_4^{2-}	81	8.96	5.43	2.46	5.58	7.91	11.01	37.11
Summer	Cl^-	85	1.53	1.48	0	0.64	1.01	2.03	8.54
	NO_3^-	88	5.36	5.00	0.18	2.43	3.69	6.82	27.63
	SO_4^{2-}	88	16.37	13.76	1.72	6.89	11.46	21.37	57.84
Autumn	Cl^-	73	1.55	1.09	0.24	0.81	1.30	1.87	5.61
	NO_3^-	73	13.75	10.96	1.50	5.94	10.69	20.53	55.64
	SO_4^{2-}	73	15.82	11.28	2.41	6.71	12.09	20.94	49.86
Winter	Cl^-	89	1.62	1.25	0.11	0.90	1.25	2.02	8.06
	NO_3^-	89	15.48	7.76	3.21	9.79	14.94	19.36	46.10
	SO_4^{2-}	89	15.26	8.81	2.90	9.64	13.43	19.08	46.42
Overall	Cl^-	328	1.43	1.31	0	0.58	1.09	1.96	8.54
	NO_3^-	328	9.72	8.66	0.18	3.39	7.10	13.69	55.64
	SO_4^{2-}	328	13.79	10.10	1.72	6.69	10.79	16.35	54.96

N – number of samples w_{avg} – average values w_{min} – minimum values w_{25} – 25 percentile
w_{max} –maximum values w_{75} – 75 percentile SD – standard deviation w_{50} - median

Table 4 summarises the results of lead, manganese and cadmium content (%) in $PM_{2.5}$ particle fraction for overall measuring period, as well as for each season.

Table 4. Relative content (%) of metallic components in overall particle mass

Measuring period	Component	N	w_{avg}	SD	w_{min}	w_{25}	w_{50}	w_{75}	w_{max}
Spring	Pb	81	0.16	0.12	0.03	0.07	0.15	0.22	0.64
	Mn	81	0.02	0.02	0	0.01	0.01	0.02	0.11
	Cd	81	0.0016	0.0011	0	0.0008	0.0014	0.0021	0.0077
Summer	Pb	91	0.31	0.46	0.02	0.09	0.18	0.35	3.40
	Mn	91	0.05	0.07	0	0.02	0.03	0.05	0.53
	Cd	91	0.0040	0.0049	0	0.0017	0.0031	0.0048	0.0323
Autumn	Pb	73	0.33	0.22	0.03	0.18	0.27	0.44	0.89
	Mn	73	0.03	0.03	0	0.01	0.03	0.04	0.11
	Cd	73	0.0020	0.0026	0	0	0.0015	0.0030	0.0161
Winter	Pb	89	0.28	0.17	0.05	0.15	0.25	0.36	0.98
	Mn	89	0.03	0.02	0.01	0.02	0.03	0.05	0.10
	Cd	89	0.0019	0.0015	0	0.0009	0.0017	0.0026	0.0061
Overall	Pb	328	0.25	0.19	0.02	0.10	0.20	0.33	1.33
	Mn	328	0.03	0.02	0	0.01	0.02	0.04	0.19
	Cd	328	0.0024	0.0027	0	0.0008	0.0019	0.0031	0.0278

N – number of samples w_{avg} – average values w_{min} – minimum values w_{25} – 25 percentile
w_{max} –maximum values w_{75} – 75 percentile SD – standard deviation w_{50} - median

In Table 5 the significant correlation coefficients (* $P < 0.05$; ** $P < 0.01$) between pollutant mass concentrations for entire year are presented, as well as for each season. Figure 1 presents the total anion (chlorides, nitrates and sulphates) mass content (%) in the High-risk particle fraction during the overall measuring period, as well as for each season.

The total metal (lead, manganese and cadmium) mass content (%) in the high-risk particle fraction during the overall measuring period, as well as for each season are shown in Figure 2.

Table 5. Significant correlation coefficients between pollutant mass concentrations

Measuring period	Correlated components	Cl^-	NO_3^-	SO_4^{2-}	Pb	Mn	Cd
Spring (N = 81)	$PM_{2.5}$	-0.316**		0.357**		0.391**	0.413**
	Cl^-		0.528**		0.311**		
	NO_3^-			0.531**	0.431**		
	SO_4^{2-}						0.266*
	Pb						
	Mn						0.319**
Summer (N = 85)	$PM_{2.5}$			0.523**			0.266*
	Cl^-					0.213*	
	NO_3^-			0.465**			
	SO_4^{2-}						
	Pb					0.275*	
	Mn						
Autumn (N = 87)	$PM_{2.5}$					0.311**	
	Cl^-		0.276**		0.247*	0.492**	0.316**
	NO_3^-			0.578**	0.344**	0.451**	0.499**
	SO_4^{2-}					0.333**	0.219*
	Pb					0.493**	0.327**
	Mn						0.389**
Winter (N = 90)	$PM_{2.5}$	0.278**	0.705**	0.618**	0.568**	0.462**	0.306**
	Cl^-		0.264*		0.312**	0.224*	
	NO_3^-			0.465**	0.492**	0.420**	0.312**
	SO_4^{2-}						
	Pb					0.849**	0.285**
	Mn						0.276**
Overall (N = 343)	$PM_{2.5}$	0.125*	0.316**	0.419**	0.272**	0.342**	0.197**
	Cl^-		0.419**	0.144**	0.395**	0.349**	
	NO_3^-			0.564**	0.628**	0.506**	0.128*
	SO_4^{2-}				0.258**	0.248**	
	Pb					0.667**	
	Mn						0.217**

* $P < 0.05$ ** $P < 0.01$ N – number of samples

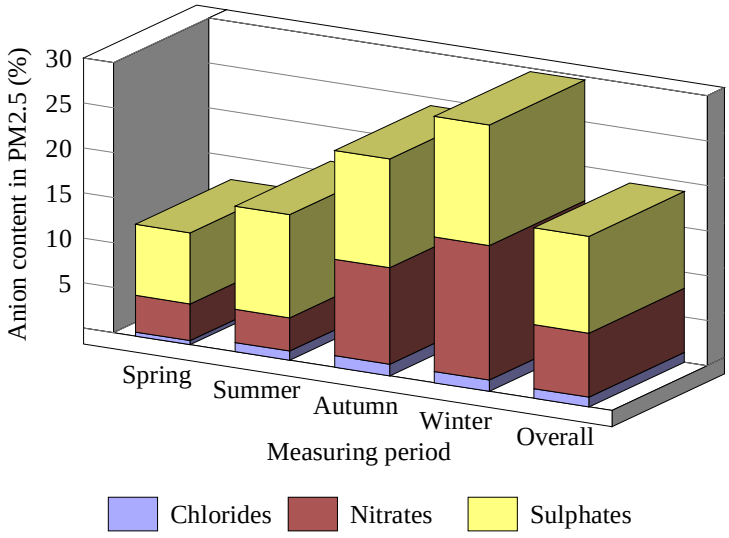

Figure 1. Overall anion mass content (%) in $PM_{2.5}$ particle fraction

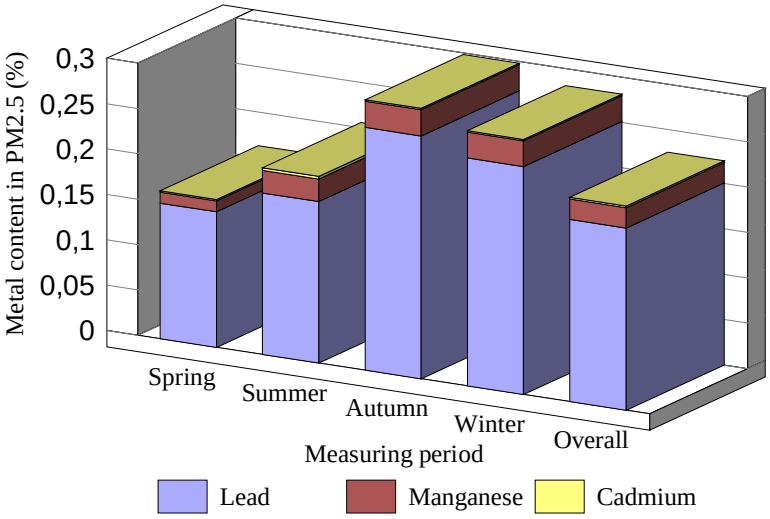

Figure 2. Overall metal mass content (%) in $PM_{2.5}$ particle fraction

DISCUSSION

Concentration levels of all pollutants showed significant seasonal differences ($P<0.001$, ANOVA, one-way analysis of variance), with high values during winter, which may be due to great emissions of pollutants and their precursors from

anthropogenic sources, combustion of fossil fuels and motor vehicle exhaust with high incomplete combustion in cooler period, except cadmium with high value in summer. The lower chloride, sulphate and manganese concentrations were found during the spring, nitrates and lead in summer and $PM_{2.5}$ and cadmium in autumn. Results of Kolmogorov test show that the mass concentration distributions of all investigated pollutants could be described by the lognormal distribution ($P<0.001$).

The content of all components in $PM_{2.5}$ particle fraction also showed significant seasonal differences ($P<0.001$, ANOVA, one-way analysis of variance). The high level of nitrate content in winter has been observed by Kaneyasu et al. (Kaneyasu, Ohta and Murao, 1995). The shifting of the NH_4NO_3 (s) $\Leftrightarrow$ HNO_3 (g) + NH_3 (g) equilibrium to the aerosol phase has been regarded -as responsible for this phenomena (Solomon, Salmon, Fall and Cass, 1992). The high level of chloride content in winter could be attributed to the thermodynamic equilibrium of NH_4Cl (s) $\Leftrightarrow$ NH_3 (g) + HCl (g) reaction (Willson, Clarke and Zeki, 1985). The high sulphate content in summer may be due to the strong solar radiation in summer, and photochemical gas-phase oxidation of gas precursor pollutant. During the winter period the aqueous-phase oxidation of gas precursor pollutant to secondary aerosols mainly take place. This process is slower compared to the photochemical gas-phase oxidation (Van Der Zee, Hoek, Harssema and Brunekreef, 1998). The higher metal content was found during the autumn (lead) and summer (manganese and cadmium) period. The lower contents of all metals were measured in spring. Results show that the mass content distribution of all investigated pollutants could be approximated to the lognormal distribution ($P<0.001$). The overall anion content median in high-risk particle fraction amounted to 19%, ranging from 12.4% during spring to 29.7% during winter period.

The overall metal content median in high-risk particle fraction was 0.22%, ranging from 0.16% in spring to 0.30% in autumn period.

The lower correlation was found between chlorides and $PM_{2.5}$ in summer and autumn, which may be due to lower chloride concentration levels. Correlation between nitrates and chlorides were no significant in summer when the concentration levels of both pollutants were lower. Sulphates significantly correlated with $PM_{2.5}$ in spring, summer and winter, and nitrates in all seasons which may be due to the higher contribution of nitrate and sulphate mass to overall particle mass. More significant correlations were found between lead and chlorides, lead and nitrates in spring, summer and winter, and lead and $PM_{2.5}$, in winter indicated that the pollutants might be originated from the same sources. Significant higher correlations between manganese and $PM_{2.5}$, and manganese and chlorides, and manganese and nitrates, and manganese and lead, indicated that the pollutants might be originated from the same source, probably traffic. The lower correlation between cadmium and $PM_{2.5}$ in autumn, indicated that the cadmium might originate from separate source.

CONCLUSION

Concentration levels of all pollutants showed significant seasonal differences with high values during the winter period, except cadmium with high values in summer. The overall anion content median in high-risk particle fraction amounted to 19%, ranging from 12.4% during spring to 29.7% during winter period. The overall metal content median in high-risk particle fraction was 0.22%, ranging from 0.16% in spring to 0.30% in autumn period. The most abundant species contributing to the $PM_{2.5}$ mass were: sulphates, nitrates, chlorides, lead, manganese and cadmium, in decreasing order of contribution.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

DEPOSITION OF ACIDIC COMPONENTS AND HEAVY METALS IN ZAGREB IN 1999-2001

J Hršak*, M Čačković, N Kalinić and I Balagović

ABSTRACT

Monthly samples of atmospheric depositions were collected over three years (1999-2001) at five different sites (city centre, northern, southern, western and eastern part of the city) in Zagreb using a Bergerhoff-type deposit gauge. After determining the total deposition, the samples were analysed for acidifying ions (Cl^-, NO_3^-, SO_4^{2-}) and heavy metals (Pb, Cd, Tl). Over the three years, total deposition varied from 18 to 518 mg/(m^{2}d), chloride content from 0 to 20.42 mg/(m^{2}d), nitrate from 0 to 10.66 mg/(m^{2}d) and sulphate from 1.00 to 20.24 mg/(m^{2}d). Lead varied from 9 to 93 μg/m^{2}d, cadmium from 0.13 to 13.72 μg/m^{2}d and thallium from 0 to 12.86 μg/m^{2}d. No correlation between acidifying ion and heavy metal content has been found. It is assumed that the deposition includes other components, such as sodium, potassium, calcium, ammonia etc., which were not measured. Croatian legislation (Ordinance, 1996) defines recommended and limit values for monthly lead, cadmium, and thallium content in deposited matter. Lead and cadmium content in deposited matter were below the recommended values at all five sampling sites. Thallium content was above the recommended value, but under the limit value at four sampling sites, and below the recommended value at one sampling site (eastern part of the city).

INDEX TERMS

Acidifying ions, Heavy metals, Total deposited matter, Recommended value, Limit value

INTRODUCTION

Deposited matter are solid or liquid particulates in the atmosphere which settle on the ground and contaminate soil, plants and materials, but do not affect people

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and animals directly. It is very important to know the quantity of deposition, especially the content of toxic substances such as acidifying ions and heavy metals lead, cadmium and thallium.

MATERIAL AND METHODS

Monthly samples of deposited matter were collected from 1999 to 2001 at five sites in Zagreb (city centre, northern part, eastern part, western part and southern part) - Figure 1, using the Bergerhoff type deposit gauge (VDI, 1972).
The samples were analysed for acidifying ions (Cl^-, NO_3^-, SO_4^{2-}) using an Ion chromatographer (Dionex DX-120) and for heavy metals (Pb, Cd, Tl) using a flame atomic absorption spectrometer (SOLAAR 969 AAS).

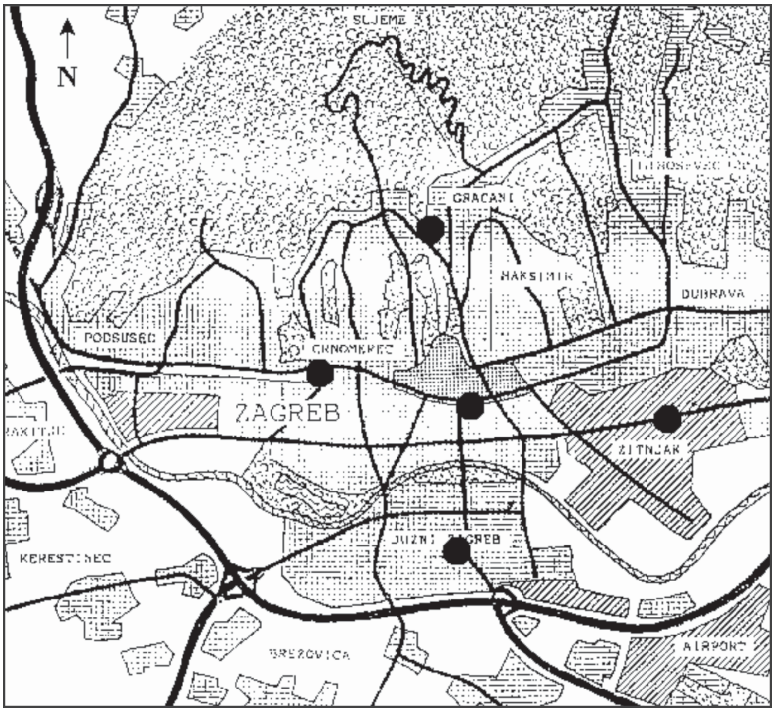

Figure 1. Sampling sites

RESULTS AND DISCUSSION

Overall monthly values of total deposited matter (TDM) ranged from 18 to 518 mg/(m^2d) during the entire measuring period and at all sampling sites. Annual values are shown in Figure 2. They kept below the recommended value defined by the Croatian Ordinance on Recommended and Limit Air Quality Values /200 mg/(m^2d)/ (Ordinance, 1996).

Overall monthly chlorides in total deposited matter (TDM) ranged from 0 to 20.42 mg/(m^{2}d) Annual values are shown in Figure 3. The Croatian Ordinance does not define recommended or limit values for chlorides.
Monthly nitrates in total deposited matter (TDM) for the period 1999-2001 ranged from 0 to 10.66 mg/(m^{2}d). Annual values are shown in Figure 4. The Croatian Ordinance does not define recommended or limit values for nitrates in TDM.
Monthly sulphates in total deposited matter (TDM) for the period 1999-2001 ranged from 1.00 to 20.24 mg/(m^{2}d). Annual values are shown in Figure 5. The Croatian Ordinance does not define recommended or limit values for sulphates.
Overall monthly lead content in total deposited matter ranged from 9 to 23 μg/m^{2}d. Annual values are shown in Figure 6. All results were below the recommended value (100 μg/m^{2}d).
Overall monthly cadmium content in total deposited matter for the same period ranged from 0.13 to 13.72 μg/m^{2}d. Annual values are shown in Figure 7 and they were below the recommended value (2μg/m^{2}d).
Overall monthly thallium content in total deposited matter ranged from 0 to 12.86 μg/m^{2}d. Annual values are shown in Figure 8 and in 1999 they kept below the recommended value (2μg/m^{2}d) except for the city centre (). In 2000, annual values did not exceed the recommended value at any site, but they rise above the recommended value in 2001, keeping, however, below the limit value set by the Ordinance.

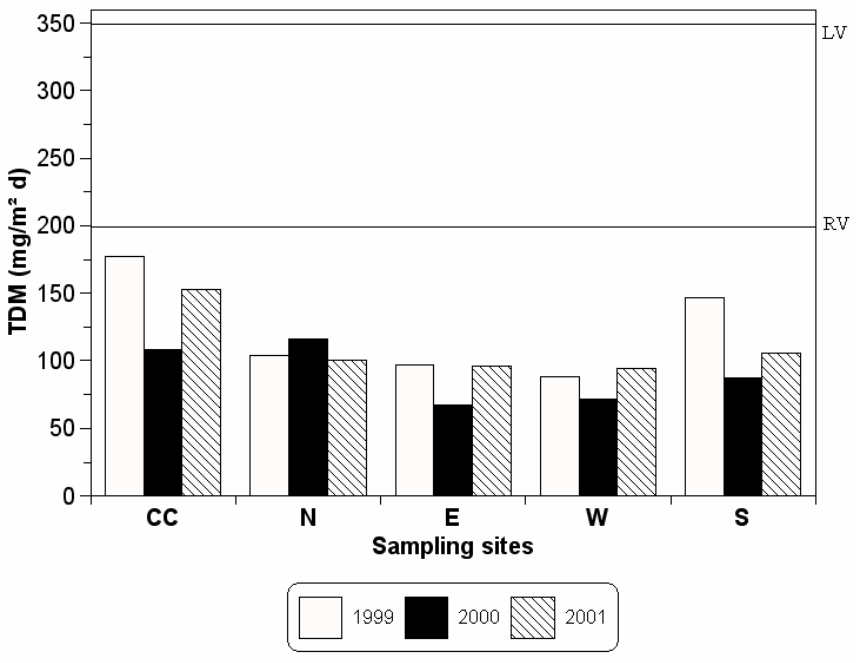

Figure 2. Annual values of total deposited matter in Zagreb from 1999 to 2001

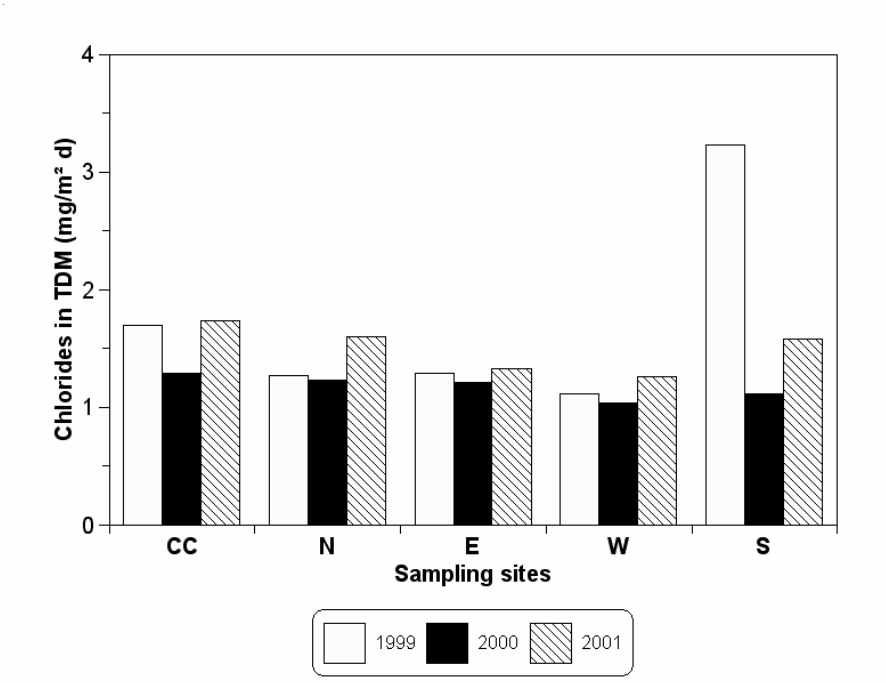

Figure 3. Annual values of chlorides in TDM in Zagreb from 1999 to 2001

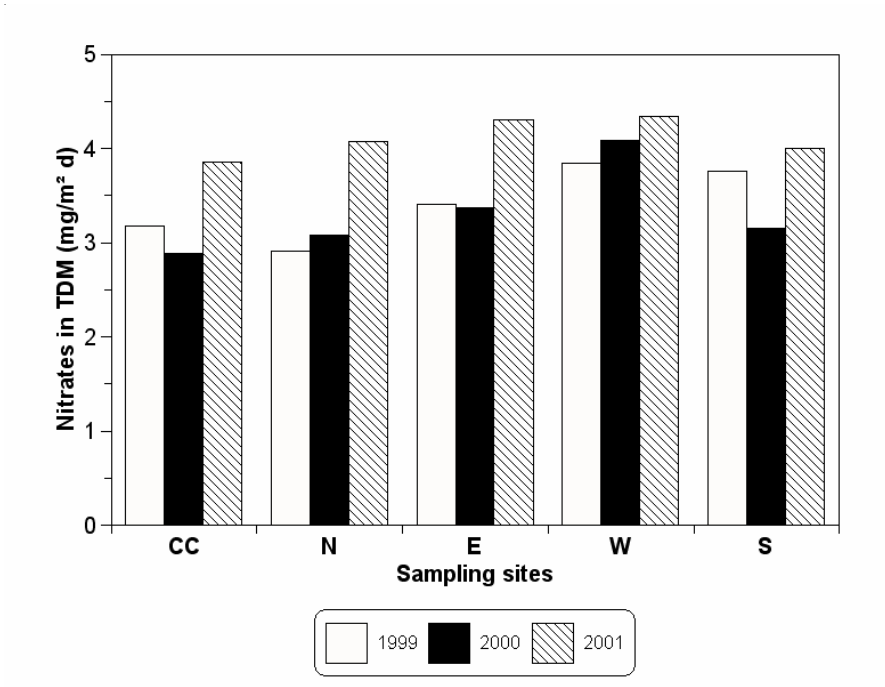

Figure 4. Annual values of nitrates in TDM in Zagreb from 1999 to 2001

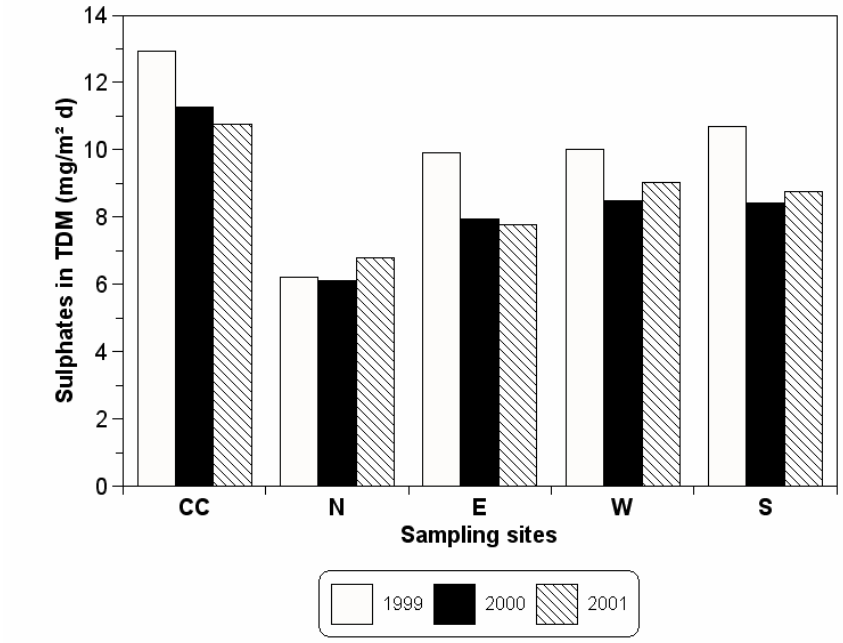

Figure 5. Annual values of sulphates in TDM in Zagreb from 1999 to 2001

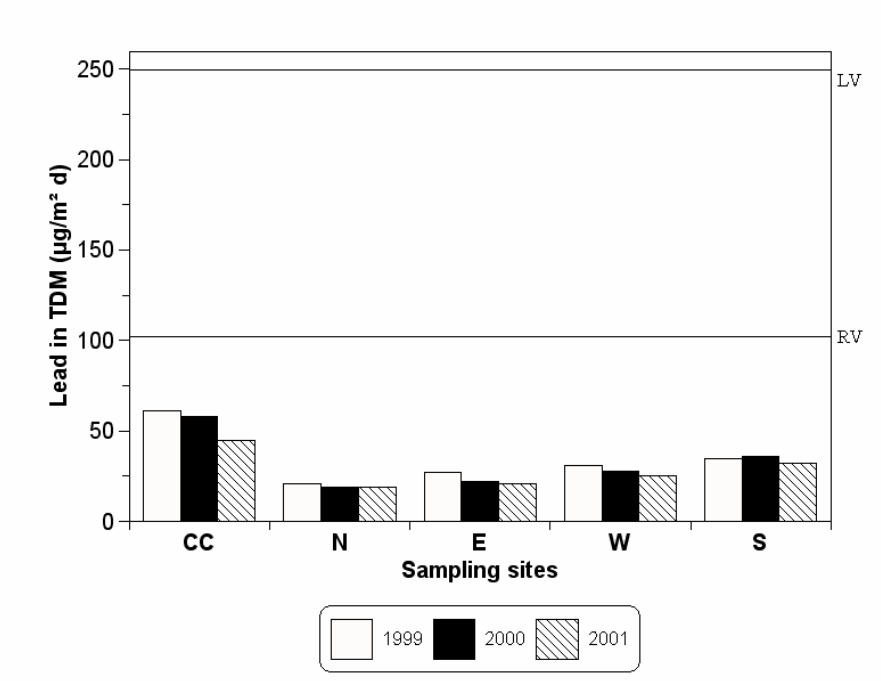

Figure 6. Annual values of lead in TDM in Zagreb from 1999 to 2001

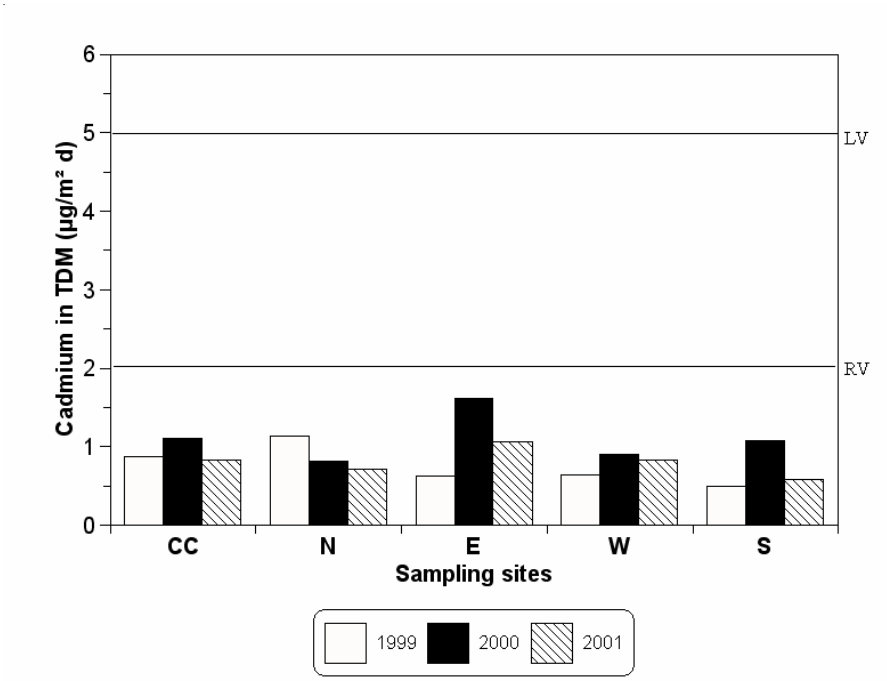

Figure 7. Annual values of cadmium in TDM in Zagreb from 1999 to 2001

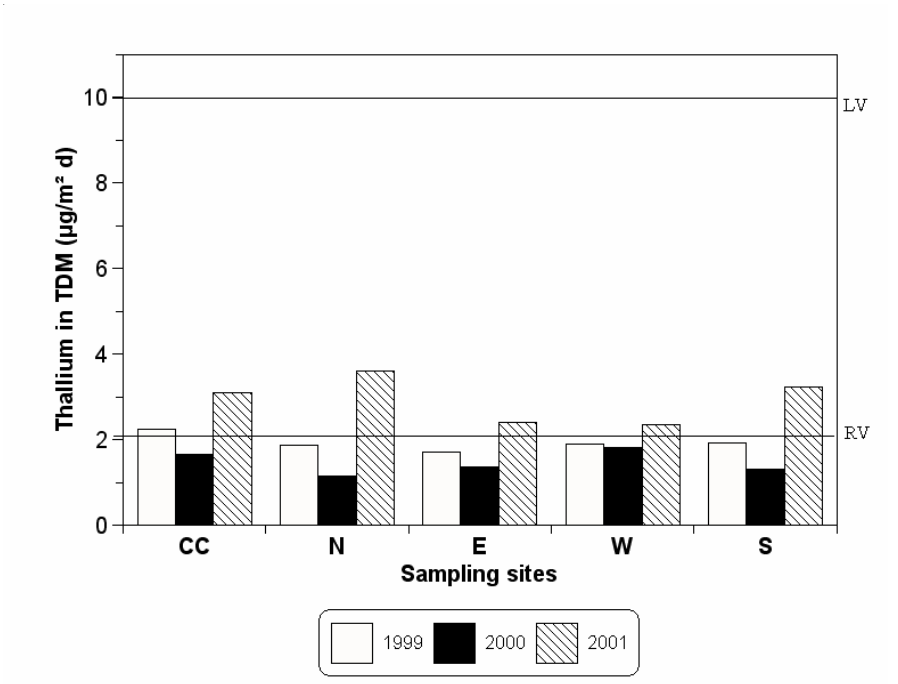

Figure 8. Annual values of thallium in TDM in Zagreb from 1999 to 2001

CONCLUSION

During the three-year period of measuring, the total deposited matter at all measuring sites was relatively low, below the recommended value. Acidifying ions (Cl^-, NO_3^-,SO_4^{2-}) were relatively high, but for them there are no recommended or limit values according to the Ordinance.

Lead and cadmium content in total deposited matter for three-year measuring period at all sampling sites was low and below the recommended value (100 $\mu g/m^2d$ for lead and 2 $\mu g/m^2d$ for cadmium). Thallium content in total deposited matter was below the recommended value (2 $\mu g/m^2d$) in 1999 except in the city centre, it was also below the recommended value in 2000 and above it in 2001 at five sampling sites.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

TOTAL BETA ACTIVITY IN THE AIR AND WET FALLOUT IN RELATION WITH SUSPENDED PARTICULATE MATTER CONCENTRATIONS

G Marović*, J Senčar, K Šega and I Bešlić

ABSTRACT

Within the scope of systematic investigations of the environment, the Radiation Protection Unit and Environmental Hygiene Unit of the Institute for Medical Research and Occupational Health in Zagreb have been conducting measurement of total beta activity in the air in the samples of rain and snow (wet fallout), as well as measurement and analysis of suspended particulate matter in the air. The samples of the atmosphere were analysed for the amount of suspended particulate matter fractions ($PM_{2.5}$ and PM_{10}) in the air. The samples were collected on a daily basis over the period of three years (from the year 2000 to 2002), at the location of the Institute. The results of total beta activity in the air showed good agreement with suspended particulate matter concentrations (best with $PM_{2.5}$). The results of total beta activity in the fallout showed good agreement with suspended particulate matter concentrations, too. Special concern was given to the possible relationship between total beta activity and suspended particulate matter concentrations in the days before and after the rain. This agreement was obvious during longer continuous wet-fallout period.

INDEX TERMS

Air pollution, radioactive matter, total beta radioactivity in the air and in fallout, suspended particulate matter

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INTRODUCTION

Radioactive matters are generally a component of the atmosphere. Radionuclides contained in the air are mainly of natural origin, either terrestrial or cosmogenic, but man-made sources are responsible for an increasing release of radionuclide amounts of fission origin to the atmosphere. After release to the atmosphere, radionuclides undergo downwind transport and mixing processes (turbulent diffusion) and eventually reach ground level where they are assessed and measured. Nuclear weapon tests from the early 1960-es have still remained most significant sources of radioactive matter discharged into the atmosphere. The Chernobyl accident caused an increase in radioactive matter in the air only in 1986, and in the following years its levels returned to the values measured over the previous years (Franić et al. 1997).

Survey and assessment of radioactivity in the air started in Croatia in 1961 and has been continued ever since, as part of an extended monitoring programme conducted by the Radiation Protection Unit of the Institute for Medical Research and Occupational Health in Zagreb. The total level of radioactive matter in the air is determined by measuring total beta activity in the air and in fallout, radiochemical analyses of selected radionuclides as well as alpha, beta and gamma spectrometric analyses. The total beta activity serves only as an initial indication of the presence of radioactivity in an analysed sample, whereas a specific radionuclide can be identified by utilization of specific radiochemical methods. Any increase in beta activity in the samples of air and fallout requires additional specific measurements and analyses aimed to determine the cause of increase in order to enable as precise as possible, determination of the dose received by the Croatian population and possible effects of ionizing radiation to human health.

Radioactive contaminants contained in the ambient air represent only a fraction of total air pollution and eventually possible human exposure. Whereas continuous monitoring of air pollution in Croatia started in the sixties, measurements of suspended particulate matter levels and heavy metals started in 1972, at first in Zagreb and later in other Croatian towns. Long-term surveys have revealed difficulties posed by collecting total suspended particulate matter when the upper limit of a particle size was in most cases undefined, and pointed to a need for precise definition of particulate matter fractions (Šega, 1999).

The paper presents results on the relation between total beta activity in air and fallout and suspended particulate matter concentrations, in order to provide a valuable data base for determination of possible health effects in Croatian population.

MATERIAL AND METHODS

Continuous air sampling, the daily volume ranging from 100 to 200 m^3, daily collected 1 m above the ground, has been carried out at the location of the Institute

for Medical Research and Occupational Health (45°50' N, 15°59' E). Air is pumped through the Schneider & Poelman filter paper (blue). In order to allow the decay of short-lived beta radionuclides the activity is measured after 120 h by a low level anti-coincidence, shielded beta counter.
Fallout samples were collected daily at the location of the Institute. The funnels used for fallout collection had 1m^2 area. The precipitation amount was measured by Hellman pluviometer.
Separation of suspended particulate matter of greater diameter size and collection of those with equivalent aerodynamic diameter less than 10 μm (PM_{10}) and less than 2.5 μm ($PM_{2.5}$) was carried out using an inertial impactor. Continuous air sampling was provided by means of Low Volume Sampler (LVS3) produced by Ingenieurburo Sven Leckel certified by CE marks EN 12341. Air (the daily volume about 55 m^3) is pumped through the glass-fiber filter (Wathman EPM 2000) diameter 47 mm.

DISCUSSION

The data presented in the paper show total beta activity in the air and fallout and determined suspended particulate matter concentrations, obtained during 2000, 2001 and 2002 by continuous daily measurement at the location of the Institute (Marović et al., 2001; Marović et al., 2003). Summary results are given in Figure 1. Results were statistically processed in order to determine functional correlation of total beta activity in the air and suspended particulate matter. The same was performed for total beta activity in fallout for the days when these data were available. Obtained correlations for the investigated period are shown in Tables 1-6 (y = kx + l; r-correlation coefficient). Table 1 shows correlations of total beta activity in the air and suspended particulate matter concentrations in the period 2000-2003.

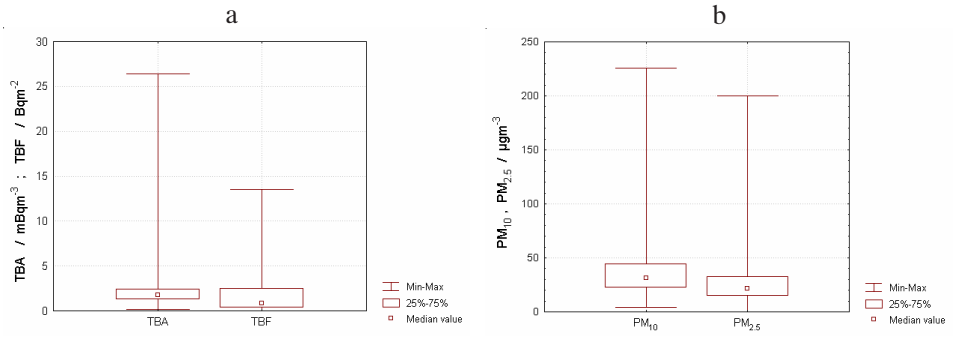

Figure 1. a) Total beta-activity in the air (TBA/mBqm^{-3}) and total beta activity in fallout (TBF /Bqm^{-2}) for the period 2000-2003; b) Suspended particulate matter concentrations (P_{10} and $PM_{2.5}$ / μgm^{-3}) for the period 2000-2003

Table 1. Correlations between total beta activity in the air (TBA / $mBqm^{-3}$) and suspended particulate matter concentrations (PM_{10} and $PM_{2.5}$ / $\mu g/m^{-3}$)

X / Y	N	r	p	k	l
PM_{10} / TBA	1089	0.4329	< 0.001	0.0261	0.9884
$PM_{2.5}$ / TBA	1089	0.4356	< 0.001	0.0293	1.1498

In the observed period (2000-2002) there were 319 rainy days and 770 days without wet fallout. Table 2 gives correlations of total beta-activity in the air and suspended particulate matter concentrations for the days without fallout.

Table 2. Correlations between total beta activity in the air (TBA / $mBqm^{-3}$) and suspended particulate matter concentrations (PM_{10} and $PM_{2.5}$ / $\mu g/m^{-3}$) in days without wet fallout

X / Y	N	r	p	k	l
PM_{10} / TBA	770	0.4515	< 0.0001	0.0282	0.9310
$PM_{2.5}$ / TBA	770	0.4618	< 0.0001	0.0328	1.1030

The days without wet fallout were separated into three subgroups: days preceding a day of wet fallout, days following a day of wet fallout and the rest of the days without wet fallout. Table 3 gives correlations of total beta activity in the air and suspended particulate matter concentrations for the 483 days with no fallout, 120 days preceding a day of wet fallout and 167 days following a day of fallout. The days following a day of wet fallout (167) were separated in the days following a day of fallout (116) and the single days without fallout, interpolated between days with fallout. Table 4 gives correlations of total beta activity in the air and suspended particulate matter concentrations for this days.

Table 3. Correlations between total beta activity in the air (TBA / $mBqm^{-3}$) and suspended particulate matter concentrations (PM_{10} and $PM_{2.5}$ / $\mu g/m^{-3}$) in days with no fallout (483), days preceding a day of fallout (120) and days following a day of fallout (167)

X / Y	N	r	p	k	l
PM_{10} / TBA	483	0.4590	< 0.0001	0.0300	0.9608
$PM_{2.5}$ / TBA	483	0.4720	< 0.0001	0.0350	1.1464
PM_{10} / TBA	120	0.3342	0.0002	0.0189	1.2984
$PM_{2.5}$ / TBA	120	0.3616	< 0.0001	0.0221	1.4152
PM_{10} / TBA	167	0.2086	0.0068	0.0104	1.1728
$PM_{2.5}$ / TBA	167	0.2273	0.0031	0.0129	1.2065

Table 4. Correlations between total beta activity in the air (TBA / $mBqm^{-3}$) and suspended particulate matter concentrations (PM_{10} and $PM_{2.5}$ / $\mu g/m^{-3}$) in days following a day of fallout (116) and single days interpolated between days with fallout (51)

X / Y	N	r	p	k	l
PM_{10} / TBA	116	0.3656	< 0.0001	0.0187	0.9554
$PM_{2.5}$ / TBA	116	0.3882	< 0.0001	0.0226	1.0225
PM_{10} / TBA	51	-0.1796	0.2072∗	-0.0083	1.6314
$PM_{2.5}$ / TBA	51	-0.1727	0.2254∗	-0.0091	1.5736

∗ p> 0.05 (correlation is not significant)

The best agreement was determined between the total beta activity in the air and $PM_{2.5}$ in days with no wet fallout (483). In the observed period (2000-2002) there was only 319 rainy days. Table 5 gives correlations of precipitation amount and total beta activity in the air and suspended particulate matter concentrations. Table 6 gives correlations of total beta activity in the air and suspended particulate matter concentrations and between total beta activity in the fallout and suspended particulate matter concentrations in days with wet fallout.

Table 5. Correlations between precipitation amount (Lm^{-2}) and suspended particulate matter concentrations (PM_{10} and $PM_{2.5}$ in $\mu g/m^{-3}$) and between precipitation amount and total beta activity in the air (TBA / $mBqm^{-3}$)

X / Y	N	r	p	K	l
Fallout / PM_{10}	1089	-0.2351	< 0.0001	-0.9050	39.3158
Fallout / $PM_{2.5}$	1089	-0.1882	< 0.0001	-0.6475	29.0262
Fallout / TBA	1089	-0.0995	< 0.001	-0.0231	2.0118

Table 6. Correlations between total beta activity in the air (TBA/$mBqm^{-3}$) and suspended particulate matter concentrations (PM_{10} and $PM_{2.5}$ in $\mu g/m^{-3}$) and between total beta activity in the fallout (TBF/Bqm^{-2}) and PM_{10} and $PM_{2.5}$ in $\mu g/m^{-3}$ in days with wet fallout

X / Y	N	r	p	K	l
PM_{10} / TBA	318	0.1949	0.0005	0.0114	1.3120
$PM_{2.5}$ / TBA	318	0.2239	< 0.0001	0.0126	1.3604
PM_{10} / TBF	318	-0.1555	0.0054	-0.0207	2.3831
$PM_{2.5}$ / TBF	318	-0.1064	0.0582∗	-0.0137	2.1016

∗ p> 0.05 (correlation is not significant)

Table 1, 2, 3, 4 and 6 show correlations between total beta activity in the air and suspended particulate matter concentrations in dependence of fallout. A distinction was made between the days with wet fallout, the days with no fallout, the days immediately preceding fallout and days after fallout (number of continuous rainy days was to small to be also taken into account). Correlations between total beta activity in the air and suspended particulate matter concentrations $PM_{2.5}$ was higher than between total beta activity in the air and suspended particulate matter concentrations PM_{10}. The highest agreement of data for total beta activity in the air and suspended particulate matter concentrations was determined for suspended particulate matter of equivalent aerodynamic diameter below 2.5 μm in the days without precipitation (483 days they excluded days preceding a day of fallout and days following a day of fallout). Future studies should include meteorological parameters to give more information about this correlation. Figure 2 illustrates histograms of total beta activity in the air and suspended particulate matter $PM_{2.5}$ and their interdependence ("scatter" diagram).

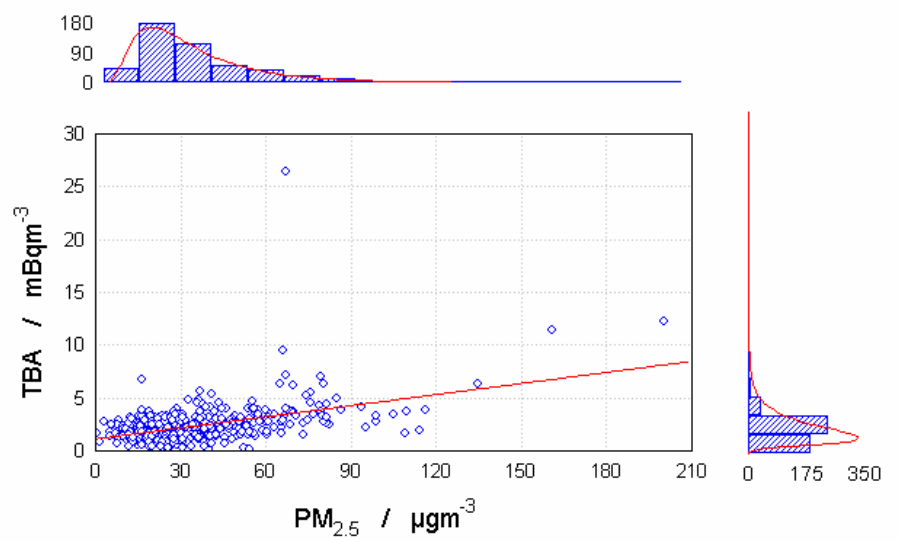

Figure 2. Scatterplot with histograms of total beta activity in the air and suspended particulate matter concentration $PM_{2.5}$

Higher correspondence of data were observed for correlations of precipitation amount and suspended particulate matter concentrations analysed for the whole period of investigation (Table 5). High agreement was determined between the total beta activity in the fallout and suspended particulate matter PM_{10} (319 days with wet fallout). Figure 3 illustrates histograms of TBF and PM_{10} and their interdependence ("scatter" diagram).

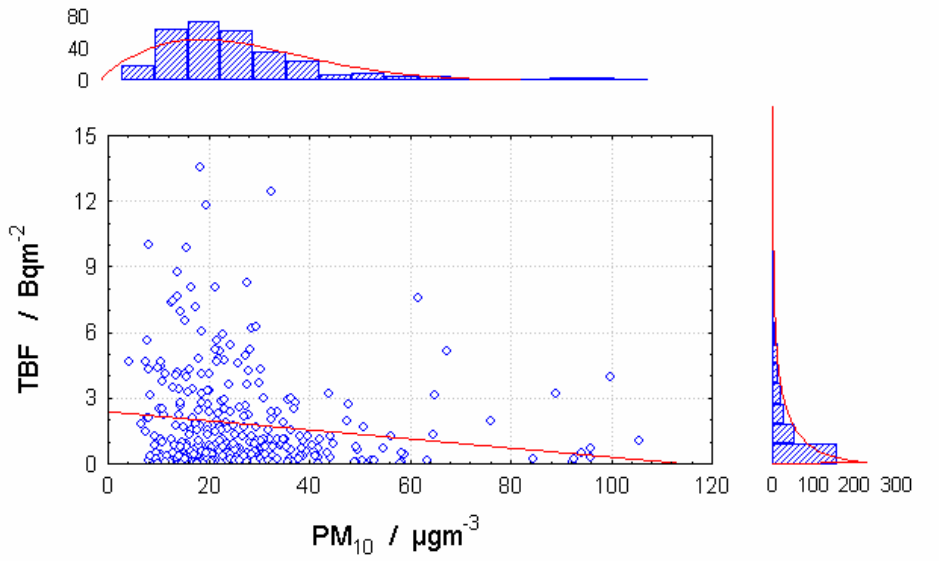

Figure 3. Scatterplot with histograms of total beta activity in the fallout and suspended particulate matter concentration PM_{10}

CONCLUSION

Preliminary investigations described in the paper showed mutual dependence of total beta activity in the air and fallout, and suspended particulate matter concentrations. On the basis of data presented it could be concluded that stronger relationships exist between total beta activity in the air and suspended particulates of smaller equivalent aerodynamic diameter, as well as between total beta activity in the fallout and suspended particulates of greater equivalent aerodynamic diameter. Agreement of the results for total beta activity in the fallout and suspended particulate matter concentrations could lead to modelling of contribution of ionising radioactive matter in suspended particulate matter concentrations due to their transfer from the atmosphere through fallout. Future studies should give more information about the possible relation between sampling and meteorological parameters, as well as means of their optimal correspondence in order to enable modelling and determination of patterns characteristic of the investigated area.

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The 14th International Conference
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Dubrovnik, CROATIA 6-10 October 2003

SEASONAL VARIATION OF AIRBORNE MOULDS IN CONTINENTAL AND MEDITERRANEAN PARTS OF CROATIA (2002)

S Pepeljnjak and M Šegvić*

ABSTRACT

Many aeromycological studies showed the presence of airspora of different allergologicaly important fungi in the air of indoor and outdoor environment. The airspora concentrations of outdoor environments depend on numerous factors including; time of day, meteorological factors, seasonal climatic factors, and type of vegetation. The aim of our study was to determine seasonal variations of the common airborne fungi, as potential allergens, of the outdoor environment in Continental and Mediterranean parts of Croatia. Samples were collected bimonthly during: February and March, April and May, June and July. In addition, sampling was done in the area of Velebit during June. Method employed in this study was exposure of Sabouraud agar plates (diameter 9 cm) to air for 1 hour, and total of 500 samples were collected. Results, expressed as CFU/h/plate, were statistically analysed by a one-way analysis of variance (repeated measures ANOVA) followed by a multiple comparison procedure (Bonferroni test). Probability values less than 0,05 ($P<0,05$) were considered significant. Higher levels of airspora were detected in June and July, with significantly higher concentration in Continental parts (43,64 CFU/h/plate), than in Primorje (25,66 CFU/h/plate) and Dalmacija (5,9 CFU/h/plate) ($P<0,001$). Lower airspora concentrations were found during April and May; in Continental part (8,18 CFU/h/plate) and Dalmacija (6,9 CFU/h/plate), these were without significant difference, and significantly lower in Primorje (3,3 CFU/h/plate) ($P<0,001$). In June, in the Velebit area, significantly lower airspora concentrations were found (18,36 CFU/h/plate), compared to those in Continental parts and Primorje

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(P<0,05), but higher than those in Dalmacija (P<0,001). In this study airspora belonging to 26 fungal genera were identified, and *Cladosporium*, *Alternaria* and *Penicillium* species dominated in all sampling sites, but with significantly higher concentrations in Continental parts (P<0,05).

INDEX TERMS

Airspora, Allergens, Moulds, Croatia, Velebit

INTRODUCTION

Fungi from a wide variety of genera have a great capacity to colonise many kinds of substrata and develop in extreme environmental conditions, on soils, plants and animal remains (Comtois, 1990). Spores from these fungi are usually airborne. The airspora concentrations of outdoor environments depend on numerous factors including; time of day, meteorological factors, seasonal climatic factors, and type of vegetation (D'Amato et al, 1984). Airspora of several species of moulds are known to induce numerous human diseases such as chronic bronchitis, asthma, fungal allergies, hypersensitivity pneumonitis and aspergillosis. Fungal allergens are found primarily in the spores, but they are also occurring in other structures, e.g. mycelia and material secreted into the environment (Horner et al., 1995). Since distribution of airborne micromycetes depends on seasonal climatic factors, the aim of this study was to determine seasonal variations of the common airborne fungi, as potential allergens, of the outdoor environment in Continental and Mediterranean parts of Croatia.

METHODS

Sampling area

Samples were collected from three geographical parts in Croatia; Modest continental climate, including Zagreb, Varaždin, Međimurje, Slavonija; Mediterranean climate North part of Adriatic coast (Primorje), including Opatija Rijeka Krk; and South Croatia (Dalmacija), including Split, Šibenik, and Zadar. Samples were collected bimonthly during: February and March, April and May, June and July. In addition, sampling was done in the area of Velebit during June (height above 1000 m). A total of 50 samples were collected in each sampling field, for each period ($\Sigma N=500$).

Sampling, isolation methods and identification

The Petri plate gravitational method was used for the isolation of airborne moulds. Sabouraud agar plates (diameter 9 cm) with antibiotic streptomycin (50 mg/L) were used as collecting media. Open plates were exposed to air for 1 hour. The plates were held at 70 cm-1,2 m. Plates were incubated on 25° C for 4-7 days and

colony forming units (CFU) in 1 h/plate were counted. Fungal species were reisolated on different agar plates (Czapek, Malt, Potato-dextrose agar) for characterisation and determination of fructification organs in accordance with keys (Raper and Thom, 1949; Booth 1971; Samson et al., 1981; De Hoog et al., 2000). Meteorological data (relative humidity and temperature) were collected from Hydrometerological Department in Zagreb (Croatia).

Statistical analysis

Results, expressed as CFU/h/plate, were statistically analysed by a one-way analysis of variance (repeated measures ANOVA) followed by a multiple comparison procedure (Bonferroni test). Correlations between CFU/h/plate and meteorological parameters were tested by using Spearman rank Correlation. Probability values less than 0,05 ($P<0,05$) were considered significant.

RESULTS

Bimonthly mean concentrations and standard deviation of airborne moulds in Continental and Mediterranean parts of Croatia (2002) are represented in Figure 1., in relation to temperature and relative humidity (Figure 2). Highest peak of airborne fungi was recorded in June and July. These concentrations were significantly higher in Continental parts (43,64 CFU/h/plate) compared to levels of airborne fungi in Primorje (25,66 CFU/h/plate), Velebit (18,36 CFU/h/plate) and Dalmacija (5,9 CFU/h/plate) ($P<0,001$). Lower concentrations were observed during April and May, and these were similar in Continent (8,18 CFU/h/plate) and Dalmacija (6,9 CFU/h/plate) ($P>0,05$), but significantly higher compared to those in Primorje (3,3 CFU/h/plate) ($P<0,001$). In February-March very high concentrations were found only in Continent (24 CFU/h/plate), while the peaks in Primorje (7,66 CFU/h/plate) and Dalmacija (6,28 CFU/h/plate) were similar and much lower ($P<0,001$). Comparing bimonthly peaks of airborne fungi for each sampling area, significant difference was found for Continental parts and Primorje. In Continent concentrations were significantly higher in February-March and June-July, than during April-May ($P<0,001$); concentrations in Primorje were similar during February-March and April-May ($P>0,05$), but significantly higher in June-July; in Dalmacija the concentrations were more or less the same during all periods ($P>0,05$). Significant correlation was not found between meteorological parameters and levels of airborne fungi ($P>0,05$).

Total of 25 fungal genera and non-sporulating sterile mycelium were identified (Table 1). *Cladosporium,* followed by *Alternaria* and *Penicillium* dominated the air mycoflora from all sampling areas. Significantly higher concentrations of cladosporia were recorded during February-March and June-July in Continent (32,18 CFU/h/plate) than in other parts of Croatia ($P<0,01$). In April-May these peaks were higher in Primorje (4,60 CFU/h/plate), compared to Continent (2,96 CFU/h/plate), and Dalmacija (1,74 CFU/h/plate) ($P<0,05$). In Velebit area (12,5

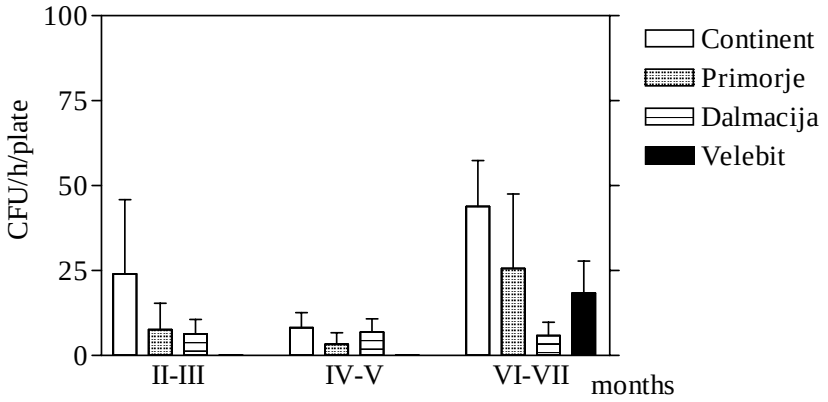

Figure 1. Concentrations of airborne moulds in Continental and Mediterranean parts in Croatia through the year 2002

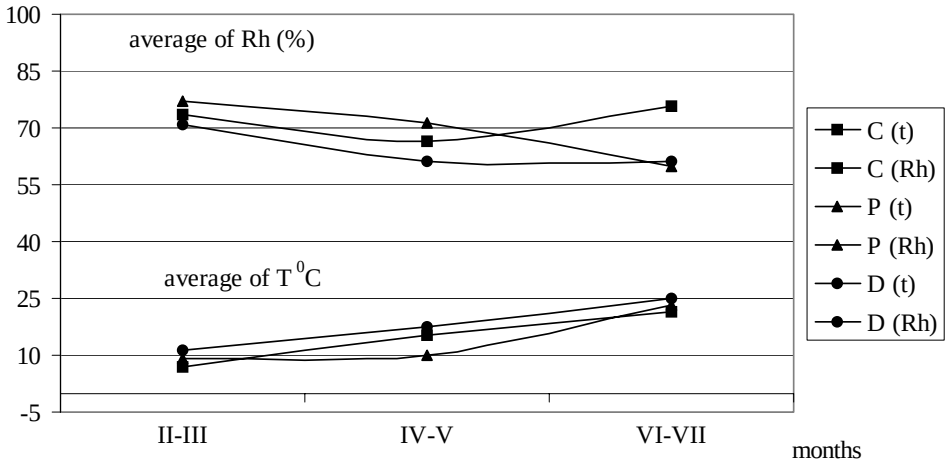

Figure 2. Averages of temerature (T°C) and relative humidity (%) in Continental and Mediterranean parts of Croatia (2002)

CFU/h/plate), and Dalmacija (0,84 CFU/h/plate), during June-July, airborne cladosporia levels were significantly lower then in Primorje (22,16 CFU/h/plate) ($P<0,01$). Highest peaks of *Alternaria* were found during June-July, especially in Continent (3,28 CFU/h/plate), than in other areas ($P<0,01$). These concentrations were similar in Dalmacija (1,34 CFU/h/plate) and Velebit (1,24 CFU/h/plate), and significantly lower in Primorje (0,44 CFU/h/plate). During February-March higher levels were found in Continent (1,60 CFU/h/plate), and during April-May in Dalmacija (1,46 CFU/h/plate) ($P<0,01$). Higher peaks of *Penicillium* were recorded in Continent (1,08-4,14 CFU/h/plate) during all periods, while in other areas concentrations of penicillia were lower than 1 CFU/h/plate ($P<0,01$).

Table 1. Occurrence of airborne fungi in Continental (C) and Mediterranean (P, D) parts and Velebit (V) (2002)

FUNGI	February-March CFU/h/plate			April-May CFU/h/plate			June-July CFU/h/plate			
	C	P	D	D	P	D	C	P	D	V
Absidia	0,04	0,22	-	0,02	0,06	0,06	0,08	0,04	0,04	0,04
Acremonium	-	0,02	-	-	-	-	0,04	-	0,04	0,02
Alternaria	1,6	0,68	0,18	0,56	0,26	1,46	3,28	0,44	1,34	1,25
Aspergillus (total)	0,14	0,16	-	0,08	0,02	0,18	0,18	-	0,78	0,1
A. clavatus	-	-		-	-	-	0,04		-	-
A. flavus	-	-		-	-	-	0,1		0,06	0,02
A. fumigatus	-	-		-	-	-	-		0,18	-
A. glaucus	0,02	-		-	-	-	-		-	-
A. niger	0,1	0,16		0,06	-	0,18	-		0,48	0,08
A. ochraceus	-	-		-	-	-	0,04		-	-
A. sulphureus	-	-		-	-	-	-		0,06	-
A. terreus	0,02	-		-	0,02	-	-		-	-
A. versicolor	-	-		0,02	-	-	-		-	-
Auerobasidium	-	-	-	-	0,04	0,04	-	-	-	-
Bipolaris	-	-	-	-	-	-	-	-	0,16	-
Botrytis	0,1	0,12	-	-	-	0,08	-	0,04	-	-
Chaetomium	-	-	-	-	-	-	-	-	-	0,02
Chrysosporium	1,54	0,58	0,3	0,26	0,3	0,26	0,08	0,2	0,24	-
Cladophora	-	-	-	-	0,02	-	-	-	-	-
Cladosporium	14,57	3,96	1,4	2,96	4,6	1,74	32,18	22,16	0,84	12,5
Culvularia	-	-	-	-	-	-	0,08	-	0,08	0,02
Fusarium	0,14	0,32	0,12	0,2	0,18	0,1	2,46	0,42	0,86	1,3
Geotrichum	-	-	-	-	0,02	0,06	-	-	-	-
Gliocladium	-	-	-	0,06	-	-	-	0,02	-	0,02
Mucor	0,08	0,16	-	0,08	0,02	0,02	0,06	0,04	0,04	0,02
Paecilomyces	0,04	-	-	0,08	-	0,02	0,1	0,08	0,08	-
Penicillium	1,08	0,62	0,14	1,68	0,26	0,46	4,14	0,08	0,18	0,34
Phoma	0,26	0,2	0,1	0,14	0,14	0,1	0,02	0,04	0,06	0,06
Pithomyces	0,58	0,1	-	0,1	0,04	0,1	0,12	0,06	0,04	0,02
Rhizopus	-	0,06	-	-	-	0,02	0,02	0,02	0,04	0,02
Sclerotium	-	-	0,04	-	-	-	0,04	0,12	0,06	0,02
Scytalidium	1,7	-	-	-	0,84	0,16	0,04	0,02	-	-
Sterile mycelia	1,54	0,3	0,32	0,28	0,56	1,22	-	0,92	0,72	1,36
Trichoderma	-	0,04	0,02	-	-	0,04	0,14	0,14	0,04	0,02
Ulocladium	0,32	0,04	0,06	0,08	0,1	0,12	0,14	0,42	0,02	0,16
Other moulds	0,3	0,6	0,62	0,32	0,2	0,04	0,44	0,4	0,2	0,52

"-" not detected"

Among other fungi, higher peaks of *Fusarium* were found in Continent and Velebit during June-July; *Chrysosporium* and *Scitalydium* in Continent during February-March. Sterile mycelium concentrations varied; in February-March it was higher in Continent, while in other months increased in Primorje, Dalmacija, and Velebit. Other fungi, including *Aspergillus*, were present in concentrations lower than 1 CFU/h/plate.

DISCUSSION

Significant increase of airborne fungi was recorded in late spring and summer in Continental parts and Primorje. These results correspond to earlier studies of outdoor air mycoflora in Croatia (Cvetnić and Pepeljnjak, 1997; Pepeljnjak and Šegvić, 2003). The increase of airborne fungi was significantly higher in Continent compared to Primorje, Dalmacija and Velebit. During this period similar concentrations were observed in Primorje and Velebit, even the sampling in Velebit area was done above 1000 m height, and we expected lower levels of airborne fungi. These findings must be due to a strong south wind during sampling time. Mycoflora monitoring in Dalmacija showed similarity, while in Continent and Primorje significant variations in concentration were found. Lower relative humidity and higher temperature in Dalmacija can be one of reasons for reduced concentrations of airborne fungi. These findings are similar to our earlier study conducted in 1998 (Pepeljnjak and Šegvić, 2003). The dominant fungi contributing to such a difference were allergologicly important species; *Cladosporium, Alternaria* and *Penicillium*. Similar results were obtained in surveys described in Croatia and other European countries (Italy, Spain, Turkey) (Asan et al., 2002; Herrero, 1997; Marchiso and Airaudi, 2001). Qualitatively, airborne mycoflora of all three parts presented 6 constant (*Alternaria, Cladosporium, Fusarium, Penicillium, Phoma, Ulocladium*), 11 common (*Absidia, Aspergillus, Chrysosporium, Mucor, Paecilomyces, Pithomyces, Rhizopus, Sclerotium, Scitalydium*, sterile mycelium, *Trichoderma*), and 8 rare fungal species (*Acremonium, Auerobasidium, Bipolaris, Botrytis, Chaetomium, Cladophora, Geotrichum, Gliocladium*). Among constant fungi (except *Alternaria, Cladosporium* and *Penicillium*), *Fusarium* was found in higher concentration in Continent and Velebit during June-July. In group of common fungal species, *Chrysosporium* and *Scytalidium* were increased in winter months. The increase of non-sporing sterile mycelium in late spring and summer in Mediterranean parts may also indicate seasonal effects of mycoflora prevalence. In addition, the presence of plants, known to produce essential oils and aerosol which showed sporistatic, fungistatic, and fungicide activity (Pepeljnjak et al., 2001), can be one of reasons for reduced airspora and increased non-sporing moulds in the air of Mediterranean parts of Croatia.

CONCLUSIONS

In late spring and summer, concentrations of airborne fungi were significantly increased in Continent and Primorje. In Dalmacija, levels of airborne fungi were

more or less the same during winter, spring and summer. Seasonal and geographical variations of airborne fungi concentration were contributed by *Cladosporium*, *Alternaria* and *Penicillium*. Decreased concentration of airspora and increased non-sporing moulds in Mediterranean parts of Croatia, are probably due to a meteorological, seasonal climatic factors and type of vegetation, which includes plant species known to produce essential oils with sporistatic, fungistatic and fungicide activity. In addition, monitoring of allergologicaly significant airborne fungi can help us to predict variations in concentration depending on meteorological, geographical and seasonal climatic factors, which is of great importance for atopic patients.

ACKNOWLEDGEMENTS

The authors would like to express their gratitude to the Hydrometeorological Department in Zagreb for providing us meteorological data. This work was supported by Croatian ministry of Science and Technology (No. 0006641).

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

WINTER AND SUMMER PAH MASS CONCENTRATIONS – COMPARISON BETWEEN PM_{10} AND $PM_{2.5}$ PARTICLE FRACTION MEASUREMENTS

A Šišović[1,*], Ž Vadjić[2], K Šega[1], I Bešlić[1] and V Vadjić[1]

ABSTRACT

The aim of this investigation was to evaluate if there were statistically significant differences between PAH mass concentrations measured in inhalable or thoracic (PM_{10}) and respirable or high-risk ($PM_{2.5}$) particle fraction. Twenty-four hour air samples were collected at one site in the northern part of Zagreb, Croatia by low-volume PM_{10} and $PM_{2.5}$ samplers (50 m^3) for a period of 30 consecutive days in winter (January) and summer (July). Glass fibre filters were used to collect PM_{10} and $PM_{2.5}$ particle fractions. The analysis was performed by HPLC and fluorescent detector with changeable excitation and emission wavelength. Samples were analysed for the following PAHs: fluoranthene (Flu), pyrene (Pyr), benzo-b-fluoranthene (BbF), benzo-k-fluoranthene (BkF), benzo-a-pyrene (BaP) and benzo-ghi-perylene (BghiP). The average mass concentration of BaP measured in winter in PM_{10} was 3.039 ng/m^3 and in $PM_{2.5}$ 3.178 ng/m^3. BghiP had a higher average mass concentration than BaP. The average mass concentration of BghiP in PM_{10} in winter was 4.081 ng/m^3 and in $PM_{2.5}$ 4.099 ng/m^3. Although the average PM_{10} mass concentrations of all PAHs, except for winter BaP and BghiP, were slightly higher than $PM_{2.5}$ concentrations, the differences between all measured PAHs were not statistically significant. The average mass concentration of BaP measured in summer in PM_{10} was 0.048 ng/m^3 and in $PM_{2.5}$ 0.049 ng/m^3 and the average mass concentration of BghiP in PM_{10} was 0.147 ng/m^3 and in $PM_{2.5}$ 0.156 ng/m^3 respectively. The average summer mass concentrations of all PAHs in $PM_{2.5}$ were slightly higher, but the differences were not statistically significant. The results of

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measurements showed that all PAHs were present in respirable (high-risk) particle fractions, regardless of the season.

INDEX TERMS

Polycyclic aromatic hydrocarbons, Benzo-a-pyrene, Particle size distribution, Seasonal influence, Meteorological condition

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) widely distributed pollutants in the atmosphere are product of incomplete combustion of fossil fuels and other organic materials. Their sources include natural processes (forest fires and volcanic eruptions) and antropogenic emissions (motor vehicles, industrial processes, domestic heating, tobacco smoke and other.

They consist of two or more benzene rings. Most PAHs with fewer rings are gases, while those with more benzene rings bind to particles according to their affinity for bounding on particles. Most of them are associated with fine airborne particles (Katz, 1980). It is generally accepted that PAHs associated with small particles ($< 1\ \mu$m) tend to result from combustion or other high temperature sources whereas large particles ($>10\ \mu$m) are likely to arise from wind action on soils and deposited dust (Sheu, 1997). Levels of PAHs concentration in the atmosphere depend on heating, traffic density, type of industrial emissions, and tend to vary with season and meteorological conditions. More than 500 PAH have been identified in the air, but only 1-20 are measured (Lee, 1981). Several compounds of this group have been classified by the International Agency for Research and Cancer (IARC) as probable (2A) or possible (2B) human carcinogens (IARC, 1987). Many developed countries started to measure PAH concentrations in the atmosphere in the mid-20th century. Benzo-a-pyren (BaP) has been the most commonly measured PAH since it is always present, and this substance was used as an indicator of the carcinogenic hazard in environment pollution.

The aim of this investigation was to evaluate if there were statistically significant differences between PAH mass concentrations measured in inhalable or "thoracic" (PM_{10}) and respirable or high-risk ($PM_{2.5}$) particle fraction during two different seasons.

METHODS

Collection of samples

Twenty four air samples were collected at one monitoring site in the Northern part of Zagreb, Croatia by low volume PM_{10} and $PM_{2.5}$ samplers ($\sim$50 m^3) for a period of 30 consecutive days in winter (January) and summer (July). Glass fibre filters were used to collect PM_{10} and $PM_{2.5}$ particle fractions. The samples were kept in the deep freeze at the temperature of -18 ^{o}C, wrapped in aluminium foil until analysed.

Sample analysis

PAH samples were extracted with cyclohexane in an ultrasonic bath for one hour, separated from undissolved parts by centrifugation and evaporated to dryness in a mild stream of nitrogen at 30 °C. Then they were redissolved in acetonitrile. A detailed procedure for the preparation of samples has been described earlier (Šišović, 1991). The analysis was performed by Varian Pro Star high-performance liquid chromatograph (HPLC) and a fluorescence detector with changeable excitation and emission wavelength, in order to optimise the selectivity and sensitivity for individual PAH species (Colombini, 1998). For preparation of calibration curves commercial PAH standard (Supelco SS EPA 610 PAHs Mix) was used. Samples were analysed for the following PAHs: fluoranthene (Flu), pyrene (Pyr), benzo-b-fluoranthene (BbF), benzo-k-fluoranthene (BkF), benzo-a-pyrene (BaP) and benzo-ghi-perylene (BghiP).

RESULTS AND DISCUSION

Figure 1. shows day-to-day variations of four PAHs mass concentrations (Flu, Pyr, BaP and BghiP), measured over 30 consecutive days in PM_{10} and $PM_{2.5}$ particle

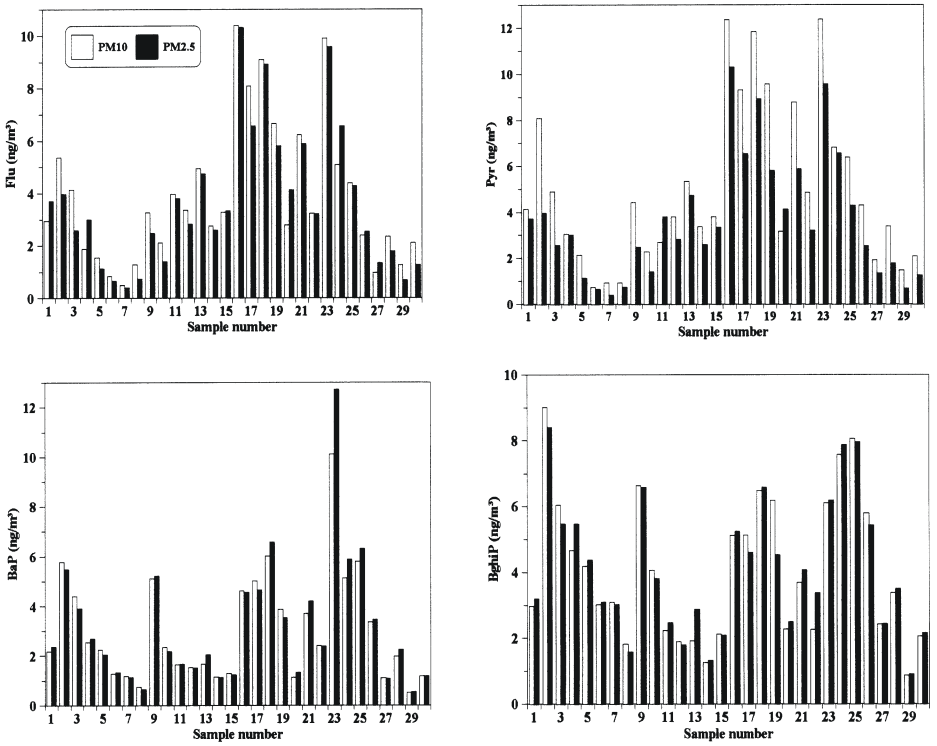

Figure 1. Day to day variations of some PAH mass concentrations measured in PM_{10} and $PM_{2.5}$ in winter

fractions in winter. Concentrations of PAHs measured in different particle size shows similar daily variations. Day to day variations mainly depend on weather conditions (wind direction, velocity and temperature variations). The average mass concentrations and other statistically important parameters of PAH measured in PM_{10} and $PM_{2.5}$ particle fractions in winter are shown in Table 1. Pyrene showed the highest average value measured in PM_{10} 4.982 ng/m^3 and the lowest average value of mass concentrations had BkF in $PM_{2.5}$ 2.098 ng/m^3. Average mass concentrations of BaP were 3.093 ng/m^3 in PM_{10} and 3.178 ng/m^3 $PM_{2.5}$. Average mass concentrations of Flu in PM_{10} was 3.905 ng/m^3 and in $PM_{2.5}$ 3.675 ng/m^3. Table 2 shows statistical parameters and difference between PAH mass concentrations (ng/m^3) measured in different particle size in winter.

Table 1. Statistical parameters of mass concentrations PAHs (ng/m^3) measured in PM_{10} and $PM_{2,5}$ in winter

PAH		N	$C_{min.}$	$C_{max.}$	**C**	STD	SE
Flu	PM_{10}	30	0.487	10.392	**3.905**	2.6437	0.4827
	$PM_{2,5}$	30	0.409	10.308	**3.675**	2.6118	0.4768
Pyr	PM_{10}	30	0.745	12.379	**4.982**	3.3833	0.6177
	$PM_{2,5}$	30	0.607	12.511	**4.654**	3.0782	0.5620
BbF	PM_{10}	30	0.453	10.332	**3.627**	2.1833	0.3986
	$PM_{2,5}$	30	0.477	9.672	**3.523**	1.9880	0.3630
BkF	PM_{10}	30	0.752	5.596	**2.142**	1.1746	0.2145
	$PM_{2,5}$	30	0.793	5.648	**2.098**	1.1390	0.2080
BaP	PM_{10}	30	0.519	10.122	**3.039**	2.1416	0.3910
	$PM_{2,5}$	30	0.561	12.732	**3.178**	2.4954	0.4556
BghiP	PM_{10}	30	0.865	9.016	**4.081**	2.1591	0.3942
	$PM_{2,5}$	30	0.907	8.398	**4.099**	2.0187	0.3686

N – number of samples
$C_{min.}$ – minimum value
$C_{max.}$ – maximum value
C – arithmetic means
STD – standard deviations
SE – standard error

Table 2. Statistical parameters and significance of difference in PAH mass concentrations (ng/m^3) measured in PM_{10} and $PM_{2,5}$ in winter

PAH	N	C ($PM_{2,5}$)	C (PM_{10})	Δ	STD Δ	SE Δ	t	P
Flu	30	3.675	3.906	0.231	0.7205	0.1316	1.75	>0.05
Pyr	30	4.654	4.982	0.328	0.6566	0.1199	2.73	<0.01
BbF	30	3.523	3.627	0.104	0.4052	0.0740	1.41	>0.05
BkF	30	2.098	2.142	0.044	0.1439	0.0263	1.68	>0.05
BaP	30	3.178	3.039	-0.139	0.5368	0.0980	1.42	>0.05
BghiP	30	4.099	4.081	-0.018	0.4927	0.0900	0.20	>0.05

N – number of sample
$C(PM_{2,5})$ – arithmetic means in $PM_{2,5}$
$C(PM_{10})$ – arithmetic means in PM_{10} SE
Δ - mean difference
STD Δ – standard deviation of mean difference
Δ – standard error of mean difference

Although the average PAH mass concentrations of all PAHs (except BaP and BghiP) were slightly higher in PM_{10}, the differences were not statistically significant ($P>0.05$) except for Pyrene ($P<0.01$). Figure 2 shows day to day variations of four PAH mass concentrations measured in PM_{10} and $PM_{2.5}$ particle fraction in summer. PAH mass concentrations in summer show similar daily variations like in winter, but the concentrations levels of all PAHs were much lower.

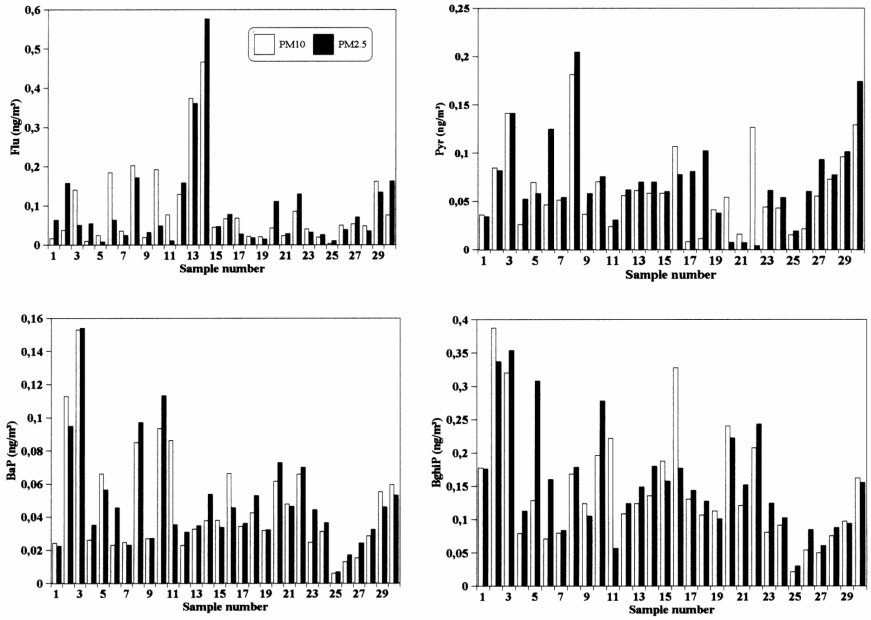

Figure 2. Day to day variations of some PAH mass concentrations measured in PM_{10} and $PM_{2.5}$ in summer

Table 3. Statistical parameters of mass concentrations PAHs (ng/m^3) measured in PM_{10} and $PM_{2,5}$ in summer

PAH		N	$C_{min.}$	$C_{max.}$	**C**	STD	SE
Flu	PM_{10}	30	0.004	0.467	**0.092**	0.1047	0.0191
	$PM_{2,5}$	30	0.008	0.577	**0.092**	0.1158	0.0211
Pyr	PM_{10}	30	0.008	0.181	**0.061**	0.0409	0.0075
	$PM_{2,5}$	30	0.004	0.205	**0.071**	0.0448	0.0082
BbF	PM_{10}	30	0.015	0.235	**0.091**	0.0530	0.0097
	$PM_{2,5}$	30	0.019	0.211	**0.094**	0.0439	0.0080
BkF	PM_{10}	30	0.009	0.131	**0.048**	0.0298	0.0054
	$PM_{2,5}$	30	0.008	0.117	**0.050**	0.0267	0.0049
BaP	PM_{10}	30	0.006	0.153	**0.048**	0.0321	0.0059
	$PM_{2,5}$	30	0.007	0.154	**0.049**	0.0306	0.0056
BghiP	PM_{10}	30	0.022	0.387	**0.147**	0.0845	0.0154
	$PM_{2,5}$	30	0.031	0.354	**0.156**	0.0797	0.0146

N – number of samples C – arithmetic mean SE – standard error
$C_{min.}$ – minimum value STD – standard deviation $C_{max.}$ – maximum value

Summarised results of PAH mass concentrations measured in PM_{10} and $PM_{2.5}$ particle fraction in summer are shown in Table 3. Average mass concentration levels of all measured PAHs were much lower than in winter. The average mass concentration of BaP measured in PM_{10} was 0.048 ng/m^3 and in $PM_{2.5}$ 0.049 ng/m^3. The average mass concentration of Flu in PM_{10} and $PM_{2.5}$ were equal 0.092 ng/m^3. The highest concentration of all measured PAHs during summer showed BghiP in $PM_{2.5}$ 0.156 ng/m^3 and the lowest BkF and BaP in PM_{10} 0.048 ng/m^3. Statistical parameters and difference between PAH mass concentrations (ng/m^3) measured in summer are shown in Table 4.

Table 4. Statistical parameters and significance of difference in PAH mass concentrations (ng/m^3) measured in PM_{10} and $PM_{2,5}$ in summer

PAH	N	C ($PM_{2,5}$)	C (PM_{10})	Δ	STD Δ	SE Δ	t	P
Flu	30	0.092	0.092	0.0003	0.0574	0.0105	0.0291	>0.05
Pyr	30	0.071	0.061	0.010	0.0377	0.0069	1.4091	>0.05
BbF	30	0.094	0.091	0.003	0.0204	0.0037	0.7991	>0.05
BkF	30	0.050	0.048	0.002	0.0096	0.0018	1.0761	>0.05
BaP	30	0.049	0.048	0.001	0.0139	0.0025	0.4841	>0.05
BghiP	30	0.156	0.147	0.009	0.0606	0.0111	0.8394	>0.05

N – number of sample
$C(PM_{2,5})$ – arithmetic means in $PM_{2,5}$
$C(PM_{10})$ – arithmetic means in PM_{10}
Δ – mean difference
STD Δ – standard deviation of mean difference
SE Δ – standard error of mean difference

Although the average PAH mass concentrations of all PAHs (except Flu) were slightly higher in $PM_{2.5}$, the differences between all were not statistically significant ($P>0.05$).

CONCLUSION

The average mass concentrations of all measured PAHs in winter (except BaP and BghiP) were slightly higher in PM_{10} than in $PM_{2.5}$ particle fraction, but the differences between the two were not statistically significant. The average mass concentrations of all PAHs in summer were slightly higher in $PM_{2.5}$ (except Flu), but the differences also were not statistically significant. Our results show that all PAHs are present in a high-risk particle fraction ($PM_{2.5}$). The findings are in good agreement with a number of other findings which showed that BaP and other PAHs, with more benzene rings, are adsorbed on small size particulate matter which directly enters the lower part of human respiratory system.

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The 14th International Conference
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NO_2 LEVELS IN CROATIAN AIR FROM 1992 TO 2001

V Šojat*, G Hrabak-Tumpa, B Gelo, D Borovečki, Z Gliha

ABSTRACT

This paper deals with the annual course of NO_2 mean daily concentrations, measured in the stations of Puntijarka and Zavižan, which operate according to the EMEP Program, and are compared to the measurements in the station of the Zagreb-Maksimir urban area.
The impact of traffic on the NO_2 daily concentration level for the Zagreb urban area has been determined through the weekly course of NO_2 concentration levels per season and in a year.
During the period of significant increase of NO_2 concentration in the Zagreb urban area, meteorological factors have been analysed, as they are one of the indicators for the efficiency of both the increase and decrease of NO_2 daily concentration levels.

INDEX TERMS

Pollution, NO_2 concentration, traffic, wind direction and speed, precipitation

INTRODUCTION

The observed values of nitrogen dioxide concentration are an integral part of the measurements conducted by The Meteorological and Hydrological Service, with the aim to systematically monitor the quality indicators of air and precipitation. The purpose of establishing the network is to monitor background pollution, remote and cross-border pollution within the framework of the obligations pursuant to international contracts (EMEP, MED-POL and GAW Programme) which have been established as part of the national network of meteorological stations.

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The stations within the Meteorological and Hydrological Service (MHS) have been registered with international programmes as the National Stations of the Republic of Croatia, pursuant to relevant requirements.
Part of the EMEP Programme relates to the systematic monitoring of NO_2, by using modified spectophotometric Saltzman's method.
The pollutants' ground-level concentrations depend on emissions into the air, as well as on the following elements: physical properties of emissions, chemical reactions in the atmosphere, geographical characteristics of the environment, and meteorological conditions.
The nitrogen dioxide emissions (NO_X, x = 1.2) into the atmosphere is still one of the major problems in air protection, despite better results achieved in reducing the presence of other pollutants in the atmosphere. The increased amount of NOx in the atmosphere is mostly the result of human activities, i.e. of economic development. Special attention is paid to nitrogen oxides, since they represent the key components for the generation of numerous compounds through various chemical transformations in the atmosphere (e.g. HNO_2, HNO_3), with a negative impact on numerous ecosystems. The impact of the new compounds on the environment is acid rains, photochemical smog, increased ozone concentration in the lowest layer of the atmosphere - the troposphere. Recently, attention has also been paid to nitrogen oxide (N_2O), due to its role in global warming of the zoosphere.
The biggest source of NO_2 air pollution is mobile – it is a vehicle (an automobile, a bus, a ship, a diesel engine, an aircraft and others – according to statistical data, NO_2 amounts to 40 % of pollution on the territory of Croatia), followed by power generation processes (about 22 %) as well as industrial combustion processes (about 10 %). The more developed the country, the higher the concentration from mobile sources, compared to the concentration from stationary sources. The main indicators of pollutants from mobile sources are carbon monoxide (CO), nitrogen oxides (NOx), hydrocarbons, CxHy, lead (Pb) in a form of organic compounds. In traffic the pollutants are released into the ground-level layer, so the ground-level concentration is increasing in correlation with the sources. The emissions from road traffic and their impact on air quality in the Republic of Croatia were studied for the needs of the European project CORINAIR (Coordinated Information System for Air Pollutants) by Jurić, Ž., and Jelavić, V. (1999). Problems caused by traffic could be, in the first place, mitigated by enhancing import of more advanced, and cleaner vehicles and by the consumption of better quality fuel. The content of nitrogen dioxide in urban areas is much higher than in rural areas (which is also presented and evidenced in this paper, in the part relating to the data obtained on the stations Zagreb-Maksimir, Puntijarka, and Zavižan). The concentrations vary, depending on the area and emission intensity in the course of the daily cycle – and primarily on human activities, and, up to a point, on weather conditions.
The interconnection between air pollution and its harmful impact on human health, and morbidity and mortality, shown in a survey on NO_2, which, together

with SO_2, hovering particles and others, are in the group of the main pollution indicators, is the main subject of many surveys and epidemiological studies.

NO_2 annual concentration course

The introduction indicates that the concentration depends on numerous factors and on meteorological conditions. This paper deals with concentration values on the stations of the Zagreb-Maksimir urban area and on high altitude stations (which are part of the network of the EMEP program Puntijarka (on top of Zagrebačka gora mountain - at 988 m above the sea level) and Zavižan (on top of Mt. Velebit – at 1594 m above the sea level).

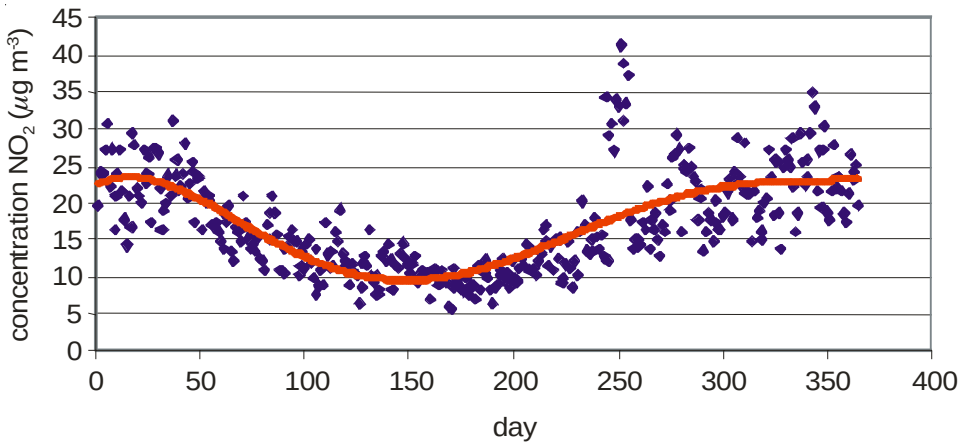

Figure 1. NO_2 Annual concentracion course, Zagreb-Maksimir, 1992-2001.

Figure 1. shows the NO_2 annual concentration course in the ten-year measurement period 1992-2001 in the Zagreb-Maksimir station. We can conclude that Zagreb has a clearly defined annual course with minimum values in the warm seasons and with a maximum course in the cold seasons. An equation was calculated showing the expected mean daily concentration on a single day in a year for the Zagreb-Maksimir area. The correlation is rather high ($r^2 = 0.56$) and the equation can describe the expected value of NO_2 concentration with a 80 % accuracy for every day in a year. The same result was obtained for Puntijarka ($r^2 = 0.55$). However, for the mountain area of Zavižan we cannot speak about a regular annual course, since the values are evenly distributed throughout the year (Fig. 2 and Fig. 3), with slightly higher concentrations at the end of the year. It can be concluded that NO_2 daily concentrations tend to slightly decrease.

As the NO_2 annual concentration course is well expressed, a correlation was made with air temperature which has an opposite annual course.

This analysis leads to a conclusion that the daily concentration does not significantly depend on air mean daily temperature (the correlation coefficient

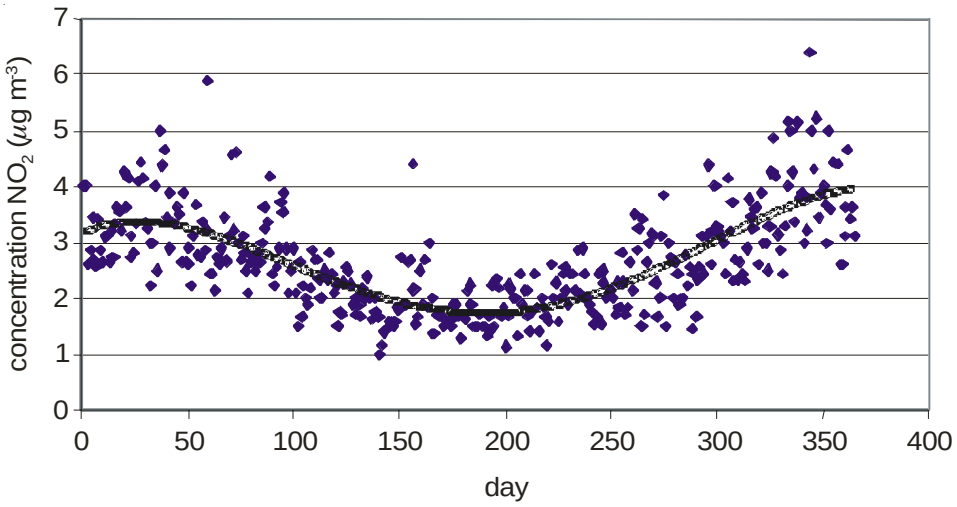

Figure 2. Annual concentration (μg m^{-3}) NO_2, Puntijarka, 1992-2001.

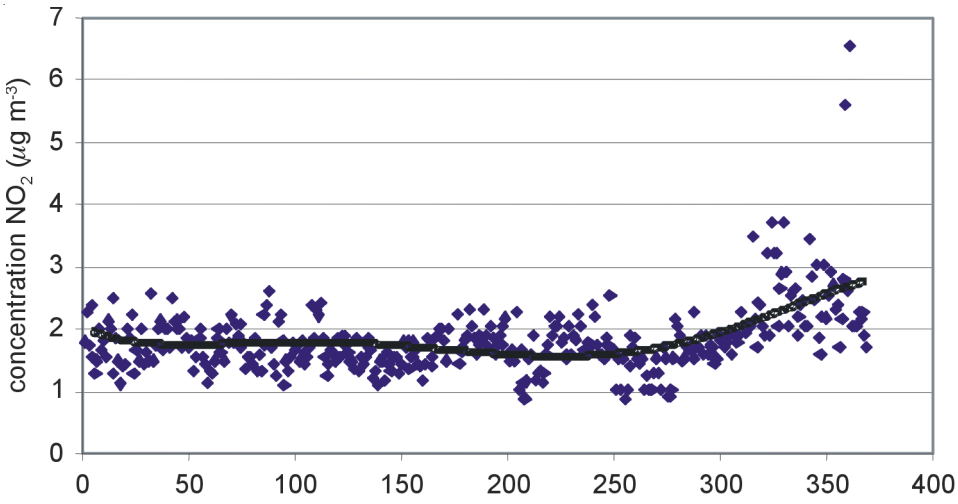

Figure 3. Annual concentration (μg m^{-3}) NO_2, Zavižan, 1992-2001.

is only about 0.10). If the daily concentration with significant increases at the beginning of September 1994 is excluded, the correlation coefficient increases and the relation obtained can be used to describe 34 % of the values measured (Fig. 4.)

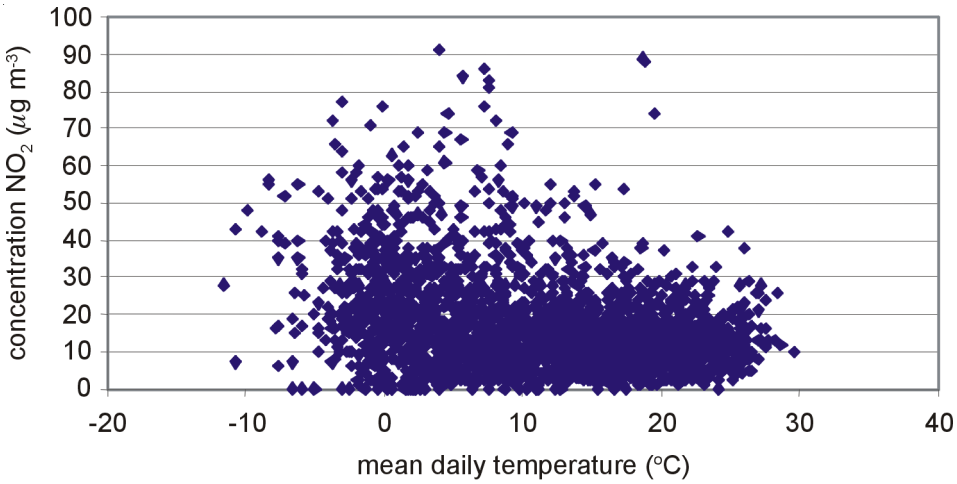

Figure 4. Air temperature and concentration NO_2, Zagreb-Maksimir, 1992-2001.

NO_2 weekly concentration course

Research carried so far has established NO_2 daily, weekly, and annual concentration courses, which are exclusively related to the distance from roads and highways, in other words to road traffic intensity. The present paper (Gelo, 1999.) provides evidence that the lowest level of pollution is present at the end of the weekend and the highest at the end of the working week.

Since the annual concentration course is relatively regular, weekly concentrations were made per season and per week for each particular season.

Looking at the whole year generally, NO_2 lowest concentrations can be expected on Sundays (20.6 μg m^{-3}), and the highest on Fridays (24.1 μg m^{-3}). It is interesting to note that, during summer, on the average, the highest concentrations were measured on Wednesdays and the daily values are two times lower than the winter values (Fig. 5.).

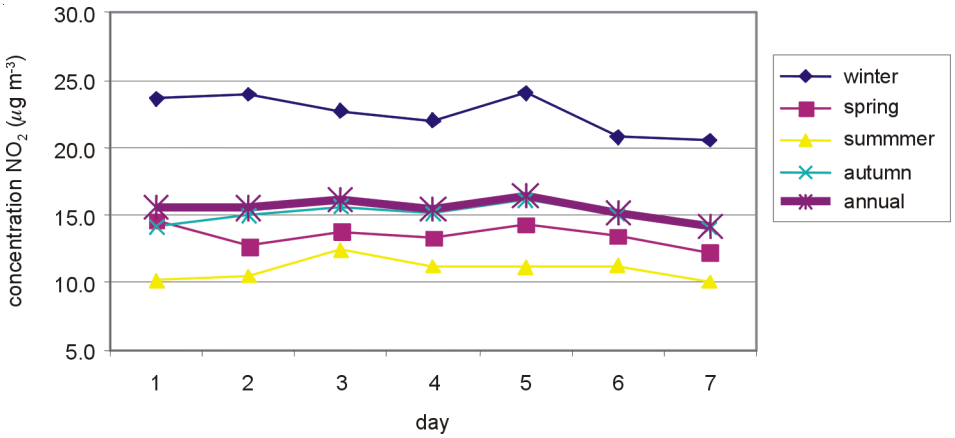

Figure 5. Weekly courses NO_2, Zagreb-Maksimir, 1992-2001.

It is clearly evident that the highest daily concentrations can be expected during the fourth week of the winter season (Christmas and New Year holidays) when the daily values on Mondays, on the average, amount to about 40 μg m^{-3}, and at weekends to about 30 μg m^{-3} (Fig.6.).
Significant daily concentration reduction in the spring season occurs in the first week (beginning of March) – on the average from 4 to only 5.3 μg m^{-3}. (which can be the result of not only less traffic but also of more days with penetration of cold air from the North – better airing in urban areas) and significant concentration increase in the fourth and fifth week (probably heavier traffic due to Easter and spring school holidays).
In the summer, daily maximum concentrations are recorded on Wednesdays, when daily concentrations are by 20% higher than on Sundays and even Mondays and Tuesdays.

NO_2 daily concentrations and weather conditions

Attempts have been made to establish a connection between the days with significantly higher daily concentrations and their respective weather conditions (meteorological factors). Mean daily air temperatures were studied, together with

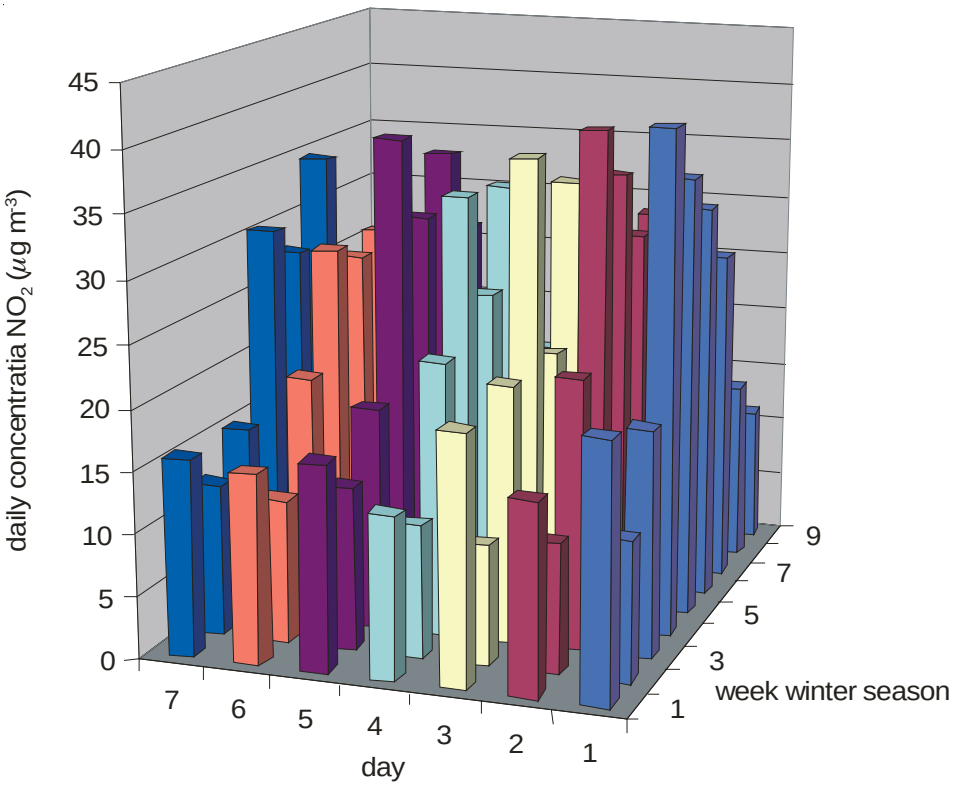

Figure 6. NO_2 Weekly Concentracion Course, Winter, Zagreb-Maksimir, 1992-2001.

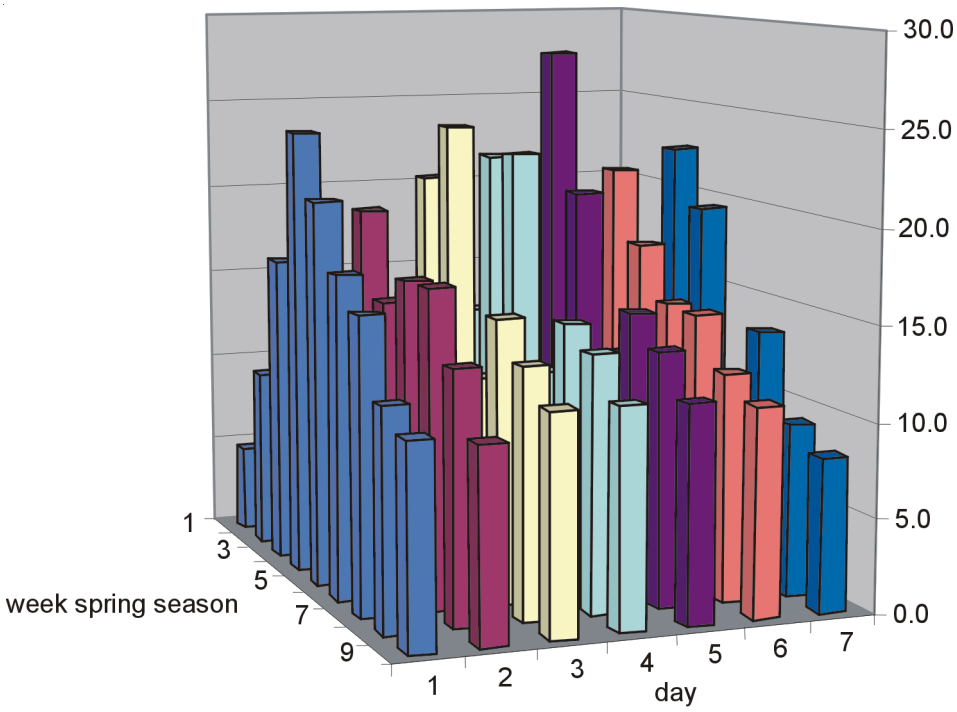

Figure7. NO_2 Weekly Concentracion Course, Spring, Zagreb-Maksimir, 1992-2001.

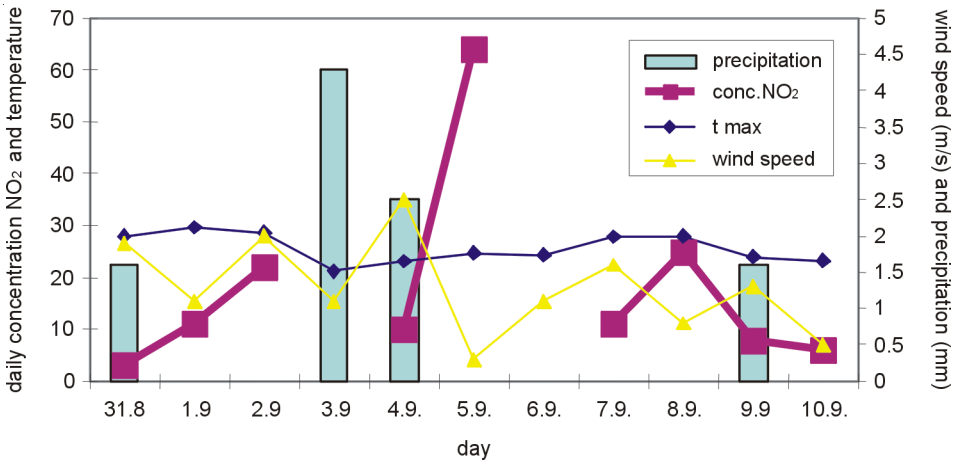

Figure 8. NO_2 daily concentration and meteorological factors, Zagreb-Grič, August 31.-September 10. 1994.

the volume of precipitation on a 24-hour basis and NO_2 concentration for the measurement period from 7 a.m. to 7 a.m.

At the beginning of September 1994, NO_2 daily concentrations were measured, which exceeded by far the recommended values (30 μg m^{-3}, because of plant protection and 80 μg m^{-3} for human protection).
On 1 September 1994, the 24-hour concentration amounted to 174 μg m^{-3}, and after the rain the following day, only 11 μg m^{-3} were measured. Increased wind speed on September 4 probably caused NO_2 daily concentration fall on September 5. Absence of precipitations and lower wind speed again caused higher NO_2 concentrations on the following days (above 160 μg m^{-3} - Fig.8.).

CONCLUSION

The impact of nitrogen oxides on the environment can be studied at the local, regional and global level. At the local level it has a direct impact on human health and the environment (material and cultural goods. At the regional level it causes «acid rains» (together with acid soil and ground waters).
At the global level, the impact is the depletion of the ozone layer and the «green-house effect» and finally climatic changes.
According to measurements conducted on a ten–year basis, a slight declining trend in NO_2 concentration can be noticed on all stations observed. Urban areas (Zagreb) show a regular distribution of the weekly and annual concentration course. A parallel pace has also EMEP area of Puntijarka station, located very near of Zagreb on 988 m above sea level. No weekly or annual course of NO_2 concentration was established on the station Zavižan of the EMEP Program.
Looking at the whole year generally, during the week, the lowest concentrations can be expected at the end of the weekend, and the highest can be expected at the end of the working week. Concentrations in the cold period of the year are twice as high as the concentrations in the warm period.
Increased wind speed and precipitations «clean« the environment, thus reducing NO_2 concentration.
Most of the values measured in the Zagreb urban area are within the limits of the recommended values. It is, however, necessary to think of how to decrease these concentrations can be decreased, since even lower concentration levels can, in the long run, have a harmful impact on people and on the environment. That is why it is necessary to enlarge the measurement program on the existing stations.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

EMISSION INFLUENCE FROM CEMENT PLANTS ON CONCENTRATIONS OF THALLIUM IN DEPOSITED MATTER IN THE AREA OF KAŠTELA BAY

T Tomić*, N Periš and A Barač

ABSTRACT

This paper presents the results of monitoring of Thallium concentration in total deposited matter (TDM) on ten measuring points of Kaštela bay including one measuring point of Omiš hinterland, during 2001 and 2002. While choosing measuring points, a distance from emission sources, population density and metereological parameters were taken in consideration. Measuring points in Kaštela bay are divided into three groups presenting eastern, central and western part of Kaštela bay. Twenty four samples were collected and analysed on TDM and Thallium content, from all measuring points. The results of measuring were compared with recommended (RV) and limit values (LV) according to the Law on Air Quality Protection in Croatia and the Ordinance on Recommended and Limit Air Quality Values. During 2001, regarding TDM the air was on the 3rd category level in the eastern part of Kaštela bay. During 2002, there was a 20% decrease of TDM concentration in the eastern part.
In regard to TDM concentration in 2002, the air in Kaštela can be put into the 2nd category level with significant difference between the eastern and the western part. The eastern part shows 60% higher level of TDM concentration in relation to RV, the central part 31% and the western part 5.5%. During 2001 and 2002, in the control area of Omiš the air was on the 1st category level regarding TDM.
In 2001 and 2002, all measuring points in Kaštela bay as well as control area showed lower level of Thallium concentration in total deposited matter in relation to RV, therefore, regarding Thallium the air can be put into the 1st category level. Thallium concentrations decrease in accordance with distance from emission sources; this is

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visible in the eastern part of Kaštela bay with levels 6 times higher than those from the western part and 11 times higher than those from the control area.

INTRODUCTION

Thallium is a metal widely spread in traces in the Earth's Crust. Environmentally, Thallium produces compounds with oxygen, sulphur and halogens. It exists in the air, water and soil. It is present in the atmosphere as Thallium hydroxide, Thallium sulphate or sulphide. Thallium remains unchanged in the atmosphere without any possibility of division into more simple particles.
Thallium is emitted in the atmosphere from plants using coal combustion as a source of energy, cement industry plants, plant production of iron and steel etc. In the eastern part of Kaštela bay there is a large exploiting field for extraction of mineral raw materials used in the cement production of three big plants. Annual production of clinkers is about 2 million tones.
The ironworks "Split", which is located in the eastern part as well, worked only partially during 2001 and 2002.
During a period of air quality monitoring in the area of Kaštela bay, imission values of metal concentrations in total deposited matter (TDM) were also tested. In the process, a special attention was directed to Thallium concentrations given the specific quality of the industry in this area.

MATERIALS AND METHODS

Since January 2001, systematic monitoring of Thallium concentrations in total deposited matter (TDM) started at a number of measuring points in the area of Kaštela bay, Split and Omiš hinterland. Three measuring points were chosen in the eastern part of Kaštela bay (Solin, area between two cement plants, Kaštel Sućurac), three in the central part (Kaštel Kambelovac, Kaštel Lukšić and Kaštel Novi), and three in the western part (Airport, Trogir, Arbanija-Čiovo island) including one measuring point in the rural part of Omiš hinterland-Tvrćica (Figure 1).



Figure 1. Kaštela bay

While choosing measuring points, population density and meteorological parameters were taken in consideration. In other words, the area of Kaštela bay is rather windy. During a winter time, the most frequent wind is *bura*, the north-eastern wind. In February, April and November the most frequent is *jugo*, the south and south-eastern wind. In a summer time, the most frequent is *maestral,* the south-western wind.
Samples of the deposited matter were collected by the Bergenhoff method. Total deposited matter was determined gravimetrically. Thallium content was determined using flameless atomic absorption spectrophotometer method.
During 2001 and 2002, 24 samples from each measuring point were collected and analysed on Thallium content.
Test results were compared with recommended and limit values of the air quality.

RESULTS AND DISCUSSION

Annual mean concentrations of TDM in measuring points of eastern part of Kaštela bay ranged from 330 to 445 mg/m^2/day in 2001 and from 397 to 261 mg/m^2/day in 2002. Table 1 shows relation between decreases in concentration and distance from source emission.
During 2001, mean concentration of TDM in the whole eastern part area was 401 mg/m^2/day thus exceeding limit value (LV). In 2002, mean concentration was 317 mg/m^2/day i.e. below LV and exceeding recommended value (RV). In relation to last measuring year, there was a 20% decrease in concentrations of TDM (Figure 2).
In measuring points of central part of Kaštela bay, concentrations of TDM ranged from 240 to 265 mg/m^2/day in 2001, and from 226 to 305 mg/m^2/day in 2002.
Mean concentration of TDM in the central part of the bay was 253 mg/m^2/day in 2001, and 262 mg/m^2/day in 2002; both being below LV and exceeding RV.
In the western part of Kaštela bay, mean concentration of TDM ranged from 179 to 263 mg/m^2/day in 2001, and 175 to 280 mg/m^2/day in 2002.
Mean concentration of TDM in the western part of the bay was 232 in 2001, and 211 mg/m^2/day in 2002; both slightly exceeding RV.
Annual mean concentration of TDM in the village Tvrćica, (control area) was 151 in 2001, and 172 mg/m^2/day in 2002; both below RV. Regarding TDM, the air is slightly polluted i.e. it was on the 1st category level.
During 2002, regarding TDM the air was moderately polluted i.e. it was on the 2nd category level in the whole area of Kaštela bay. However, it must be emphasized that there are significant differences in testing areas of TDM concentrations.
TDM concentrations in the eastern part of Kaštela bay exceed RV for 60%, in the central part for 31% and in the western part for only 5.5%.
In 2001, annual mean concentrations of Thallium in the eastern part of the bay ranged from 1.025 to 1.58 μg/m^2/day with maximal values from 5.32 to 9.42 μg/m^2/day. During 2002, annual mean concentrations ranged from 0.813 to 1.69 μg/m^2/day with maximal values from 2.35 to 5.32 μg/m^2/day (Table 1).

Table 1. The amount of total deposited matter (mg/m^{2}day) and metals (μg/m^2/day) for years 2001 and 2002.

MEASURING POINT		T.D.M. mg/m^2/day		Tl μg/m^2/day	
		C	Cm	C	Cm
Solin	2001	330	763	1,28	7,00
	2002	261	372	0,813	2,35
Između tvornica	2001	445	716	1,025	5,32
	2002	397	501	1,29	5,38
K.Sućurac	2001	430	1000	1,58	9,42
	2002	292	438	1,69	2,970
K. Kambelovac	2001	265	522	0,662	5,37
	2002	255	372	0,538	1,731
K. Lukšić	2001	240	588	0,170	0,669
	2001	226	532	0,451	2,55
K. Novi	2001	253	299	0,192	0,425
	2002	305	574	0,316	1,035
Zračna luka	2001	256	427	0,217	0,950
	2002	175	306	0,29	2,01
Trogir	2001	163	522	0,142	0,574
	2002	280	768	0,285	0,654
Čiovo	2001	179	295	0,119	0,250
	2002	179	307	0,259	2,33
Tvrčica	2001	151	262	0,108	0,390
	2002	172	335	0,121	0,390

Mean concentration of Thallium in the eastern part of the bay was 1.295 μg/m^2/day in 2001 and 1.264 μg/m^2/day in 2002 i.e. below RV (Figure 3).

During 2001, annual mean concentrations of Thallium in measuring points of central part of Kaštela bay ranged from 0.192 to 0.662 μg/m^2/day with maximal values from 0.425 to 5.57 μg/m^2. During 2002, annual mean concentrations ranged from 0.316 to 0.538 μg/m^2/day with maximal values from 1.035 to 2.55 μg/m^2/day. Annual mean concentration of Thallium in the whole central area of the bay was 0.341 in 2001, and 0.435 μg/m^2/day in 2002 i.e. both below RV.

In 2001, annual mean concentration of Thallium in measuring points of western part of Kaštela bay ranged from 0.119 to 0.217 μg/m^2/day with maximal values from 0.250 to 0.950 μg/m^2/day. During 2002, annual mean concentrations ranged from 0.259 to 0.285 μg/m^2/day with maximal values from 0.654 to 2.33 μg/m^2/day. In the whole western part area of Kaštela bay, Thallium concentration was 0.159 in 2001, and 0.269 μg/m^2/day in 2002 i.e. both below RV.

Annual mean concentration of Thallium in the village Tvrčica, during 2001, was 0.108 and maximal 0.390 μg/m^2/day. During 2002, annual mean concentration of Thallium was 0.121 and maximal 0.390 μg/m^2/day thus significantly below RV.

During 2001 and 2002, annual mean concentrations of Thallium in all measuring points were below recommended values. Figure 3 clearly shows that concentrations

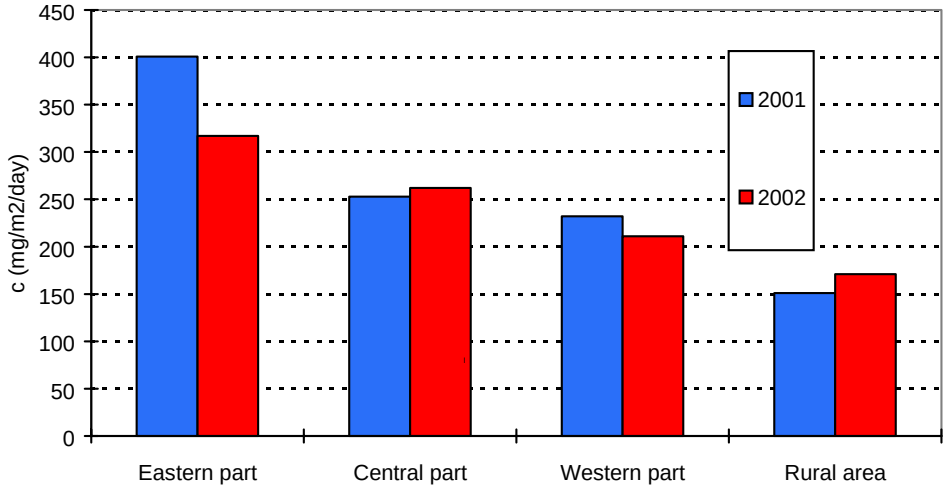

Figure 2. Annual mean concentrations of total deposited matter in 2001 and 2002

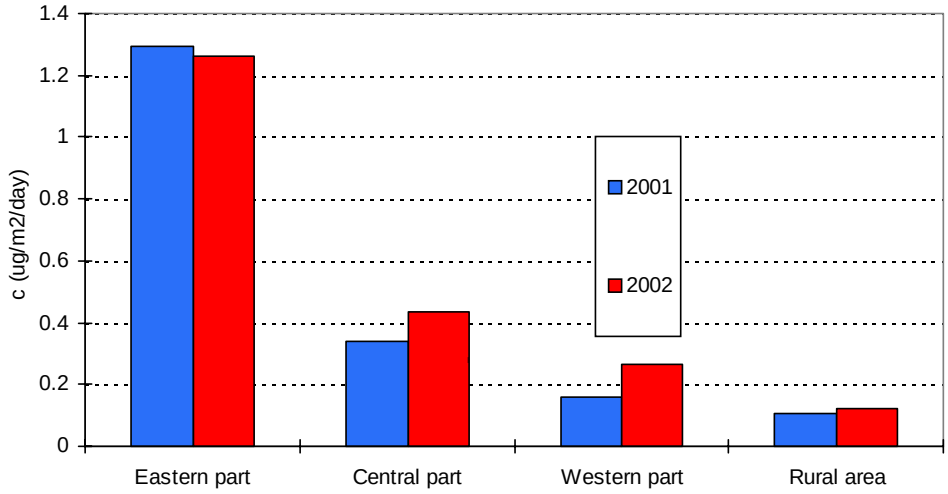

Figure 3. Annual mean concentracions of Thallium in total deposited matter in years 2001 and 2002

of Thallium decrease in accordance with distance from emission sources. Annual mean concentrations of Thallium in the eastern part are 3.3 times higher than those in the central part, and 6 times higher than those in the western part of Kaštela bay. In relation to control area, Thallium concentrations are 11 times higher. It should be pointed out that significantly higher Thallium concentrations in TDM were measured in Zagreb area, which indicates that elevated levels are consequences of various activities.

CONCLUSION

The results of measuring of total deposited matter as well as Thallium in total deposited matter (TDM) during 2001 and 2002 in the area of Kaštela bay and Omiš hinterland have been compared with limit and recommended values of the air quality. They show that the air in Kaštela bay area can be put into the 2nd category level regarding total deposited matter with 60% higher level of TDM concentration in relation to RV in the eastern part, 31% in the central part, and 5.5% in the western part. The air in control area belongs to the 1st category level regarding TDM. The results of measuring of Thallium in TDM show that the air in all testing areas can be put into the 1st category level. Thallium concentrations decrease in accordance with distance from emission source and they are 6 times higher in the eastern part of Kaštela bay than those from the western part and 11 times higher than those from the control area.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

ORGANOCHLORINE PESTICIDES AND PCB CONGENERS IN SUSPENDED PARTICULATE MATTER COLLECTED IN ZAGREB

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ABSTRACT

Semivolatile persistent organochlorine (OC) compounds were determined in samples of atmospheric particles PM_{10} collected daily during the year 2002 at one location in the northern, residential part of Zagreb. The compounds analysed were hexachlorobenzene (HCB), α-, β-, and γ-hexachlorocyclohexane (α-HCH, β-HCH and γ-HCH), 4,4'-DDT, 4,4'-DDE, 4,4'-DDD and 20 polychlorinated biphenyl (PCB) congeners, including six indicator congeners (PCB-28, PCB-52, PCB-101, PCB-138, PCB-153, and PCB-180) and fourteen other toxicologically significant congeners (PCB-60, PCB-74, PCB-77, PCB-105, PCB-114, PCB-118, PCB-123, PCB-126, PCB-156, PCB-157, PCB-167, PCB-169, PCB-170 and PCB-189). Twenty-four-hour samples of PM_{10} particle fractions were collected on two glass microfibre filters from approximately 100 m^3 of ambient air per filter at the average air flow rate of 70 L min^{-1}. Fourteen filters with particle samples collected during seven consecutive days were combined for chemical analysis. OC compounds associated with particles were accumulated by ultrasonic extraction with 1:1 acetone: *n*-hexane mixture. The extracts were purified with sulphuric acid and analysed by high resolution gas chromatography with electron capture detection. The most frequently detected particle bound compounds in air were HCH isomers (γ-HCH in 100 %, α-HCH in 96 % and β-HCH in 88 % of samples), DDT type compounds (4,4'-DDE in 87 %, 4,4'-DDT in 79 % and 4,4'-DDD in 38 % of samples) and HCB (in 85 % of samples). The median concentrations in air of different OC pesticides sorbed in PM_{10} ranged from 0 to 6 pg m^{-3}. The most frequently detected PCB congeners were PCB-28 (in 65 % of samples), PCB-60 (in 63 % of samples), PCB-101 (in 58 % of samples) and PCB-180 (in 56 % of

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samples). The highest mass concentration was determined for PCB-28: 101 pg m^{-3}. The decreasing trend in mass concentrations of particle bound β-HCH and total PCBs with increasing air temperature was mostly related to the lower particle mass concentrations at higher temperatures.

INDEX TERMS

Organochlorine pesticides, polychlorinated biphenyls (PCBs), suspended particulate matter, PM_{10}

INTRODUCTION

Organochlorine (OC) pesticides and polychlorinated biphenyls (PCBs) belong to the widespread highly persistent, lipophilic and semivolatile environmental micropollutants. They can be transported long distances by circulation of air masses, precipitation of particles onto which pollutants are sorbed and wet depositions washing them out from the atmosphere. Their association to airborne inhalable particles with an equivalent aerodynamic diameter <10 μm (PM_{10}) and respirable particles with an equivalent aerodynamic diameter <2.5 μm ($PM_{2.5}$) is of special concern because the potential toxicity of particles varies not only with their size but also with chemical composition. Non-volatile organochlorine compounds such as hepta- and octachlorinated dibenzo-*p*-dioxins and dibenzofurans, were found to be more or less completely particle bound in the atmosphere and on average 92 % of these compounds were associated with particles with aerodynamic diameters smaller than 2.9 μm (Kaupp and McLachlan, 2000). Particles of that size contained also 60-95 % of particle bound semivolatile less chlorinated congeners, for which significant fractions were present in the gas phase. Concentration levels of PCBs determined in the atmospheric fine particles $PM_{2.5}$ in the urban environments of Chile were even higher than gas-phase PCBs measured in the atmosphere of other urban areas around the world (Mandalakis and Stephanou, 2002). Particle size distributions of total PCBs were found to be bimodal (Lee *et al.*, 1996) with the highest peak in the particle size range between 5.6 and 10.0 μm, and the second peak in the particle size range between 0.31 and 0.52 μm.

Our measurements of OC pesticides and PCBs in samples of suspended particulate matter collected from October 2000 to May 2001 at a location in the northern residential part of Zagreb, indicated that these compounds were mainly sorbed in respirable $PM_{2.5}$ fraction (Vasilić *et al.*, 2001). The abundance and levels of OC compounds in respirable ($PM_{2.5}$) and inhalable ($PM_{10.5}$) particle fractions were not significantly different. A significant decrease of particle mass concentrations as well as of concentrations of some OC pesticides with increasing air temperature indicated the possibility of seasonal variations in levels of particle bound OC compounds in the air.

In continuation of this study we have measured organochlorine pesticides and specific PCB congeners in weekly samples of PM_{10} atmospheric particles collected

at the same location in the year 2002. This paper describes the measurement results of hexachlorobenzene (HCB), α-, β-, and γ-hexachlorocyclohexane (α-HCH, β-HCH and γ-HCH), 1,1,1,-trichloro-2,2-di(4-chlorophenyl)ethane (4,4'-DDT), 1,1-dichloro-2,2-di(4-chlorophenyl)ethene (4,4'-DDE), 1,1-dichloro-2,2-di(4-chlorophenyl)ethane (4,4'-DDD), and 20 polychlorinated biphenyl (PCB) congeners, including six indicator congeners (PCB-28, PCB-52, PCB-101, PCB-138, PCB-153, PCB-180) and fourteen other toxicologically significant congeners (PCB-60, PCB-74, PCB-77, PCB-105, PCB-114, PCB-118, PCB-123, PCB-126, PCB-156, PCB-157, PCB-167, PCB-169, PCB-170, PCB-189). The abundance and levels of different OC compounds in PM_{10} fraction are compared and analysed with respect to the variations in air temperatures during the sampling periods.

METHODS

Sampling

The samples of PM_{10} atmospheric particles were collected daily from January to December 2002 at a station located in the northern residential part of Zagreb. Twenty-four-hour samples of PM_{10} particle fractions were collected parallelly on two glass microfibre filters (Whatman Glass Microfibre Filters), 90 mm in diameter, from approximately 100 m^3 of ambient air per filter at the average air flow rate of 70 L min^{-1}. The coarse particles were removed by means of an inertial impactor. The filters were wrapped in aluminium foil and kept at -18 ^oC, until analysis.

Sample analysis

Fourteen filters with particle samples collected during seven consecutive days were extracted together three times in the row with 120 mL of 1:1 acetone:*n*-hexane mixture in an ultrasonic bath for 15 min and finally washed with additional 20 mL of extracting solvent. The combined extracts were evaporated to dryness under a gentle stream of nitrogen. Immediately before gas chromatographic analysis the dry residue was redissolved in 1.00 mL of *n*-hexane and washed with 1 mL of concentrated sulphuric acid. The *n*-hexane layer was separated and analysed simultaneously on the Rtx-5MS and Rtx-1701 fused silica gas chromatographic columns, 60 m x 0.25 mm i.d., film thickness 0.25 μm. The analytes were detected with a ^{63}Ni electron capture detector. The Rtx-5MS column provided good separation and reliable quantitation of all analytes. The extract analyses on the Rtx-1701 column served only for qualitative confirmation because of insufficient resolution of several analyte peaks.
Blank samples of pure glass microfiber filters were prepared, treated and analysed in the same manner as the real samples.

RESULTS AND DISCUSSION

Due to the low levels of OC compounds in atmospheric fine particles, the sensitivity of their determination depends on the mass of particle samples. The

mass of particles collected on a glass microfiber filter from 100 m^3 of air during a period of 24 hours was to low for a reliable and sensitive analysis of particle bound OC pesticides and PCB congeners. The collection of particles from larger air volumes, e.g. from 700 m^3 of air drawn through a filter during seven consecutive days, failed because of observed volatilisation losses leading to an underestimation of particle bound OC compounds (Vasilić *et al.*, 2002). High amounts of PCBs may volatilize from fine particles during aerosol sampling and the volatilization losses strongly depend on partial pressure of individual PCB congener and air temperature (Mandalakis and Stephanou, 2002).

Sufficiently high determination sensitivity was achieved by extraction of two combined sets of seven one-day particle samples collected during a week from a total air volume of approximately 1400 m^3. The ultrasonic extraction with 1:1 acetone: *n*-hexane was not uniformly, but still satisfactory efficient for trace enrichment of different OC compounds from atmospheric particles. The extraction recoveries were determined by analysis of filters with particles spiked with nanogram amounts of analytes. At mass fraction levels of 0.06-1.66 ng mg^{-1} the recoveries of OC pesticides ranged from 38 % for 4,4'-DDD to 74 % for α-HCH and g-HCH (RSD=20-33 %). The recoveries of PCB congeners, determined at single congener mass fractions ranging from 0.13 to 0.75 ng mg^{-1}, were 38 to 72 % (RSD=5-46 %). The lowest recovery was obtained for PCB-101 and the highest for PCB-114. Detection limits of particle bounded OC compounds in air, estimated by analysis of real samples, ranged from 0.02 pg mg^{-3} for α-HCH and PCB-180 to 0.2 pg mg^{-3} for β-HCH and PCB-126.

The mass concentrations of total suspended PM_{10} in 52 weekly samples collected and analysed in the year 2002 ranged from 11.7 to 78.7 $\mu g\ m^{-3}$ (median 27.0 $\mu g\ m^{-3}$). The concentrations decreased significantly ($r=0.663$, $P<0.05$) with increasing air temperature. The highest value was measured in December at -2.1 °C and the lowest in July at 21.6 °C. Mean temperatures for the sampling weeks ranged from -3.6 °C to 24.2 °C (median 11.8 °C).

The mass concentrations of particle bound OC pesticides and PCB congeners in weekly samples of PM_{10} are summarised in Tables 1 and 2, respectively. All results are corrected for recovery and recalculated to normal conditions. The most frequently detected particle bound compounds in air were HCH isomers (γ-HCH in 100 %, α-HCH in 96% and β-HCH in 88 % of samples), DDT type compounds (4,4'-DDE in 87 %, 4,4'-DDT in 79 % and 4,4'-DDD in 38 % of samples) and HCB (in 85 % of samples). The median concentrations in air of different OC pesticides sorbed in PM_{10} ranged from 0 to 6 pg m^{-3}. The ratio of α-HCH:γ-HCH is an indicator of recent versus old usage of HCH isomers and of the distance from the input sources over which the HCH isomers may have been transported. In most (75 %) of PM_{10} samples analysed in this work this ratio was lower than unity (0.005-0.922) indicating a higher input of the γ-HCH into the atmosphere as a consequence of local usage of lindane, the insecticide formulation containing γ-HCH as the active ingredient. In two samples a-isomer was not detected at all.

However, in 11(21 %) out of 52 analysed PM_{10} samples the α-HCH:γ-HCH ratio was ≥1 (1.01-2.12). DDE:DDT ratio was lower than unity in 42 % of analysed PM_{10} samples indicating that there had been a recent input of DDT into the atmosphere probably as a consequence of the long-range transport from tropical areas. These findings were in good agreement with low DDE:DDT ratios found in air samples collected at the same location in 1997, 1999, and 2000 (Herceg Romanić and Krauthacker, 2000; Herceg Romanić and Krauthacker, 2003).

Table 1. Mass concentrations of organochlorine pesticides in 52 weekly samples of PM_{10} fraction collected in Zagreb from January to December 2002

Compound	Mass concentration / pg m^{-3}		
	n	Range [a]	Median
HCB	44	0.28 - 24,5	6.24
α-HCH	50	0.02 - 15.6	1.73
β-HCH	46	0.48 - 28.8	4.82
γ-HCH	52	0.31 -19.0	3.22
4,4'-DDE	45	0.07 - 17.0	2.43
4,4'-DDD	20	1.18 - 20.7	0
4.4'-DDT	41	0.12 - 8.39	3.60
∑ DDT	48	0.87 - 41.5	7.70

n – number of positive samples; [a] ranges apply to positive samples; 0 – below the detection limit; ∑DDT – sum of 4,4'-DDE, 4,4'-DDD and 4,4'-DDT

The most frequently detected PCB congeners were PCB-28 (in 65 % of samples), PCB-60 (in 63 % of samples), PCB-101 (in 58 % of samples) and PCB-180 (in 56% of samples). The highest mass concentrations were determined for PCB-28 (101 pg m^{-3}) followed by PCB-101 (76.4 pg m^{-3}). These two congeners together with PCB-52 contributed largely to the sum of six indicator congeners detected in all air samples collected at the same location in 2000 (Herceg Romanić and Krauthacker, 2003b). Compared to the air samples the PCB levels in PM_{10} samples were considerable lower. The mass concentrations of PCBs in air, expressed as the sum of six PCB indicator congeners, ranged from 10.7 to 577.0 pg m^{-3}.
Seasonal variations in levels of particle bound OC compounds in air were tested by linear regression of OC pesticide and PCB congener mass concentrations with average air temperatures during the sampling periods. A significant ($P<0.05$)

decrease in compound mass concentrations with increasing temperature was observed for PCB congeners PCB-28, PCB-52, PCB-169, PCB-101, PCB-138, and PCB-180, for the sum of six indicator congeners, and for the sum of all 20 analysed congeners. Among OC pesticides a significant negative correlation was observed only for b-HCH. However, as in the earlier study (Vasilić *et al.*, 2001), this trend was more related to the lower particle mass concentrations in air during the period of air higher temperatures than to the seasonal variations in levels of compounds associated with particles.

Table 2. Mass concentrations of PCB congeners in 52 weekly samples of PM_{10} fraction collected in Zagreb from January to December 2002

Compound	Mass concentration / pg m^{-3}			Compound	Mass concentration / pg m^{-3}		
	n	Range [a]	Median		n	Range [a]	Median
PCB-28 [b]	34	0.50-101	2.67	PCB-138 [b]	24	0.15-5.76	0
PCB-52 [b]	23	0.06-5.65	0	PCB-153 [b]	23	0.09-2.83	0
PCB-60	33	0.08-14.4	1.01	PCB-156	3	1.65-3.67	0
PCB-74	18	0.39-35.8	0	PCB-157	20	0.28-7.17	0
PCB-77	22	0.16-14.1	0	PCB-167	0	0	0
PCB-101 [b]	30	1.13-76.4	3.78	PCB-169	12	0.29-4.65	0
PCB-105	8	0.29-2.49	0	PCB-170	1	2.91	0
PCB-114	6	0.06-1.79	0	PCB-180 [b]	29	0.02-3.07	0.08
PCB-118	22	0.54-11.8	0	PCB-189	0	0	0
PCB-123	11	0.24-5.13	0	Σ 6 PCB	48	0.12-111	12.3
PCB-126	19	0.70-4.32	0	Σ 20 PCB	52	2.39-131	22.6

n – number of positive samples; [a] ranges apply to positive samples; [b] PCB indicator congeners; 0 – below detection limit; Σ 6PCB – sum of six indicator PCB congeners; Σ PCB – sum of 20 PCB congeners

CONCLUSION

Mass concentrations of OC pesticides and PCBs in atmospheric PM_{10} particle fraction collected in the northern part of Zagreb were characteristic for global environmental pollution. A local input was indicated only for γ-HCH as a consequence of its frequent local usage. However, a decrease in environmental γ-HCH levels may be expected in the near future due to the recent ban of lindane usage in Croatia. The study performed in 2002 has not indicated pronounced seasonal variations in levels of any particle bound OC compound. The decreasing trend in mass concentrations of β-HCH and total PCBs with increasing air

temperature could be accounted for the decrease in PM_{10} mass concentrations at higher temperatures, and, consequently, with a decrease in particle bound OC compounds in the atmosphere.

ACKNOWLEDGEMENTS

This work was supported by the Ministry of Science and Technology of the Republic of Croatia through the Projects 0022002 and 0022003.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

SEASONAL VARIATIONS OF OZONE MASS CONCENTRATIONS IN THE AIR OF ZAGREB

S Žužul*, G Pehnec, M Čačković and V Vadjić

ABSTRACT

This paper presents the results of measurements of ozone in the air of Zagreb, Croatia. Twenty-four hour samples were taken at four sampling sites (city centre, northern, western and southern part of the town) for one month during each season (winter, spring, summer and autumn) of 2001. The samples were collected in carbonate alkali absorption solution of sodium nitrite (active sampling). Nitrite ion reacts with ozone, forming nitrate which is determined by ion chromatography. Regardless of the sampling location, ozone concentrations significantly differed ($P<0.001$) between seasons, showing higher values in summer and lower values in winter. Throughout the sampling period, ozone concentrations were low, and did not exceed the recommended value for the 98th percentile (110 μg m^{-3}), given in The Ordinance on Recommended and Limit Air Quality Values, at three sampling sites. The recommended and the limit values were exceeded only in the city centre, the limit values in summer (two times) and the recommended values in summer (three times) and in autumn (two times).

INDEX TERMS

Air quality, ozone, sampling site, seasonal variations

INTRODUCTION

Ozone is a secondary air pollutant, being formed in the troposphere from primary precursor pollutants (e. g. in motor vehicle engine exhaust) such as nitrogen oxides (NO_x) and hydrocarbons. Based on epidemiological studies and laboratory

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exposure studies on animals and humans, ozone is recognized as a public health problem (R.B. Devlin *et al.*). As a strong oxidant, it may cause harmful health effects and damages on plants and materials. Extensive measurements of ozone levels in the troposphere began during the last few decades. It was found that ozone levels during the summer season in urban areas in Europe and in the USA, often exceeds recommended and limit air quality values given by laws of the European Union and Guidelines for Air Quality by WHO (EEA,1998; EEA 2000; WHO 2000).
The aim of this paper is to investigate seasonal variations of ozone concentrations in the air of Zagreb, Croatia. Results will be interpreted with respect to relevant Croatian laws (Ordinance, 1996).

METHODS

Measurements of ozone concentrations were carried out in 2001 for one month during each season:

– winter: 10th January - 10th February – spring: 6th April - 6th May
– summer: 16th July - 16th August – autumn: 4th October - 4th November

Ozone concentrations were measured at four sampling sites in Zagreb:

North - residential part, with modest traffic and small population density
South - densely populated residential part of the town
West - industrial part of the town
Center - densely populated area with high traffic density

The twenty-four hour samples were collected by sucking the air through carbonate alkali absorption solution of sodium nitrite, pH 11. The flow through the absorption solution was set to 0.2 - 0.5 L min^{-1}. Nitrite ion reacts with ozone, forming nitrate. The nitrate ion was analysed using Dionex DX-120 ion chromatographer with conductivity detector (Pehnec, 2003).

RESULTS AND DISCUSSION

The results of ozone concentration are shown in Table 1.
The results show low concentration values during the whole sampling period. The highest concentrations were measured at the sampling site located in city center. The maximum daily average value was 162.7 μg m^{-3} and it was recorded in summer. High levels of ozone mass concentrations in city centre during the whole sampling period are probably the result of intense automobile traffic and poor ventilation of the street. At the sampling site located at the southern part of the town, the maximum daily average value was also recorded in summer and it was 46.0 μg m^{-3}. The maximum daily average value of 106.6 μg m^{-3} at the sampling site in western part of the town was measured in autumn while the same value for the sampling site in northern part of the town was 72.7 μg m^{-3}, measured in spring.

Table 1. Mass concentrations of ozone (μg m^{-3})

Sampling site: north					
	spring	summer	autumn	winter	total
N	25	26	30	28	109
C±STD	40.1±15.3	19.2±6.8	27.9±14.9	9.0±7.6	23.8±16.3
C_m	3.7	4.4	2.5	3.0	2.5
C_{50}	37.2	20.3	30.0	7.1	22.0
C_{98}					61.6
C_M	72.7	36.8	57.8	45.2	72.7
Sampling site: south					
	spring	summer	autumn	winter	total
N	31	32	32	32	127
C±STD	2.3±2.1	17.0±9.1	5.3±4.7	0.8±0.8	6.4±8.3
C_m	0.3	6.5	0	0	0
C_{50}	1.3	14.0	3.9	0.8	2.5
C_{98}					30.6
C_M	7.7	46.0	16.7	3.4	46.0
Sampling site: west					
	spring	summer	autumn	winter	total
N	31	32	32	32	127
C±STD	11.7±6.9	36.6±18.2	42.3±29.6	2.2±1.9	23.3±24.4
C_m	4.0	15.7	6.6	0	0
C_{50}	11.0	25.7	30.0	2.0	16.8
C_{98}					83.4
C_M	28.8	68.7	106.6	7.8	106.6
Sampling site: center					
	spring	summer	autumn	winter	total
N	31	25	32	32	120
C±STD	20.6±14.7	67.3±45.9	34.4±28.1	5.4±5.0	29.9±34.5
C_m	2.3	6.2	6.7	1.5	1.5
C_{50}	14.3	57.0	28.8	2.7	19.3
C_{98}					140.2
C_M	58.7	162.7	135.2	22.1	162.7

N - number of samples C±STD - average values ± standard deviation C_m - minimum value
C_{50} – 50th percentile C_{98} – 98th percentile C_M - maximum value

The minimum daily averages of ozone concentrations were below 1 μg m^{-3} and they were measured at sampling sites in southern and western part of the town during winter sampling period.

One way analysis of variance shows significant statistical difference ($P<0.001$) in mass concentrations of ozone between sampling sites during each sampling period. Mass concentrations of ozone were high at the sampling site in city center and low at the sampling site located in the southern part of the town. Significant statistical difference ($P<0.001$) between seasons was also found. Values were elevated during summer sampling period and low during winter sampling period at all sampling sites. Higher ozone concentrations in summer months are consequence of high temperatures and intense sunlight which both have positive influence on forming ozone.

The Ordinance on Recommended and Limit Air Quality Values based on the Croatian Law on Air Quality Protection defines the following values for ozone:

Recommended value of 98th percentile (RV_{98}) = 110 μg m^{-3}, for average time 24 hr
Limit value of 98th percentile (LV_{98}) = 150 μg m^{-3}, for average time 24 hr.

The RV_{98} and LV_{98} values are used to categorize the air quality of the area with respect to ozone:

1st category - clean air (concentration values, C_{98}, are below RV_{98})
2nd category - moderately polluted air (concentration values, C_{98}, are above RV_{98} but below LV_{98})
3rd category - polluted air (concentration values, C_{98}, are above LV_{98}) (Ordinance, 1996).

The limit value was exceeded only in the city centre on two occasions during the summer sampling period, amounting 1.7% of measured results (Table 2). The excess of recommended value was also recorded only at the sampling site in city centre and that was on two occasions in autumn and three in summer (4.2% of measured results).

Table 2. Frequency of days with high average daily concentration of ozone.

	Frequency of days with concentrations of ozone higher than μg m^{-3}			
	110		150	
sampling site	N	%	N	%
north	-	-	-	-
south	-	-	-	-
west	-	-	-	-
center	5	4.2	2	1.7

Throughout the overall measuring period, the 98th percentile value for sampling sites located at the southern, northern and western part of the town did not exceed RV_{98}. Therefore, the air at that three sampling sites was clean with respect to ozone, that is, it was of the 1st category of air quality. The 98th percentile value for the sampling site located in the city center exceeds the RV_{98} but not the LV_{98}, so the air was of the 2nd category with respect to ozone findings. The results of air quality categorization should be taken with caution because the mass concentrations of ozone were not monitored for the entire year.

CONCLUSION

The results show that the mass concentrations of ozone varied with seasons, with elevated values during the summer period at all sampling sites. The highest concentrations were measured at sampling location in city center where they

exceeded the recommended value for the 98th percentile. The mass concentrations of ozone at sampling sites located at the southern, northern and western part of the town were low throughout the whole measuring period and they did not exceed the recommended air quality values.

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Global and Regional Environment

The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

A PRACTICAL PERSPECTIVE ON LOCAL AIR QUALITY MANAGEMENT IN THE UK

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ABSTRACT

A system of air quality management was introduced into the United Kingdom in the late 1990's. There is an overarching national strategy but the primary duty to assess and review air quality against air quality objectives is placed with local government. Such a system has many benefits, particularly that the assessment of air quality is made using local knowledge and the results are more likely to obtain public acceptance. There are also certain disadvantages with the local approach described, for example the fact that it focuses on individual air pollutants. It is argued that this could lead to the wider air quality issue being marginalised and/or not treated properly by the policy makers.

In this paper, the development of regional responses to air quality management is discussed as well as the advantages that such initiatives can provide. Recognising that there is still much we need to understand about air quality management, the paper describes briefly the "tools" needed in order to deliver improvements in air quality more "holistically". These tools not only include scientific knowledge, but also expertise related to the establishment of local government partnerships able to deliver improved air quality across a region or an "airshed" more efficiently.

KEYWORDS

National policy, Regional strategies, Air Quality Management Areas, Airsheds

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INTRODUCTION

In response to growing evidence that air pollution poses a risk to human health and the wider environment, international and national initiatives have been developed in order to achieve improvements in ambient air quality. Concern has arisen regarding pollution impacts related to acid deposition, ground-level ozone, heavy metals, volatile organic compounds, particulates, etc. Recognising that many air pollutants have a transboundary nature, the international community has responded by establishing agreements, which have been translated (to a certain extent) by national governments into pragmatic local initiatives.

In European Union, following the adoption of the air quality "framework" directive on ambient air quality assessment and management (European Council, 1996/62/EC), a series of air quality objectives to protect human health and ecosystems have been established. Member States and their local authorities are required to monitor air quality, provide information to the public, and introduce mitigation plans where ambient levels fail to meet the prescribed criteria.

In addition, the Convention on Long-Range Transboundary Air Pollution (UNECE, 1979) led to adoption of the "Gothenburg Protocol" for the abatement of acidification, eutrophication and ground-level ozone. In European Union, the National Emission Ceilings directive (European Council, 2001/81/EC) and the directive on the limitation of emissions of certain pollutants into the air from large combustion plants (European Council, 2001/80/EC) set legally binding emission ceilings for each Member State for each of the pollutants covered by the Gothenburg Protocol. These emission ceilings are set at a level at least equal to, and in many cases more ambitious than, those required by the Gothenburg Protocol.

Currently, European Union work on air quality is being co-ordinated under the Clean Air For Europe (CAFÉ) programme. This programme is set to review the implementation of air quality directives and the effectiveness of air quality programmes in EU countries. Furthermore, CAFÉ aims to improve air quality monitoring and public information, as well as to promote relevant scientific research. As an example of current research, the INTEGAIRE project (Integrated Urban Governance and Air Quality Management in Europe), within the framework of CLEAR (Cluster of European Air Quality Research), explores solutions to key challenges for urban governance and air quality management throughout Europe (www.integaire.org).

Overall, this accumulation of policies regulating and improving air quality in Europe may have resulted in a fragmented approach for some countries. As a result, as the UK National Air Quality Strategy acknowledges, there is a plethora of terms, definitions and concepts whose application and relation to each other is at best unclear and at worse confusing or even contradictory (DETR, 2000). This paper sets out to briefly discuss how a framework strategy can deliver improved air quality and whether air quality can be obtained by adopting a more holistic approach. It draws from the experience in the UK, where a method of air quality management was introduced five years ago.

THE UNITED KINGDOM APPROACH

In the UK, the National Air Quality Strategy provides a framework to understanding the impact of eight pollutants and establishes who is responsible for reducing emissions. The pollutants included in the strategy are: carbon monoxide, lead, 1,3-butadiene, benzene, sulphur dioxide, nitrogen dioxide (NO_2), particulates (PM_{10}), and ozone.

The national strategy explicitly acknowledges that in order to tackle these pollutants, we need to work on many fronts involving all sectors of society. Integral to the strategy is that local government must review and assess air quality in their locality against future objectives, which reflect national expert opinion and are in agreement with the relevant EU directives.

Where a local authority identifies a location where it predicts that an air quality objective is unlikely to be met, then it must declare an Air Quality Management Area (AQMA) and work with the local community to design and implement an action plan to improve air quality (DEFRA, 2003).

Implicit behind this approach is that the majority of air quality improvements will be achieved by the adoption of international and national initiatives, such as those included in the EU Auto-Oil II Programme related to the development of legislation controlling vehicle emissions and fuel quality (European Commission, 2000). It was thought that where local authorities declared AQMAs, that would be mainly because of local air pollution emissions.

The devolved UK system has many advantages:

1. Separation between policy makers and the local authorities. Potentially the local authorities become the watchdog of air quality.
2. The process over time generates experts in air quality spread throughout the community, potentially providing better decision making in the future.
3. Air quality management is based upon local knowledge, delivering solutions proportionate to the problem at the appropriate level.
4. The appropriate tools (monitoring equipment, dispersion models, emission inventories) can be used to assess local air quality.
5. Local acceptance, as local authorities are more accountable than a national organisation.

However, there are deficiencies with this approach:

1. Local authorities are charged with many and often contradictory duties and functions. For instance local government is charged with enabling economic development and the provision of new housing.
2. Local air quality management requires a long term commitment and perspective, yet because of the democratic nature of local government and the ever growing burden of new initiatives, air quality can quickly loose its importance, slipping into a specialist “backwater”.

3. The very term "air quality" causes confusion, often compounded by terms such as "poor", "good", "low", "high". This apparent lack of consistency and the use of scientific terminology can cause confusion and misunderstanding for the elected representatives and the public.
4. The National Air Quality Strategy places the emphasis in assessing and reporting local air quality rather than in finding practical solutions, developing regional pollution control strategies, etc.
5. Ground-level ozone and greenhouse gas emissions are not tackled at a local level (Vardoulakis et al., 2003).

LOCAL AIR QUALITY AND APPROPRIATE SCALE

In the UK, approximately 120 AQMAs have been declared so far, most of them relating to exceedences of the NO_2 and PM_{10} objectives.. Many of these locations are beside major roads in urban areas, principally in large conurbations (Beattie et al., 2002). The UK approach of tackling air pollution at a local scale would appear more effective where a hotspot is mainly attributable to a single source, whether that be a point source or a line source such as a local road.
However, on reviewing the status of air quality in the UK, a number of themes are emerging regarding the management of air quality. These themes, which may be recognisable elsewhere, are to some extent interrelated:

1. In the draft report "Nitrogen Dioxide in the United Kingdom" by the UK Air Quality Expert Group (AQEG, 2003) concern is expressed that to achieve an overall improvement in air quality each pollutant should not be treated in isolation. The report argues the need to explore and understand the implications of air pollution "trade-offs". The AQEG argue that the general approach of focussing on one air pollutant at a time could lead to contradictory management strategies that improve air quality for one pollutant or in one location at the expense of other air pollutants or other locations. The AQEG is of the opinion that a more flexible and holistic approach to air quality management is required.
2. In many parts of the UK, air quality is principally determined by underlying regional background concentrations of air pollutants rather than by the local contribution. Particularly where exceedences of air quality standards are associated with pollution episodes, such as winter or summer smog events. Yet, the present regime requires local authorities to design and implement management plans that can only address the local contribution. The danger is that such management plans may be inappropriate in addressing the main underlying cause of the exceedences. Consequently, improved air quality will not be achieved and air quality management will loose local acceptance.

3. Many of the AQMAs are declared due to exceedences beside major roads, often of regional, national and international importance. The users of these roads are not just local residents. Therefore, to manage the wider traffic flow, it is necessary to engage with agencies and organisations at a regional, national and possibly international level. Plans that address only local derived pollution will be perceived as punishing the victim.
4. Local authorities are tasked with many, often contradictory, tasks. There is a perception that if local authorities were to base decisions solely on the delivery of improved air quality, then other objectives such as urban regeneration or the reuse of brownfield sites would not be achieved. Conversely, by introducing air quality standards, developers may begin to seek development to the air quality ceiling. Instead of improving air quality this approach will cause a deterioration of air quality over a wider area. This may lead to an increase in the long-term concentration of secondary pollutants such as ozone and secondary particulates.

DEVELOPING REGIONAL APPROACHES TO AIR QUALITY MANAGEMENT

In response many local authorities are forming partnerships to develop regional or sub-regional approaches to air quality management. These groups originally were formed to ensure consistency in assessing air quality, to share costs and to exchange information. As these initiatives developed, regional groupings have begun to recognise the importance of regional co-operation (Air Rives Manche, 2000).

Even with regional groupings, when it comes to action and strategies to improve air quality, it appears that advantages of a local system might begin to wane. With the current guidance and administrative systems in the UK, local government may be unable of providing the necessary improvements in air quality as:

1. The present approach to air quality management focuses on each pollutant in isolation. This may unwittingly lead to higher concentrations of a different air pollutant elsewhere.
2. The UK has a large numbers of vehicles on its roads; it is difficult for local authorities to control these mobile sources that each day may cross many regional boundaries.
3. Where an AQMA has been declared partly because of higher levels of imported background pollution, any resulting action to reduce local emissions is unlikely to obtain local acceptance.

Yet to "throw the baby out with the bath water" and abandon the current devolved approach to a more centralised system would ensure the loss of the many advantages listed previously.

A WAY FORWARD

In response to these possible failings, perhaps we should begin to explore some of the following areas of research and administration in order to support and complement a local approach:

1. Developing conceptual models that enable decision-makers at many levels to assess air quality as a whole rather than on a pollutant by pollutant basis.
2. By developing a holistic approach to air quality, we may be able to assess more effectively the wider benefits of permitting development in existing air quality hotspots, in order to avoid development to air quality ceilings.
3. To consider air quality within its wider meteorological context. By establishing why and when air pollution exceedences may occur across a region, we can then design and implement strategies that deal with such episodes.
4. Design and implement strategies that enable a progressive decrease in background air pollution. For instance, future concentrations of urban NO_2 may not decrease as predicted. This may occur due to slowly increasing of background ozone concentrations altering the relationship between NO_2 and NO_x and the move toward catalytically-regenerative particulate traps that are being retrofitted to diesel powered vehicles. (AQEG, 2003)
5. Considering linking air quality to other parameters of environmental derogation and community safety. The majority of AQMAs are due to traffic-related air pollution. Those living in these areas, already recognise that the quality of their environment is poor. They may not only suffer from air pollution, but also from road traffic noise, community segregation and road accidents. Approaching AQMAs on a broader scale may ensure greater public acceptance.

In order to achieve a more holistic approach, we may need to consider the concept of "airsheds" with regard to pollutants observed within a geographical area, taking into account their residence time and ability to form secondary pollutants.
We need to consider what are the pollution sources related to an airshed. Particularly with regard to transport related pollution. We may define airsheds local action but enabling a wider perspective of air quality management. A wider range of organisations and skills would need to be established to understand the chemical and physical processes taking place in the airsheds. In order to develop and implement air quality management plans, a far wider range of organisations would need to become involved, including the Highways Agency, the Environment Agency, etc.

CONCLUSION AND IMPLICATIONS

The existing air quality management system in the UK provides many advantages, but there appear to be a number of possible weaknesses. This paper describes briefly the present approach to managing air quality in England, focusing on

some of its shortcomings. It suggests that a more holistic approach to air quality management should be adopted and explores alternatives that build upon the devolved regime, linking into local, regional, national and international strategies. Although the current regime is still in its early days, it would be appropriate to undertake a critical review of whether the system is capable of improving air quality at local hotspots. We believe that modifications not only need to address technical aspects of air pollution, but also administrative regimes that enable the integration of air quality considerations throughout local government, regional organisations and national agencies.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

ATMOSPHERIC POLLUTION MAP IN A WIDE INDUSTRIAL AREA: MONITORING AND FORECASTING BY MEANS OF GROUND-BASED REMOTE SENSING DATA

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ABSTRACT

A statistical methodology to forecast air pollution is developed for a wide industrial area on the Eastern Sicilian coast, Italy, monitored by a network of 29 stations measuring the pollutant concentration and meteorological data at ground level. The thermal and wind vertical profiles of the lower atmosphere are measured continuously by a Radio Acoustic Sounding System (RASS) and by a phased array SODAR, respectively.
Specially designed software has been developed in order to store hourly profiles and pollutant measurements, to give a graphical presentation of major selected features and to obtain the pollution inducing conditions of the area surrounding the station, ignoring the amount of emission. The developed model works out the distributions of atmospheric parameters correlated to pollution conditions and uses them to compute the pollution probability combining atmospheric parameters forecasted with those measured by remote sensing systems referred to the last three hours. The predictability of these parameters is discussed. Forecast maps describing air pollution concentration for the three stations most representative of the area are obtained.

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INDEX TERMS

Radio–acoustic remote sensing, atmospheric pollution, statistical model, pollution forecast.

INTRODUCTION

The possibility to forecast the distribution of pollutant concentration near the ground with high spatial detail offers the opportunity to constantly monitor and manage the territory.

Air quality modeling procedures includes: analytical (Gaussian), numerical (Eulerian or Lagrangian), statistical or empirical, and physical models. Models measuring the dispersion of pollutant in atmosphere (Carruthers et al., 1994; Ferrero et al., 2000; Tinarelli et al., 1994); can forecast the behavior of the substances emitted from identified sources, using data from meteorological instruments. These models can supply the distribution of pollutant concentrations on the ground, and are used for the management of thermoelectric power plants, industries, etc. and are useful in case of exceptional events such as a highly dangerous pollutant escape.

A specially designed model, with forecasting abilities of air pollution, has been developed, working independently from the knowledge of the sources (Biamino et al., 2001). This model uses temperature and wind vertical profiles, measured by RASS and SODAR, and concentration data from ground stations. The local values are correlated to the characteristics of the thermal profile and the direction and* intensity of the wind at a selected altitude. On the basis of stored and statistically analyzed data, the model is able to forecast the pollution in the area surrounding the ground station.

THE INTERCONNECTED GROUND STATIONS NETWORK

Figure 1 shows the industrial area on the East Coast of Sicily in Italy where many companies are working and where chimneys of different heights emit various kinds of smoke. There are 29 measuring stations distributed over a wide area (~ 40 x 25 km^2) mainly near urban zones. The measured quantities are concentrations of SO_2, NO_X, NO_2, NO, CO, O_3, H_2S, CH_4, NMHC (non-methane hydrocarbons), THC (total hydrocarbons), etc. Moreover, the stations contain instruments measuring atmospheric parameters at ground level: temperature, wind direction and velocity, rain intensity, radiation etc.

A remote sensing station is also operative near the center of the area including a RASS and a SODAR systems in order to measure temperature and wind vertical profiles in real time.

The RASS system is able to measure the vertical profile of temperature, with continuity, good resolution and low cost, avoiding all the limitations of traditional systems (e.g. radiosondes on tethered balloons, airborne thermo-probes, meteorological towers, etc). Our RASS operates with pulsed acoustic waves and continuous electromagnetic waves (Bonino et al., 1981; Trivero et al., 2000). The

SODAR computes wind profile measuring the Doppler shift, due to air speed, of a known frequency emitted acoustic wave.

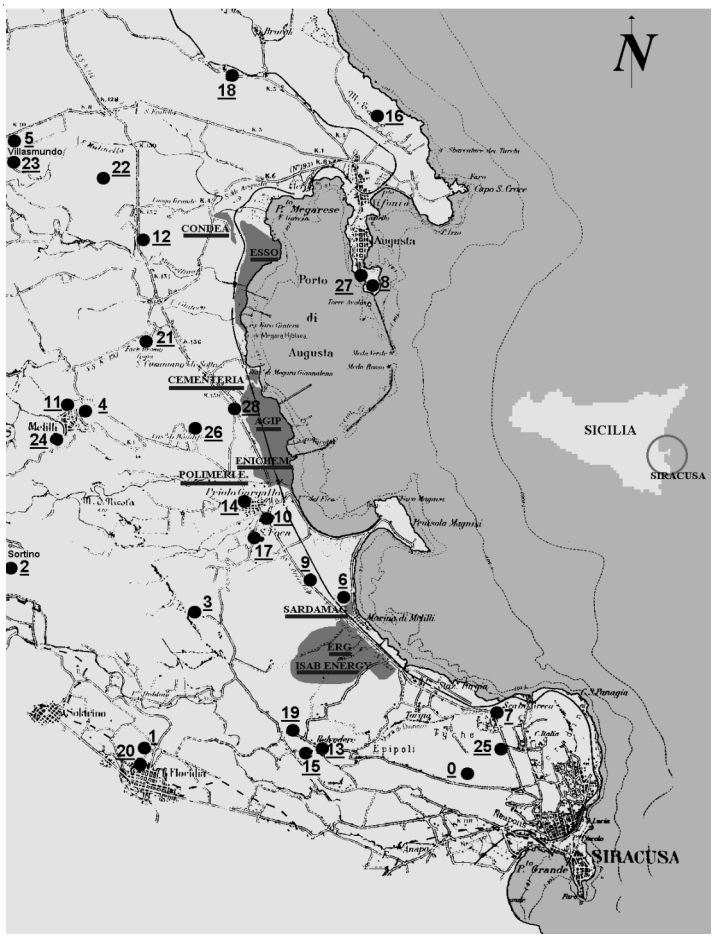

Figure 1. Map of the industrial area. The numbers from 0 to 28 refer to the measuring stations.

THE MODEL

An interactive, specially designed software has been developed with the aim of storing the data, giving a graphical representation of different parameters and yielding statistics and pollution forecast. The software works on the basis of the data supplied by RASS, SODAR and survey stations; the data is imported from several formats supplied by the various systems and is stored on a single database, relative to a time period specified by user.

The program is able to plot: temperature and wind components at four selected altitudes, top and bottom thermal inversion and stability altitudes, inversion and

stability indexes; SO_2, NO_2, O_3, NMHC concentration values measured by ground stations; pre-alarm, alarm and emergency conditions.
The rationale for the choice of the parameters needed to forecast pollution conditions has been the search of the atmospheric layers stability in conjunction with the wind direction.
When a stability condition occurs over a chimney top, trapping of smoke is expected. The altitude of the stable layer is important for pollutant diffusion. For example if there is a ground based thermal inversion with inversion and stability top levels under smoke sources, we have no pollution. Otherwise, smoke emitted under inversion and stability top is trapped near the soil. In these conditions, if in addition a layer of instability in the first tens of meters from the ground is established, then the upward and downward turbulent flows can determine the fall back of the smoke emitted from the chimneys. For this reason the analysis of RASS temperature profile becomes a fundamental element. The wind direction and intensity at the altitude of smoke plumes furnished by SODAR then indicates areas involved.
The data has been acquired over more than 6 years, with hourly regularity.
We calculate the distributions of atmospheric parameters for concentration values exceeding a high threshold and the second when the concentration is under a low threshold.
Figure 2 shows the horizontal wind direction at an altitude of 150 m when concentration of SO_2 rises over 80 μg/m^3 (pollution probability density curve *p(x)* – gray dots) and fall under 20 μg/m^3 (clean air probability curve *q(x)* – dark dots). The curves are well separated and clearly indicate the direction of the wind inducing pollution.

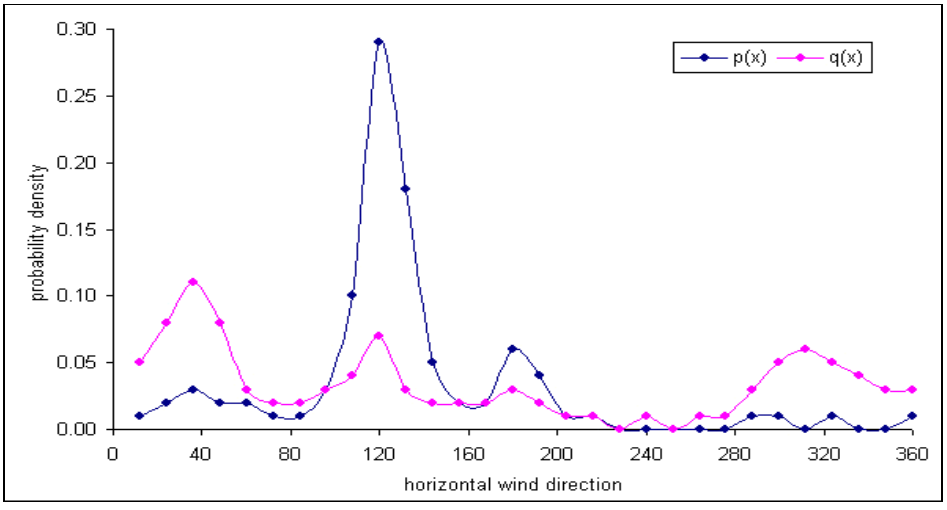

Figure 2. On y-axis: pollution probability density curve *p(x)* (for concentration of SO_2 over 80 µg/m^3 - light gray dots) and clean air probability curve *q(x)* (for concentration of SO_2 under 20 µg/m^3 - dark dots) at an altitude of 150 m for Villasmundo station during the summer on the period 1996-2001; on x-axis: horizontal wind direction.

The probability is obtained with the following formula:

$$p_x = \frac{p(x)}{p(x) + q(x)} \tag{1}$$

Similar distributions are obtained for the other parameters. Some paired curves $p(x)$ and $q(x)$ are separated; others completely overlap, indicating the importance of parameters useful for pollutant forecast. Using all the paired distributions we evaluate the ability of each parameter in predicting pollution. Table 1 indicates the predictability factors (in arbitrary units): the higher values correspond to a major predictability capacity.

Table 1. Predictability factor - Villasmundo during the summer

Parameter	*factor*
horizontal wind direction	0.152
temperature at ground level	0.101
stability index	0.080
base inversion temperature	0.073
top inversion altitude	0.070
top inversion temperature	0.068
top stability temperature	0.063
base to top inversion index	0.062
temperature at 150 m	0.058
top stability altitude	0.057
horizontal wind intensity at 150 m	0.056
base inversion to top stability index	0.050
base inversion altitude	0.047
vertical wind component at 150 m	0.033
top inversion to top stability index	0.029

Similar values are obtained for Melilli and Belvedere stations during the summer and winter months.

Another way to obtain the pollution distributions consists in modifying the measured pollutant concentrations by the following formula:

$$s' = 1 - e^{-\frac{s}{s_0}} \tag{2}$$

were (s') is the modified concentration, ranging from 0 to 1, (s) is the actual concentration and (s_0) a reference value in mg/m^3 .

The statistical distribution (histogram) for each meteorological parameter is finally obtained averaging all the measured values included in a chosen interval weighted with the (*s'*) value.
These statistics constitute a rare collection of a long temporal series of atmospheric parameters, correlated to pollution conditions. With the developed software it is easy to obtain analogous statistics for every station of the interconnected network. A single remote sensing point, for RASS and SODAR, is more than satisfactory even in a large area, because the temperature and wind spatial variations are at a minimum when far from the ground.
The statistical distributions of the first four parameters in Table 1 are used to compute the pollution compound probability. The probability is found by multiplying the values corresponding at the time and in the two previous hours, properly weighted.
Figure 3 shows an example of the forecasting ability of the system. The plots in the diagrams show meteorological parameters used to compute the pollution compound probability, the SO_2 concentration (fig. 3a – from top to bottom: temperature of ground level, base and top inversion altitude, stability index, horizontal wind direction, SO_2 concentration) and the pollution probability forecast (fig. 3b - green line) compared with modified pollutant concentration (red line).

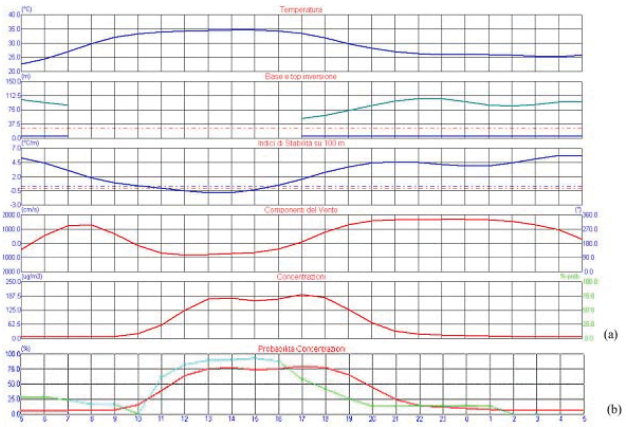

Figure 3. Plots of parameters measured or calculated from profiles and the forecasted pollution calculated from statistical distributions vs. time (hours).

Now the problem is to use this methodology in real time to forecast the alarm conditions. First of all we need to forecast the trend of meteorological parameter in the following hours. We implemented a routine able to do this using both a mathematical algorithm and meteorological forecast. The results are shown in Figure 4. Starting from to 10 a.m. the grey line indicates this evolution for the following 5 hours to be compared with measured data.

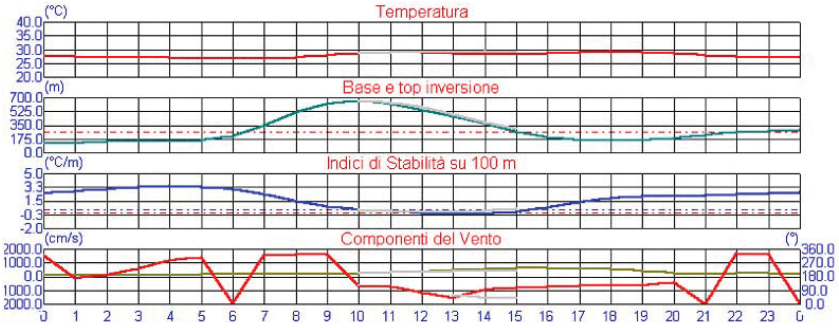

Figure 4. Time evolution (forecast of parameter in the following hours).

The pollution probability for the following hours is then calculated using the time evolution for the selected parameters.
The methodology is easy to apply and able to determine the probability in an automated way.
The data significance can be extended to the area surrounding the station; using more stations, we can obtain a pollution map.

CONCLUSIONS

The developed system is characterized by a remarkable versatility and can be used, more than synthetics archives, like a database in order to search for the best conditions of alarm generation. The examples shown illustrate its potentialities, in spite of intrinsic restrictions like the lack of temporal continuity of RASS and SODAR data that stretches to modify the weights, the vastness of the explored territory etc. Despite this, the forecast ability is reliable.
The analysis system, continuing to store information, gradually "learns" and is able to refine on the choices also in time changing situations (e.g. new sources, or seasonal cycles).

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

POLICIES AIMED AT IMPROVING AIR QUALITY IN URBAN AREAS

G Calabrò*, P Currò

ABSTRACT

The objective of reaching a good standard of air quality in urban areas is a complex problem and one which is difficult to solve.
Respecting the limits laid down by the law and enacting measures to cope with emergencies do not appear to be sufficient to guarantee clean air and to prevent damage to people's health and to the environment.
Drastic changes are needed in the way we produce and use goods and services. This is possible by intervening to limit the sources of pollution and by integrating environmental policies, economic incentives and technological innovation.
In this study we consider the possible contributions to improving air quality in urban areas made by environmental policies and alternative technology in transport. In particular, we will deal with the contributions connected with use of biomasses and alternative energy source.

INDEX TERMS

Air quality management, sustainable mobility, pollution in towns, biofuels, alternative transport

INTRODUCTION

The problem of air quality in urban areas is complex and difficult to solve. Emission sources are numerous and not always controllable, and hundreds of foreign substances are released into the atmosphere, containing many different physical, chemical and biological properties. The problem also concerns internal, domestic, industrial and work environments, with various dimensions and on a local and global level.

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Many laws exist to protect the atmosphere and public health, on a national and community level. On an international level, agreements and protocols have been drawn up with the aim of reaching certain qualities on a global level. An important incentive to environmental policy on a global level is the Kyoto Protocol, against the greenhouse effect and climatic changes, and the Montreal Protocol against the thinning of the stratospheric ozone layer, i.e. the ozone hole.
The European Union has already included the environmental problem in its policy, incentivating ways to reconcile economic growth with safeguarding environmental quality, within a sustainable development.
Urban environments are particularly prone to acoustic and atmospheric pollution, the latter especially connected with energy and transport.
Most of the population is concentrated in towns, where great quantities of resources and energy are consumed producing emissions and refuse which is also exported beyond its borders. Movement of people and goods is responsible for most of the particulate (70-80%) and contributes more than 60% of the urban emissions of nitrogenous oxides (NO_x) and volatile organic compounds (VOC) and more than 90% of carbon monoxide (CO) and other pollutants.
Air quality is mainly tied to traffic intensity, which must be managed by using alternative transport instead of private cars. The situation is more o less similar in urban areas in all developed countries and, in some and in large metropolitan areas of developing countries, the danger level is higher. Every country should therefore cooperate and contribute to solve problems in a global context besides on a local level, because pollution knows no frontiers and any intervention must be related to different contexts, and responsibility must be shared.
Evaluation of the risk to health due to the presence of dangerous substances in the air requires accurate information and data, elaborated on valid models of exposure of the population in general living in urban areas congested by intense traffic and industrial activity, and people working in open or confined areas or who move during working hours.
National, community or international laws establish limits for many specific dangerous substances regarding levels of professional exposure during production, distribution and use, and levels of external exposure. The aim is to maintain these levels of exposure at values low enough to exclude damage to health and to the environment. In order to evaluate real risk, the problem is to fix a “biological zero” which, unlike a utopistic “analytic zero”, represents the danger level at which a given contaminant has harmful effects.
More inter-disciplinary studies and research are needed to monitor dangerous substances present in the air, to verify the respect of limits and for biological monitoring.
The European Union is carefully following the situation of air quality in metropolitan areas of many towns where situations of constant emergency exist. European environment official Margot Wallstrom declares that they indicate “the difficulty Europe faces in efficiently handling problems of atmospheric pollution

and the need to put into practice a series of long-term radical measures. Besides laws, structural measures are needed to allow interventions not only in emergencies". CE Directive 96/62 of The Council, adopted by Italian law under law n. 351 4 August 1999 concerning the evaluation and management of air quality, for example, defines and establishes aims of atmospheric air quality to prevent or reduce harmful effects on human health and the atmosphere. CE Directive 99/30 establishes the procedures to harmonize the monitoring of concentrations on a European level in order for State Members to exchange information and to inform the public and optimise any action necessary to minimize the effects of pollution.
The new European Union regulations which came into force in 2005 make its compulsory for State Members to inform the European Commission when danger levels are exceeded. They also introduce more restrictive parameters which are more suitable to safeguard public health and which verify if the measures taken by State Members, if danger levels of air quality are exceeded, are sufficient to guarantee public health.

PRESENT SITUATION IN URBAN AREAS AND PROSPECTIVES

Air quality requires a policy of integrated management. Many of the polluting substances present in the air of urban areas [carbon monoxide (CO), nitrogenous oxides (NO_x) benzene, aromatic polycyclic hydrocarbons, particulate] are daily monitored at fixed and mobile stations and restrictive measures must be taken when values exceed danger levels.
It is obvious that it is not enough to monitor and control the few regulating parameters relative to so-called large pollutants in order to have reassuming information on the quality of the air we breathe. The air constantly deteriorates due to dangerous chemicals directly emitted into the air or formed as a consequence of chemicals and/or photo-chemical reactions.
Air quality is the result of a complex interaction between anthropic factors, such as urban structures and weather conditions like turbulence, atmospheric stability, temperature, humidity etc.
Processes of dispersion and dilution of the substances released into the air and the chemical and photo-chemical reactions occurring in the atmosphere depend on these factors. For some pollutants, 70-80% of emissions on a national level occur within urban areas. The structure of towns, the spreading of centres of activity and residential areas and the increasing need for mobility of people and goods, which is a characteristic of modern society, contribute in a significant way to the deterioration of air quality. This is especially true in Italy, where the main means of land transport is carried out on roads. Private cars are the most widely used means of transport. The use of cars has determined a model of behaviour which is a symbol of freedom and prestige which people find difficult to renounce. The role of cars in our society has meant a boom in the number of cars on the roads, and an increase in energy consumption, equal to a third of our national energy consumption. The present

system of mobility of people and goods based on vehicles and individual transport, is the main cause of acoustic and atmospheric pollution in towns. Cars are responsible for 23% of national polluting gas emissions and for 40% of greenhouse effect emissions, energy waste and traffic congestion which make our towns unsafe and impossible to live in. We must not underestimate that two or three-wheeled vehicles do not pollute less than cars, and the European Union has considered the reduction of polluting emissions of two or three-wheeled vehicles in the Directive 2002/51/CE dated 19 July 2002. Greater attention has been paid to hydrocarbons and carbon monoxide, ignoring emissions of particulate and benzene, whose contribution to the pollution of urban areas is rather significant.

Initiatives are being studied and experimented with the aim of promoting the quality of air and of life in towns, by improving traffic conditions, the energy efficiency of means of transport, by incentivating use of alternative environmental-friendly fuel, by limiting the use of private cars and encouraging the use of public transport, thus favouring a sustainable mobility.

The car industry has realized the environmental problem and has taken this variable into consideration, making it part of its strategy. The laws in force have been taken into account, and modern technological solutions have been carried out foreseeing even more restrictive laws. The car industry has widened its horizons, planning vehicles and engines and even the quality of fuel. One of the central factors vital to the improvement of air quality is the reduction of the consumption of traditional combustion and emissions, locally and globally. In this field, European industries are in the lead, with an average consumption of 7,4 lts/100 kms against the 7,5 of Japanese industries and 10,8 of the USA. It has been undertaken to further reduce this consumption by 20% by 2010. In Italy the present quantity of 7,4 lts/100 kms should go down to 5,5 lts/100 kms in 2010. Fiat has realised a prototype of a car called "Ecobasic" which proposes several technological solutions allowing a reduction in consumption down to 3 lts/100kms. Lower consumption means fewer polluting emissions and a reduced carbon dioxide emission which is one of the greenhouse effect gases. The European Automobile Construction Association (EACA) has stipulated a voluntary agreement to lower the present level of carbon dioxide from 186 to120 g/km by 2008, in order to minimize the greenhouse effect. The car industry has also promoted strategies regarding the reduction of the weight and improvement of the aerodynamics of cars, the introduction of new vehicles functioning on alternative energy, and the financing of tree-planting, because trees are a natural absorber of carbon dioxide to counteract the greenhouse effect. The petrol industry has improved the characteristics of fuel, for example by eliminating lead and lowering sulphur and other pollutant contents. The general use of catalytic exhaust pipes will also contribute decisively to improve the air quality in urban areas. Despite great progress in the field of internal combustion engine vehicles and in the quality of fuel and ever-increasing scrictness of anti-polluting laws, the situation in urban areas is still unsustainable. This is mainly due to traffic congestion and the high number of non-catalytic cars still on the road.

The use of alternative combustion, richer in hydrogen, like natural gas on a middle-long term, or bio-fuel on a short-middle term (eco-fuels), or hydrogen on a long term or the use of electric vehicles can contribute to improve air quality. Many large European cities already have public and private transport functioning on natural gas, bio-diesel or sulphur-free gasoline or electric engines.
Transport by means of electric engines is efficient and economical and can compete with petrol-driven transport with greater environmental benefits, at least in urban traffic. Electric vehicles on the market nowadays use lead accumulators which recharge on normal electrical sockets. Electric battery vehicles have a limited autonomy which is 100-150 kms and have a limited market. They are used for vehicles destined for public transport or daily public transport on short distances. The role of batteries for electric vehicles will probably become less important in the future. Alternatives are ultra-condensers which accumulate energy quickly, fly-wheel which accumulate energy in a moving rotor and combustible cells which generate electricity on board.
Despite several problems, auto-traction hydrogen appears to be a promising alternative to carbon fossils, because it does not emit polluting or greenhouse effect substances. Free hydrogen is not available in nature, but can be produced by water electrolysis or methane reforming. The most promising methods is water-electrolysis, using electricity obtained by renewable sources.
Ireland has moved in this direction, inaugurating the first public auto-traction hydrogen pump in April 2003, obtained by water-electrolysis using geothermal or hydroelectric energy. Hawaii has decided to reduce their dependence on petrol, and in 2000 a plan was formed to plan the production of hydrogen from water to be used in combustible cells. Over the next three years, in Italy, Milan will realize a hydrogen citadel at Bicocca, and experimental hydrogen buses already circulate in Turin. London and Berlin are planning to have the first public buses running on the new fuel before 2005.
A change in the traction system using hydrogen as an energetic vector means great adjustments and a rationalization of the whole system of energy production, leaving behind traditional fossil fuels and changing to renewable energy sources such as photovoltaic, eolic, and biomass energies. This would drastically reduce the energy dependence in Europe and Italy where we find about 84% of the total energy consumption. Economic incentives are needed in the form of contributions to citizens from local administrations, the State or the European Union in order to overcome the consolidated advantages of traditional vehicles and to favour the development and public and private transport of new alternative traction vehicles.

RATIONALIZATION OF URBAN TRAFFIC

Environmental consequences due to urban traffic, such as atmospheric and acoustic pollution and congestion, must be efficiently contrasted in order to improve the quality of life, to fight environmental damage and to protect historical centres and the development of tourism. This can be done by offering an attractive

alternative to the use of private cars, promoting and improving the quality of public road and rail transport. The use of trains would remove thousands of cars from the roads thereby improving air quality and safety. This requires interventions organized by regions in order to overcome emergencies when danger-levels are exceeded and improved structures: new underground trains, trolley buses, cycle lanes etc in order to compensate alternative transport. Some towns have already adopted measures to face traffic congestion emergencies; for example, sometimes there is not much parking space available for offices, so as to make it less practical to use cars. Sometimes fast lanes have been installed for private cars which practise car sharing. In some cases employers or firms help employers by organizing transport or financing collective transport. Alternative actions aimed at lowering traffic congestion by limiting the use of individual cars are:

- **Car sharing**: use of rented cars (even at hourly rates);
- **Car pooling**: sharing of cars belonging to various people for the same journey;
- **Ride matching (Rm):** a group of people who share a car on the basis of each person's needs and availability;
- **Commuter plan**: plan of journeys to and from work;
- **Guaranteed ride home program (Grh):** system which guarantees people who go to work without their car reassurance to get home in an emergency;
- **Park and road pricing**: policy of taxation on roads and parking.

The Urban 2000 program, decided by the EU for Italy, plans to finance plans to improve the environment, such as:

- the reorganization of the transport system, including pedestrian areas, intelligent systems of traffic control;
- the realization of public transport with a high energy efficiency;
- the creation of cycle tracks and environmental corridors.

The factors on which to concentrate for sustainable mobility and a reduction in pollution are: planning, technology and an integrated approach in urban and transport policies.

CONCLUSIONS

The must serious problem that national and local authorities must solve to safeguard air quality in large urban areas is traffic control.
A new approach is the promotion of clean vehicles using environmental-friendly fuel and the development of good public transport which is comfortable, rapid, flexible and ecological and satisfies traveller's requirements.
Research and developments have led to progress in the creation of new vehicles fuelled by alternative energy, with reduced emission levels which are at present used in many European towns. Extension to private cars and lorries could improve

air quality in urban areas. In order to favour this new approach to the management of air quality in urban areas, the European Union has published a green book on the safety of energy supply and has proposed the substitution of 20% of classic fuel with alternative fuel by 2020 as an aim for road transport.
The following measures have been presented by the Commission to promote the policy of alternative transport:

- a Directive to gradually introduce a minimum percentage of compulsory consumption of bio-fuel in every State Member. At first 2% is suggested leaving a maximum flexibility: use of bio-fuel mixed with fossil fuel or pure bio-fuel. In this way, unforeseen effects on engines and the environment are avoided. The second phase foresees a percentage of 6% in the penetration of bio-fuel by 2010;
- new Community regulations concerning fiscal drags for bio-fuels, bearing the need to make national fuel taxation equal in mind. This proposal will help State members create the necessary economic and legal conditions to reach the aims indicate in the proposal in the previously mentioned Directive. According to this proposal, member States will be able to foresee calibrates fiscal drags, according to accounts, local conditions and their technological choices;
- policies of incentivation for the purchase of more environmental friendly vehicles.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

THE IMPACT OF CURRENT TREND OF CLIMATE CHANGE ON AIR POLLUTION POTENTIAL IN TAIWAN

CM Chang*, LN Chang, KT Kuo and SC Lu

ABSTRACT

The diffusion of air pollutant of a region depends heavily on local weather conditions. Therefore it is interesting to compare air pollution potential among various climatological zones in Taiwan. A simplified climatological dispersion model (TCM) is used to estimate long term average ground pollutant concentration. The maximum ground concentrations are used as an index for the intercomparison of the air pollution potential. Predefined typical stacks with various heights and emission rates are assumed to be the pollution sources.
Hourly meteorological data for four representative CWB weather stations are used in this study. Current trend of the climate change in Taiwan during the last decade(1991-2000) and its impact on air pollution potential are studied. Taiwan is situated in the East Asian monsoon region, with north-easterly winds prevailing in winter and south-wetly winds prevailing in summer.
The north-south oriented central mountain range which has an average elevation of about 2000 m complicates the local circulation patterns on the island. Consequently, regional variation of climate condition and air pollution potential is quite significant. Among four climate zones in Taiwan north, central, south and east, the north and east regions are more favorable for air pollution diffusion with maximum average ground concentration about half that of the central and south regions.
During the last decade, central and east regions slow trend of improving air pollution potential, i.e, more favorable for pollutant diffusion in the region, with yearly rate of decreasing maximum concentration of 3.6% and 0.3% respectively. Meanwhile, a reverse trend is find in north and south regions, with increasing rates of 1.1% and 0.55% respectively, Finally, the seasonal variation of the air pollution potential and its decadal trend is discussed.

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INDEX TERMS

Climate Change, diffusion, air pollution potential

INTRODUCTION

Air Pollution in a region depends on the emission of pollutants and local meteorological conditions. Recently, air pollutant emission in Taiwan is well under controlled. Yet, episodes of high air pollution concentrations in a particular region may still be observed during favorable weather situations. The probability of air pollution episodes occurring may be estimated based on simple atmospheric dispersion models with proper meteorological data and predefined typical air pollution sources. For the present study, the Taxes Climatological Model (TCM) (U.S.Department of Commerce, 1980) is used to calculate the maximum long period mean pollution concentrations for each of the four climatological regions in Taiwan. Representative hourly meteorological data from Central Weather Bureau (CWB) stations in each of the regions in period 1991 to 2000 is employed for model calculations. The calculated maximum air pollutant concentrations are then used as an index comparing air pollution potentials among the four different regions. Current trend of the climate change for each region during the last decade and its influence on air pollution potential are examined. Interseasonal and interannual variations among different regions are discussed.

1. Atmospheric Diffusion Model

The Texas Climatological Model (TCM) is designed to predict the ground level and long-term concentrations of atmospheric pollutants. Calculations are based on the steady state Gaussian plume equation, Briggs plume rise formulations for buoyant and momentum dominated plumes (Briggs, 1969), the empirically derived Pasquill-Gifford (Pasqill,1974) vertical dispersion coefficients, and a meteorological joint frequency function. This model has been approved by USEPA and is used widely in Taiwan.

A rectilinear array with 1km×1km grid size and 40 km×40km in area is used for the calculation of air pollution concentration. A predefined pollution source is located at the center of the array.

2. Sources and meteorological condition

The sources adopted in this work were five stacks of different heights from 20 to 200 meters, and with different emission boiler sizes and emission rates (Yokoyama et al., 1987) (see Table 3.1). The meteorological data adopted in this study included hourly wind direction, wind speed and cloud amount for the period 1991-2000. All data were provided by the CWB.

Table 3.1 Assumed stacks

No. element	1	2	3	4	5
H (m)	20	50	100	100	200
D (m)	0.5	2	3	3	7
Q (g/sec)	2	6	10	400	800
T (°C)	100	100	100	150	200

Remarks:
H: stack height D: diameter Q: emission rates T: temperature
The air pollutant is assumed to be SO_2

RESULTS OF THE MODELING AND DISCUSSION

This study, hourly meteorological data from four CWB weather stations (Fig 4.1), namely Taipei (North), Taichung (Central), Kaoshiung (South) and Hualien

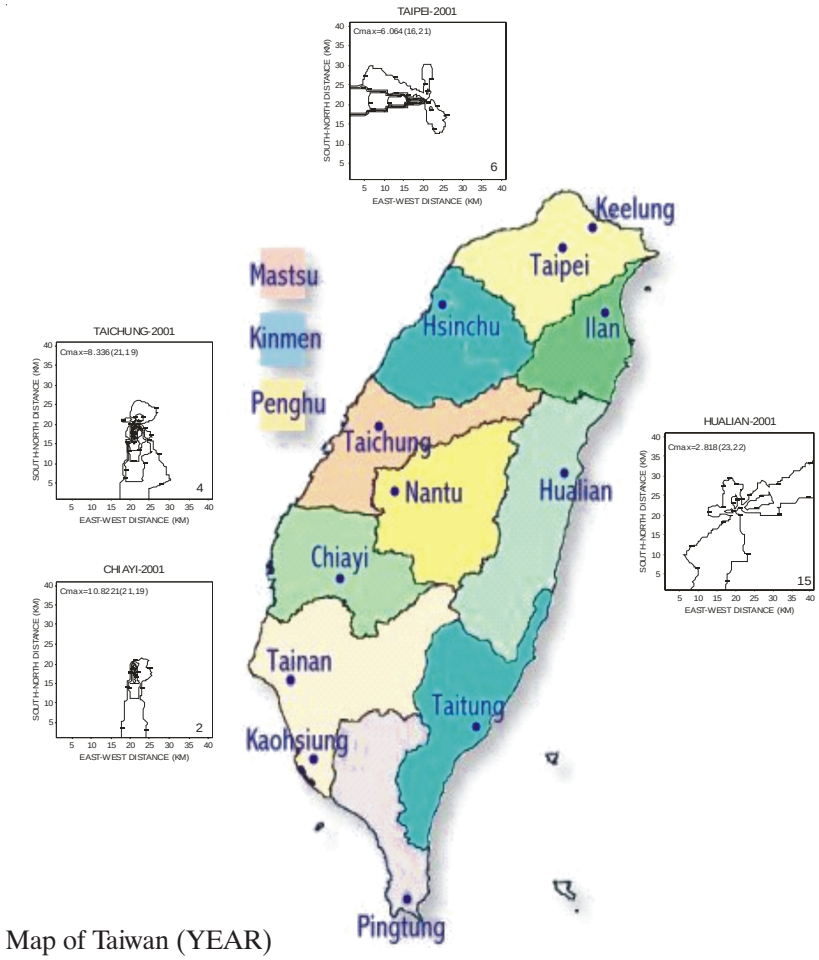

Fig 4.1 Map of Taiwan (YEAR)

(East) for the last decade (1991-2000) and a set of standard air pollution emission inventory (SO_2 for this study) are applied to TCM model. The model simulated seasonal and annual maximum average SO_2 concentration are used as air index for intercomparision of the air pollution potential among four climate regions of Taiwan.

Since the air pollution emission rates are fixed throughout the simulation period and are the same for every region, the temporal and spatial variation of air pollution potential are solely due to the variation in meteorological condition of each region. Table 3 4.1-3.4.4 and Fig 3.4.1-3.4.4 summarize annual and seasonal average temperature, wind speed and maximum average ground SO_2 concentrations (and its grid point location) from 1991 to 2000 for each station.

1. Comparison of the annual and seasonal air pollution potentials among different regions

In spite of the interannual variation, Taichung (Central) show highest annual and seasonal maximum average SO_2 concentrations. This can be attributed to lower wind speed throughout the year in this region. Hualien (East) on the other hand show lowest SO_2 concentration during winter, spring and autumn when north-easterly monsoon prevail and the wind is strong. The SO_2 concentration in Hualien become higher during the summer when south-westerly monsoon prevail and Hualien is then on the lee side of the Central mountain range, and the wind is weak.

Taipei(North) influenced by both north-easterly monsoon during winter, spring and autumn and south-westerly monsoon during summer show low SO_2 concentration throughout the year.

2. Interannual variation of the air pollution potential

2.1 Taipei (North)

From Table 3.4.1 and Fig 3.4.1 we observe a decreasing trend of wind speed and increasing trend of temperature for Taipei station during the last decade. The annual maximums average SO_2 concentrations show a slight increasing trend of about 1.38% per year. Significant increasing trend of SO_2 concentration were also observed during this period with an increasing rate of 1.11% per year for winter, 1.94% per year for summer and 3.85% per year for autumn.

2.2 Taichung (Central)

From Table 3.4.2 and Fig 3.4.2 Taichung area show significant trend of decreasing SO_2 concentrations with a rate of 3.59% per year for annual average and 2.66%, 2.51% and 5.02% per year for those of winter, spring and autumn, respectively. The summer value of SO_2 concentration show only minor variation through out the decade. It is interesting to note that, there were no significant trend of variation of average temperature and wind speed in Taichung area during the last decade, The trend of SO_2 concentration variation must be due to the variation of cloud amount which affect the stability of the atmosphere.

2.3 Kaoshiung (South)

Interannual variations of average temperature and wind speed were observed for Kaoshiung station (Table 3.4.3 and Fig 3.4.3), but no significant trend of increasing or decreasing can be identified. In the mean time, minor trend of increasing annual average SO_2 concentrations at a rate of 0.55% per year was observed.

There were trend of increasing seasonal average SO_2 concentration for winter, spring and autumn with decreasing trend for summer.

2.4 Hualien (East)

Hualien area experienced rather significant interannual fluctuation in average wind speed and temperature, during the last decade (Table 3.4.4 and Fig 3.4.4), The air pollution potential variation responds quite well with that of the wind speed. There was an increasing trend for interannual variation of the winter average maximum SO_2 concentrations at a rate of 1.23% per year. The trend is not sighificant for the other seasons.

CONCLUSION

This study, we adopted the TCM Diffusion Model to calculate the long term mean SO_2 concentration, which is then used as an index for comparing interannual variation of air pollution potential in four climatological region in Taiwan. Clearly, the air pollution potential is strongly influenced by local circulation and atmospheric stability. The locations and values of the maximum concentrations for each area vary significantly between seasons, The mountain valley in central Taiwan and inland areas located downwind of the mountain range are regions of high air pollution potential (Che-Ming Chang et al., 2002).[5]

Taiwan is situated in the East Asian monsoon region, with north-easterly winds prevailing in winter, spring and autumn and south-westly winds prevailing in summer. The north-south oriented central mountain range which has an average elevation of about 2000m complicates the local circulation patterns on the island. Consequently, regional variation of climate condition and air pollution potential is quite significant. Among four climate zones in Taiwan, the north and east regions are more favorable for air pollution diffusion with maximum average ground concentration about half that of the central and south region .

During the last decade(1991-2000), central and east regions show trends of improving air pollution potential, i.e, more favorable for pollutant diffusion in the region, with an yearly rate of decreasing maximum concentration of 3.6% and 0.3% respectively. The trend of decreasing SO_2 concentration is primary due to the change of cloud amount and thus the atmospheric stability. Meanwhile, a reverse trend is find in north and south regions, with increasing rates of 1.1% and 0.55% per year respectively. The trend is related to the weaking of the wind speed.

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Table 3.4.1 Average wind speed, temperature and simulated results of maximum average SO_2 concentrations in 1991-2000 for Taipei (north)

season	Year	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	average	Increasing rate per year
Annual	Wind speed (ms^{-1})	3.9	3.3	2.9	3.0	3.0	2.7	2.9	2.6	2.5	2.7	2.8	2.94	1.38%
	Temperature (℃)	21.9	21.6	21.3	21.5	21.8	22.4	22.5	22.6	23.6	23.0	23.2	22.31	
	SO_2 conc. (ppb)	4.9943	4.2262	2.7193	3.7580	3.4734	4.9684	5.7001	3.5029	4.1719	4.7363	4.6909	4.27	
	Grid point location of Max. SO_2 concentration	14,17	14,17	14,18	14,17	14,18	20,19	14,19	15,20	15,19	14,18	15,20		
Winter	Wind speed (ms^{-1})	3.8	3.7	2.7	3.4	3.1	2.8	3.0	2.6	2.6	3.0	3.0	3.06	1.11%
	Temperature (℃)	16.5	14.9	14.8	14.6	16.3	15.5	16.1	16.6	17.4	16.9	17.6	16.11	
	SO_2 conc.(ppb)	6.5301	5.2942	3.2589	5.0016	3.9728	6.3558	6.7953	4.6060	4.9368	6.7212	4.9656	5.31	
	Grid point location of Max. SO_2 concentration	12,18	12,18	12,18	12,18	13,20	13,20	14,19	13,20	14,17	14,18	14,21		
Spring	Wind speed (ms^{-1})	3.7	3.8	2.7	2.7	2.7	2.4	2.9	2.7	2.2	2.7	2.6	2.83	0.26%
	Temperature(℃)	20.7	21.2	20.3	20.4	20.2	21.2	20.4	22.0	23.0	21.9	21.6	21.17	
	SO_2 conc. (ppb)	4.7632	5.2968	4.2590	3.5614	3.8702	5.7338	5.5332	4.5631	4.1177	4.4244	4.4865	4.60	
	Grid point location of Max. SO_2 concentration	12,18	14,17	12,21	12,18	12,18	20,19	13,20	14,19	18,19	14,18	14,17		
Summer	Wind speed (ms^{-1})	3.5	2.5	2.5	2.1	2.9	2.2	2.2	2.3	2.1	2.0	2.2	2.41	1.94%
	Temperature (℃)	28.6	28.5	28.4	29.0	28.4	28.7	28.8	27.4	29.3	28.4	28.6	28.55	
	SO_2 conc. (ppb)	2.8714	5.2270	4.0544	4.3672	3.0576	8.8600	7.3369	3.9096	4.6516	4.6527	4.2175	4.84	
	Grid point location of Max. SO_2 concentration	20,22	20,22	20,22	19,22	21,19	20,19	20,19	21,19	21,20	22,20	20,22		
Autumn	Wind speed (ms^{-1})	4.4	3.3	3.6	3.6	3.5	3.2	3.4	2.6	3.0	3.1	3.2	3.35	3.85%
	Temperature (℃)	21.7	21.8	21.7	21.9	22.2	24.0	24.6	24.1	24.6	24.7	25.0	23.30	
	SO_2 conc. (ppb)	7.0593	4.6739	4.4202	5.4351	4.4854	5.1938	8.2354	5.7934	6.5849	6.6989	8.5419	6.10	
	Grid point location of Max. SO_2 concentration	14,18	14,18	14,18	14,18	15,19	15,20	15,20	15,19	15,19	15,19	15,20		

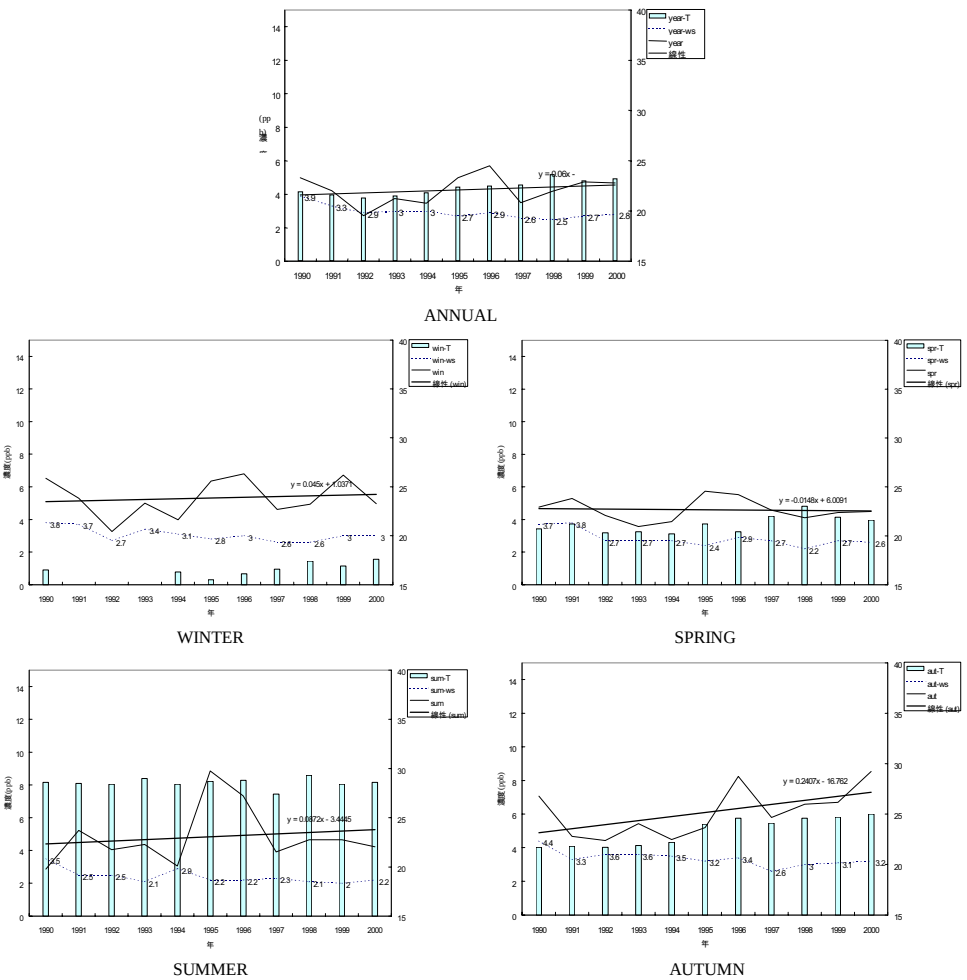


Figure 3.4.1 Interannual variation of the air pollution potential, average temperature and wind speed for Taipei (north) during 1990-2000

Table 3.4.2 Average wind speed, temperature and simulated results of maximum average SO_2 concentrations in 1991-2000 for Taichung (central)

season	Year	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	average	Increasing rate per year
Annual	Wind speed(ms^{-1})	1.6	1.6	1.6	1.7	1.6	1.7	1.7	1.6	1.6	1.7	1.7	1.65	-3.59%
	Temperature (℃)	23.6	23.8	23.2	23.6	23.6	23.1	23.4	23.5	24.5	23.7	23.9	23.63	
	SO_2 conc. (ppb)	10.8547	11.6462	10.8284	9.1318	9.0394	9.8524	10.0473	9.2943	7.9875	7.7551	8.0911	9.50	
	Grid point location of Max. SO_2 concentration	20,18	20,18	20,18	20,18	20,18	20,18	20,18	20,18	20,18	20,18	20,18		
Winter	Wind speed (ms^{-1})	1.8	1.6	1.7	1.8	1.6	1.8	1.8	1.7	1.7	1.9	1.8	1.75	-2.66%
	Temperature (℃)	18.4	17.9	17.1	17.5	18.8	16.5	17.3	17.6	18.6	17.8	18.2	17.79	
	SO_2 conc. (ppb)	13.9116	13.6933	14.4263	12.2701	11.0895	12.5433	14.7159	11.2831	9.9367	11.3129	10.8101	12.36	
	Grid point location of Max. SO_2 concentration	20,18	20,18	20,18	20,18	20,18	20,17	20,18	20,18	20,18	20,18	20,18		
Spring	Wind speed (ms^{-1})	1.5	1.5	1.5	1.6	1.6	1.6	1.6	1.5	1.5	1.6	1.6	1.55	-2.51%
	Temperature (℃)	22.3	24.0	22.8	22.7	23.3	22.6	21.7	23.7	24.4	23.7	23.1	23.12	
	SO_2 conc. (ppb)	10.7550	10.4243	8.4818	7.9986	8.1265	8.6271	9.3443	9.4889	7.8189	8.7020	8.1869	8.90	
	Grid point location of Max. SO_2 concentration	20,18	20,18	20,18	20,18	20,18	20,18	20,18	20,18	20,18	21,18	20,18		
Summer	Wind speed (ms^{-1})	1.6	1.5	1.6	1.8	1.6	1.7	1.8	1.5	1.6	1.6	1.6	1.63	0.80%
	Temperature (℃)	28.0	28.8	28.2	28.6	28.1	28.2	28.8	27.8	28.9	28.1	28.2	28.34	
	SO_2 conc. (ppb)	6.4525	7.3550	7.0057	8.0400	7.2784	6.0757	8.5238	7.1687	7.9701	8.1358	6.3922	7.31	
	Grid point location of Max. SO_2 concentration	20,22	22,21	22,21	22,21	21,21	21,21	21,21	21,21	21,21	20,21	21,22		
Autumn	Wind speed (ms^{-1})	1.5	1.6	1.8	1.6	1.6	1.7	1.7	1.5	1.6	1.6	1.8	1.64	-5.02%
	Temperature (℃)	25.0	24.2	24.2	25.4	24.4	24.9	25.8	25.0	25.8	25.5	25.7	25.08	
	SO_2 conc. (ppb)	13.6642	17.3239	14.5332	13.3600	11.7021	12.6440	12.8985	10.2742	11.0280	8.9588	10.2458	12.42	
	Grid point location of Max. SO_2 concentration	20,18	20,18	20,18	20,18	20,18	20,18	20,18	20,18	20,18	20,18	20,18		

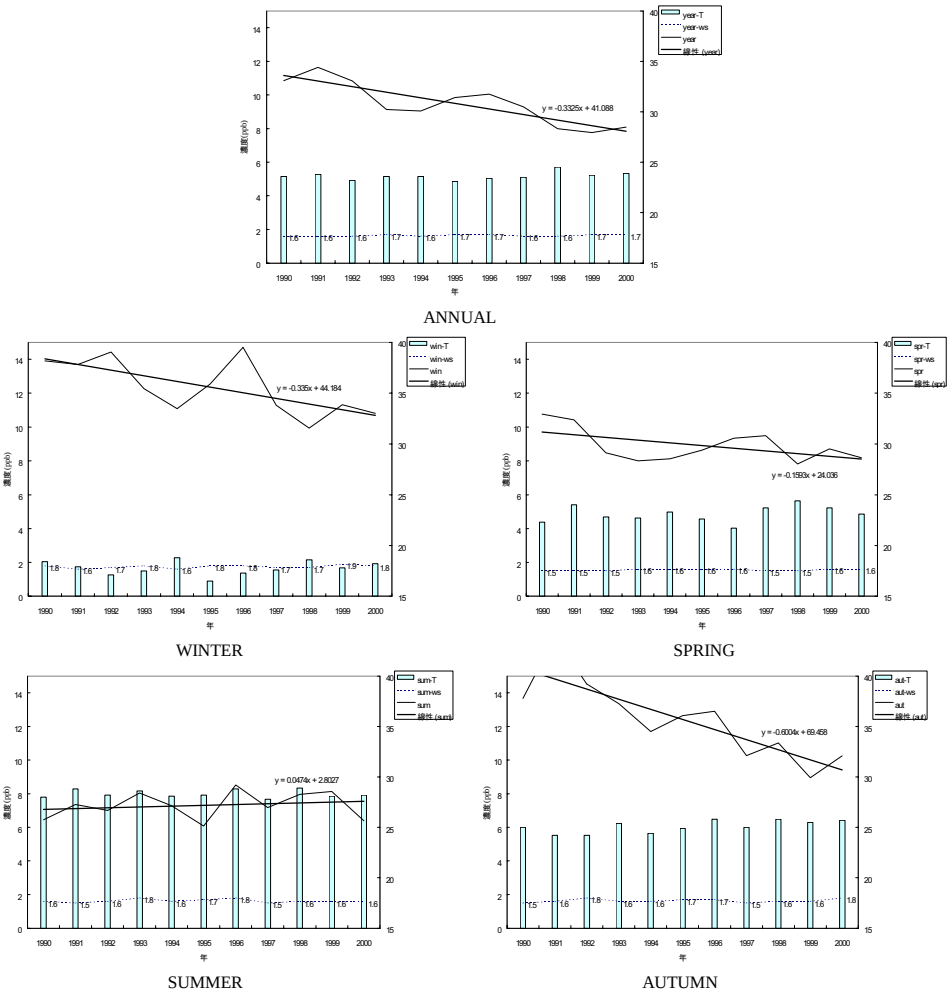
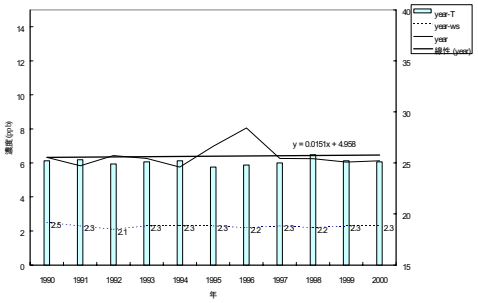


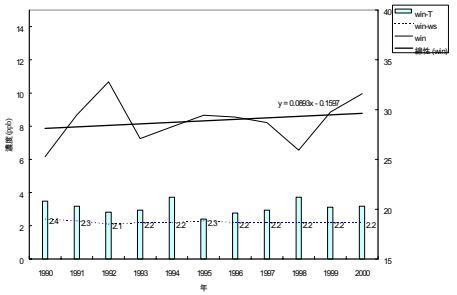
Figure 3.4.2 Interannual variation of the air pollution potential, average temperature and wind speed for Taichung (central) during 1990-2000

Table 3.4.3 Average wind speed, temperature and simulated results of maximum average SO_2 concentrations in 1991-2000 for Kaoshiung (South)

season	Year	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	average	Increasing rate per year
Annual	Wind speed (ms^{-1})	2.5	2.3	2.1	2.3	2.3	2.3	2.2	2.3	2.2	2.3	2.3	2.28	0.55%
	Temperature (℃)	25.2	25.3	24.9	25.1	25.2	24.6	24.8	25.0	25.8	25.2	25.1	25.11	
	SO_2 conc.(ppb)	6.3234	5.8291	6.4293	6.2686	5.7572	6.9800	8.0621	6.2686	6.2510	6.0532	6.1229	6.40	
	Grid point location of Max. SO_2 concentration	22,19	22,19	22,19	22,19	22,20	22,19	22,20	22,20	22,19	22,19	22,18		
Winter	Wind speed (ms^{-1})	2.4	2.3	2.1	2.2	2.2	2.3	2.2	2.2	2.2	2.2	2.2	2.23	1.08%
	Temperature (℃)	20.8	20.3	19.7	19.9	21.2	19.0	19.6	19.9	21.2	20.2	20.3	20.19	
	SO_2 conc. (ppb)	6.1656	8.6850	10.6761	7.2482	7.9680	8.6608	8.5474	8.2178	6.5551	8.8542	9.9633	8.32	
	Grid point location of Max. SO_2 concentration	22,19	20,18	20,18	20,18	20,18	20,18	22,19	20,18	20,18	20,18	20,18		
Spring	Wind speed (ms^{-1})	2.6	2.4	1.9	2.3	2.4	2.3	2.1	2.3	2.2	2.3	2.2	2.27	3.21%
	Temperature (℃)	24.7	26.1	25.2	24.8	25.2	24.8	24.0	25.4	25.9	25.8	25.2	25.19	
	SO_2 conc. (ppb)	6.4483	8.0589	5.9060	8.0061	6.2379	6.8115	8.4679	9.1461	7.1291	9.4257	9.0736	7.70	
	Grid point location of Max. SO_2 concentration	22,18	22,19	20,22	22,19	22,19	22,20	22,19	22,20	20,22	22,19	22,18		
Summer	Wind speed (ms^{-1})	2.8	2.5	2.3	2.5	2.7	2.6	2.6	2.6	2.5	2.4	2.3	2.53	-0.46%
	Temperature (℃)	28.9	29.3	29.1	29.4	28.4	28.6	29.3	28.4	29.2	28.5	28.4	28.86	
	SO_2 conc. (ppb)	5.9475	8.2078	7.5409	8.0791	8.1555	7.5004	8.8603	9.1449	6.7540	6.1464	6.7664	7.55	
	Grid point location of Max. SO_2 concentration	22,19	20,22	22,19	20,22	20,22	22,20	22,20	20,22	20,22	20,22	22,20		
Autumn	Wind speed (ms^{-1})	2.4	2.1	2.2	2.2	2.1	2.1	1.7	2.1	2.1	2.1	2.3	2.13	1.45%
	Temperature (℃)	26.2	25.6	25.5	26.3	25.9	26.2	27.1	26.3	27.1	26.3	26.6	26.28	
	SO_2 conc. (ppb)	7.2225	5.6742	8.0141	6.8336	7.9868	7.9549	15.2526	8.6424	7.9897	5.6486	7.2878	8.05	
	Grid point location of Max. SO_2 concentration	22,19	22,18	22,19	22,20	22,20	22,19	22,20	22,20	22,20	22,19	22,19		



ANNUAL



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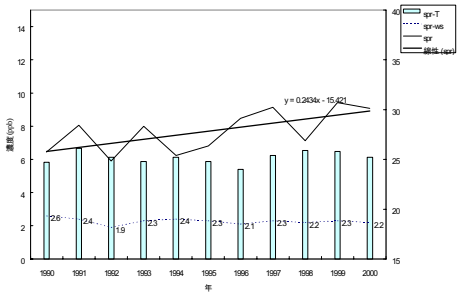

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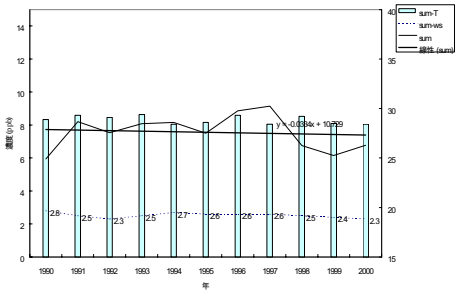
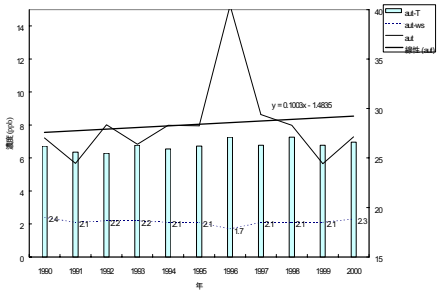


SUMMER

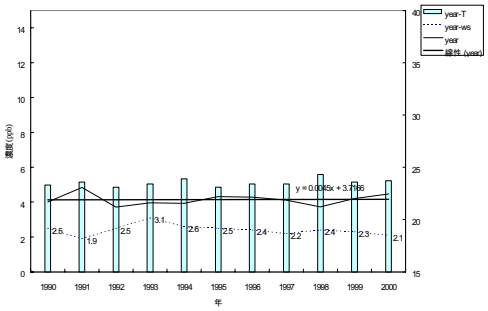


AUTUMN

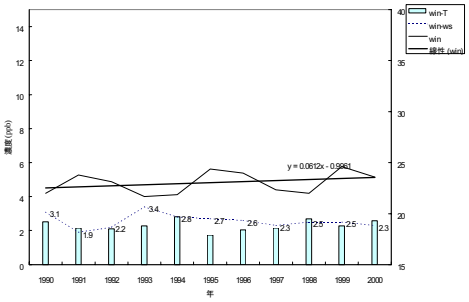
Figure 3.4.3 Interannual variation of the air pollution potential, average temperature and wind speed for Kaoshiung (South) during 1990-2000

Table 3.4.4 Average wind speed, temperature and simulated results of maximum average SO_2 concentrations in 1991-2000 for Hualien(East)

season	Year	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	average	Increasing rate per year
Annual	Wind speed (ms^{-1})	2.5	1.9	2.5	3.1	2.6	2.5	2.4	2.2	2.4	2.3	2.1	2.41	-0.29%
	Temperature (℃)	23.3	23.6	23.1	23.4	23.9	23.1	23.4	23.4	24.3	23.6	23.7	23.53	
	SO_2 conc. (ppb)	4.0115	4.8371	3.7112	3.9659	3.9394	4.3213	4.2921	4.1227	3.7305	4.2073	4.4700	4.15	
	Grid point location of Max. SO_2 concentration	18,20	19,19	19,19	18,20	22,21	18,18	18,18	18,18	21,21	18,18	19,21		
Winter	Wind speed (ms^{-1})	3.1	1.9	2.2	3.4	2.8	2.7	2.6	2.3	2.5	2.5	2.3	2.57	1.23%
	Temperature (℃)	19.2	18.6	18.5	18.8	19.7	17.9	18.4	18.6	19.5	18.8	19.3	18.85	
	SO_2 conc. (ppb)	4.1921	5.2775	4.8806	4.0113	4.1138	5.6180	5.3852	4.4028	4.1927	5.7694	5.1467	4.82	
	Grid point location of Max. SO_2 concentration	18,18	18,18	19,19	16,17	22,21	16,17	17,17	18,18	17,16	18,18	18,18		
Spring	Wind speed (ms^{-1})	2.8	2.0	1.5	2.9	2.5	2.6	2.2	2.1	2.3	2.2	1.8	2.26	-0.95%
	Temperature (℃)	22.0	23.5	22.5	22.3	23.3	22.6	21.7	23.0	23.7	22.7	22.5	22.71	
	SO_2 conc. (ppb)	4.0035	6.1049	6.8526	4.6258	4.3938	3.4833	5.2354	5.2684	5.1063	4.9054	4.4677	4.95	
	Grid point location of Max. SO_2 concentration	20,22	19,19	19,20	18,20	19,22	21,21	18,18	18,18	21,21	18,18	22,21		
Summer	Wind speed (ms^{-1})	2.0	1.9	2.7	3.0	2.6	2.2	2.3	2.3	2.3	2.2	2.2	2.34	0.15%
	Temperature (℃)	27.8	28.3	27.7	28.2	28.2	27.5	28.5	27.4	28.7	28.1	28.0	28.04	
	SO_2 conc. (ppb)	7.8068	8.9394	6.7710	6.9477	7.3504	7.3690	11.1690	7.4090	7.0059	7.0180	8.3439	7.83	
	Grid point location of Max. SO_2 concentration	18,20	19,21	19,21	18,20	19,21	19,21	19,22	19,21	19,21	19,21	19,22		
Autumn	Wind speed (ms^{-1})	2.2	1.8	3.6	3.0	2.5	2.4	2.3	2.2	2.6	2.3	2.2	2.46	0.24%
	Temperature (℃)	24.2	23.8	23.9	24.3	24.5	24.5	25.0	24.4	25.2	24.7	25.2	24.52	
	SO_2 conc. (ppb)	4.3193	6.1479	3.6914	3.3969	5.4396	7.4038	5.3257	4.7178	4.1595	4.4024	5.1821	4.93	
	Grid point location of Max. SO_2 concentration	18,18	19,19	17,16	22,22	18,18	18,18	18,18	19,21	19,18	18,18	19,21		



ANNUAL



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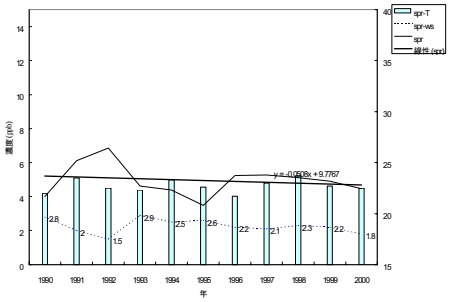

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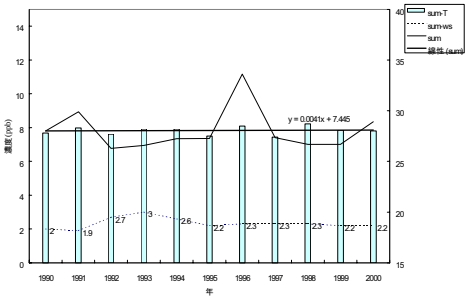

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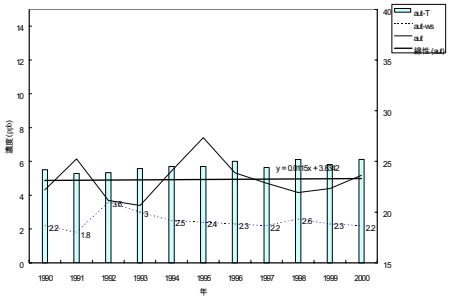

AUTUMN

Figure 3.4.4 Interannual variation of the air pollution potential, average temperature and wind speed for Hualien (East) during 1990-2000

The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

TRANSPORT, ENERGY AND ENVIRONMENT: THE ROLE OF NATURAL GAS

A Di Lorenzo*

ABSTRACT

The tight links between energy consumption and environmental impact have been thoroughly acknowledged and assessed, particularly involving exploitation of energy sources, operation of transportation networks and control of air quality. Energy sources, basically fossil fuels, often involve critical issues of economic and political concern. Simply put, is generally wise to widen the kinds of available fuels, both for strategic and environmental reasons.
The environmental impact involves both global (CO_2) and local (pollution) effects. The overall trend of CO_2 reduction is addressed and supported by two related guidelines: A) the increase of energy conversion efficiency, through improvements of combustion technology, and B) the reduction of the fuel carbon / hydrogen ratio C/H.
Both guidelines involve a shift towards increasing use of **natural gas**.
On the other hand, better fuel quality, advanced combustion technologies, enhanced emissions control, all cooperate to improve air quality, particularly in high – population – density urban and traffic – congested areas.
As a result, the perspective of a progressive increase of natural gas exploitation is foreseen and widely accepted for the next decade, particularly within the EU energy policy.
The paper presents a project between EU and Mediterranean and Middle East Countries on "Transport, Energy and Air Quality in Urban Areas". Aims and objectives of the project are:

a) To help change of the current trend of environment degradation in the Mediterranean Region;

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b) To contribute to the sustainable development of the Region, to the protection of the Mediterranean environment, and to the improvement of the health and the welfare of the population;

c) To contribute to the further integration of environment concerns in all other policies;

d) To contribute to create opportunities for new employment.

THE EURO – MEDITERRANEAN PROJECT

This project aims at identifying and exploiting solutions based on innovative technologies and strategies that can help the developing countries in the Mediterranean area pursuing an eco-sustainable development and to affect positively the air quality reducing pollution in congested urban areas.
Its feasibility is connected with the assessment of the social (and environmental), economic and financial benefits produced by a policy directed at substituting old vehicles (public transport buses and other public transport means, taxis, private cars, motorcycles, etc.) with vehicles characterized by lower polluting emissions with the objective of:

- Exploiting the NG resources, which are already relatively abundant in South Mediterranean and Middle East Countries;
- Reducing the environmental impact of urban transport in city areas, disentangling the growth in urban economies from transport demand;
- Increasing the efficiency and the quality of public transport services.

The introduction of NG will certainly contribute to improving the air quality, reducing also noise production and exploiting a natural resource largely available in that Areas (TAB. 1).
In the course of the analysis, the project will provide and measure the economic evaluation of environmental externalities, estimating the costs of the project implementation, on one side, and the benefits of substituting the current means of transport with new vehicles fuelled by NG on the other side.
Given the complexities that a full implementation of the project might bring about at the country level in that Countries context, it seems quite reasonable to identify some cities as a case study.
The perspective of a progressive increase of natural gas exploitation is foreseen and widely accepted for the next decade, particularly within the EU energy policy.
The use of natural gas, mainly for urban transports, for his chemico – physical characteristics, allows the reduction of CO_2 emission and a very low environmental impact.
The Figure 1. shows the amount of CO_2 and unregulated emission reduction when natural gas is used instead of gasoline; in addition are compared the effect of different fuels and engines on ozone promoters formation, on acid rain2 formation and on global warming index (GWI).

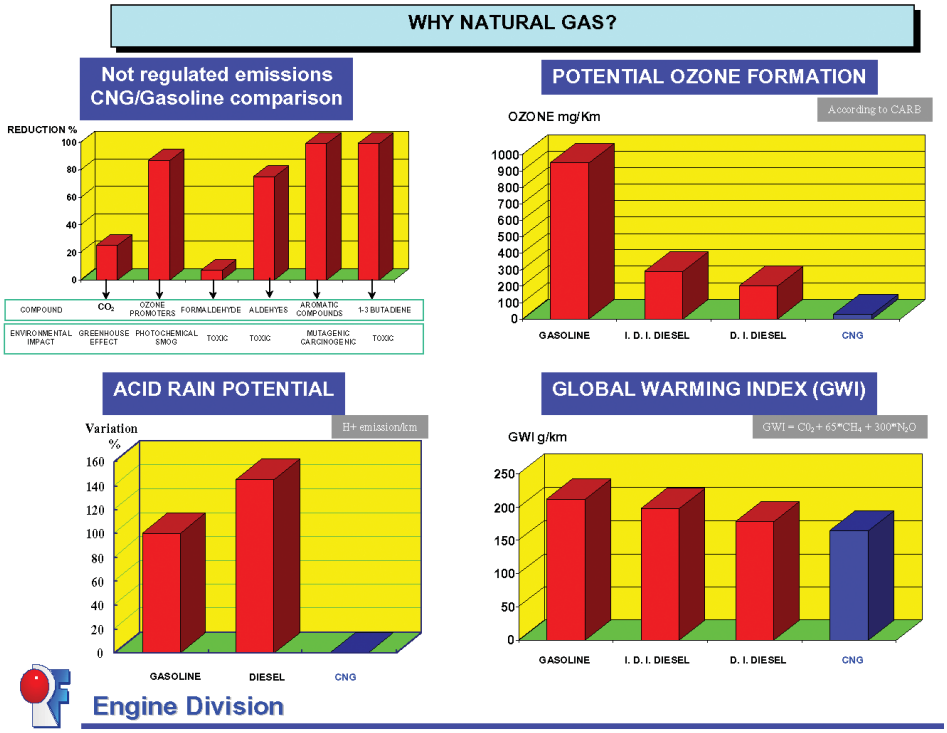

Figure 1. Amount of CO_2 and unregulated emission reduction when natural gas is used instead of gasoline

Table 1. Natural gas reserues in south mediterranean and middle east countries

1. Algeria	4.522.000
2. Libya	1.314.000
3. Egypt	1.996.000
4. Syria	5.410.000
5. Iraq	3.109.000
6. Iran	23.002.000
7. Saudy Arabian	5.791.000
8. Qatar	8.495.000
9. Kuwait	1.492.000
10. United Arab Emirates	6.003.000

According to the proposed methodology, the working programme will include:

- The collection of all available data on urban transport;
- The analysis of environmental issues such as, for example, type and amount of fuel consumption, emissions dispersion and concentrations for different types of vehicles and vehicle use in different days and year periods, etc.;
- Using the ExternE (a well known European project aiming at evaluating the effects of air pollution due to transport activities in urban areas) results to measure the economic evaluation of environmental externalities, the project will provide an estimate of the costs of the project implementation and the benefits of substituting the old means of transport by new ones; as regards costs, estimates will be provided of the related investment costs; examples of benefits are calculated in terms of the differential between the economic costs of each pollutant before and after the implementation of the substitution procedures or in terms of the reduction of the total amount of fuel consumption due to the use of more efficient transport means. The economic effects of the substitution programme will not only concern air pollution but also acoustic pollution as well as, to the extent that new buses would likely increase the efficiency of public transport versus private one, the congestion costs and the overall polluting emissions related to urban traffic.
- The final outcomes of the cost/benefit analysis will be the Net Present Value (NPV), which is calculated summing up the present values of net future benefits and the Internal Rate of Return (IRR), which is the discount rate that makes the NPV equal to zero (in other words, the rate at which the present value of benefits equals the present value of costs). As it is well known, the project will be acceptable if IRR results greater than the social discount rate adopted;
- For the economic evaluation of benefits the ExternE results will be applied to the exposure-response functions that will emerge from the traffic flows evolution during the implementation of the substitution programme.

The analysis of the results will help the local public authorities to make a choice between different alternative strategies of maximization of the urban quality of life. Such a kind of project will very likely have positive direct and indirect impacts on local urban economy by increasing the attractiveness of that cities in the tourism sector as well as in the industrial one, boosting thus the creation of new jobs in the local market.

Today four bilateral agreemt between Italy and Third Countries of Mediterranean Area are in progress:

1. Bilateral agreement between Iran and Italy, through EU – NAPOLI Programme and IFCO, IPCO, Iran.
2. Public transport policy and measures that could improve the air quality in major cities in Syria: a case study Damascus

3. Bilateral agreement between Egypt and Italy on "Transport and Energy Policy and Air Quality in Urban Areas": Alexandria and Egypt.
4. Bilateral Cooperation between Morocco and Italy on "The elaboration of an Air Quality Planning For the Grand Casablanca Region".

The Italian technology for the use of Natural Gas in vehicles

The Italian industry has been engaged since long time in the use of NG in road vehicles. Just before the 2nd World War, automobiles, trucks and even railway cars were converted for use of natural gas as a fuel. At that time, the motivation was the shortage of oil, and no worry existed to achieve the best possible engine performance, and no consideration was given to the environmental issues connected to the fuel.

The very first use of NG gave rise after the war to the first patents of small companies for pressure regulators, valves and fittings besides other accessories for the gas installation on board. With the expanding grid of NG distribution all over the country, the technology of the filling stations included more and more the compression directly from the grid, taking thus full advantage of the peculiar way of distribution.

All the know-how acquired promoted the Italian industry as a leader worldwide, with very important "daughter companies" in other countries, mainly in south and north America where, as in the case of Argentina, the NG vehicles found a wide distribution.

For several years this was the only way of using NG as a fuel until the appearance of OEM (Original Equipment Manufacturer) NG cars.

This has been and still is a business of significant value; the conversion sector totalling in Italy some 50.000 vehicles per year, mainly on old and big cars. The technology of the conversion equipment, fitted in the after market, has evolved from the very first carburettor-like solutions, with introduction of catalysts and electronics under the pressure of stricter emission limits. Therefore, the gas equipment has evolved to rather complex multiunit injection electronic systems that interfaces with the gasoline electronic control unit, and that takes advantage of the same catalyst and guarantees good performance of the engine, switching automatically the fuel from gas to gasoline. In this way, the NG loosed the image of a "poor fuel" gaining thus increasing popularity and incentives for its better environmental impacts.

The Italian industry can now supply almost perfect systems for conversions of old cars and existing engines. It should, however, be noted that the conversion is valid only for gasoline engines. Diesel engines require so many modifications, so that the after market conversion is not viable, and might give rise to serious reliability problems.

OEM vehicles: starting from the mid nineties, some of the major manufacturers, in particular FIAT, have developed and included in their catalogues the NG

versions of some of their most popular cars. The great advantage of a car built for the use of NG is that the system is fully integrated: the cylinders are included in the car body. The integration of electronics for gasoline and gas operation is deeper, giving thus rise to better performance both in efficiency and in emissions, with a big potential for further improvements. The most modern injection system (electronic phased multiunit) is used, and the testing procedures of prototypes guarantee the best quality and reliability.
As for what concerns heavy-duty vehicles, the OEM solution is the only viable one since no retrofitting or conversion is advisable in after market for diesel engines. By now a whole range of vehicles is available from the Italian industry, starting from the delivery vans to the urban buses and to the big garbage collection trucks.

Refuelling stations: a full range of filling stations is now available in Italy, starting from the compressors to the ancillary equipment, fuel dispensers, automatic billing and so on.
The technology of construction is based, today, on a modular structure that contains gas metering, electrical connections and monitoring system, gas storage that is fully assembled in the factory in the shape of a container (in steel or concrete according to local legislation) and is fully tested before shipment and can be assembled on place very easily, on a "turnkey" basis. The advantage is obviously the "modular structure", which can be expanded according to needs.
In particular, the group of Italian experts may co-operate in implementing:

- The creation of CNG fleets of buses, taxis and light duty vanes, fork lift, waste collection trucks, motorbikes, etc.;
- Innovative fleet depots, including refuelling infrastructures and maintenance facilities;
- Logistic and design of refuelling stations, with particular attention to uniform design and selection of standardized solutions, equipment to minimize installation, start up, commissioning time and to maximize inter-changeability with minimum component variety;
- Best practice in operation maintenance of the refuelling stations, with particular care to safety, upgraded and computerized diagnostics, to maximize efficiency;
- Best practices in fleet operation and maintenance;
- Training of operators (engineers, technicians, drivers, etc.).

In conclusion, the Italian NGV (Natural Gas Vehicles) industry, whose most significant companies are grouped in the "NGV System Italy" Consortium, represents a leader in the NG vehicles field, and is presently strongly expanding in various countries in the Middle East as well as in the Far East regions (examples are: Iran, India and China).
A full know-how is now available for complete designs of filling stations and car conversion equipment, and a whole range of OEM vehicles is now available.

A possible path to the introduction of natural gas in transport system could be:

A. Retrofitting of existing gasoline engines as far as practicable;

B. Introduction of OEM models for the new vehicles. This is mandatory for heavy-duty vehicles, since in this case no transformation procedures are advisable.

The Italian research on Natural Gas Engines

Since 1983 Istituto Motori is involved in activities concerning the topics of alternative fuels, especially natural gas (NG). The NG, being constituted essentially by methane and small amount of propane and inert gases, typically no toxic compound, is characterised by very low environmental impact. This together with negligible emission of particulate matter in the exhaust gases of NG engines reduces drastically the harmfulness of its utilization.

The chemico - physical characteristics of NG allow the reduction of fuel consumption and CO_2 emission in spark ignition engines. The gaseous status allows a satisfactory behaviour in transient condition operation without mixture enrichment. Moreover the utilization in heavy duty engines feeding, typically diesel engines, implies a noise reduction.

The first research activities carried out in Istituto Motori, leads to the realization of lean burn engines for passenger cars, with high turbulent combustion chamber, characterised by same performance of equivalent gasoline engine and the lower emission and fuel consumption. Considering the market difficulties of NG vehicles for their lower operating range and small amount of refuelling stations the subsequent research activities were carried out on heavy duty engines for urban buses. In fact for that type of vehicle, especially if belonging a urban fleet, it is possible to overcome easily the mentioned problems. At the beginning of the ’90 years, with the financial support of public and private institutions, it was developed a first prototype of NG heavy duty engine for Florence city bus.

During the second half of ’90 years, in cooperation with IVECO and CRF, a NG heavy duty stoichiometric engine with three way catalyst and electronic fuel control was optimised in order to satisfy the voluntary emission limits, named EEV, posed by European Commission for very ecological vehicles. In cooperation with Italian and foreign Universities some studies on combustion are developed. Recently, cooperating with a specific institution on human health (Istituto Superiore di Sanità) the real toxicological and mutagenic impact of NG for transportation: has been investigated: the impact of NG is quite negligible in comparison with diesel fuel alone or in mixture with vegetable oil. Actually, in the framework of European program, researches concerning the enhancement of NG engine efficiency and life of catalyst after-treatment system are under development. Finally, in agreement with Italian government guide lines, the research activities for the development of the second generation of NG engine are scheduled in the framework of next three years plan.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
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A STUDY ON RISK ASSESSMENT OF ROAD TUNNEL FIRES BY FULL-SCALE AND LABORATORY TESTING

B Fabiano*, F Currò, D Cazzola, E Palazzi, R Pastorino and M Del Borghi

ABSTRACT

Heavy good traffic by road has continually increased over many years and owing to population or environmental impact reasons, the actual number of road tunnels has grown in many countries. It must be remarked that, due to the sharp reduction of vehicle pollutant emissions, the ventilation of road tunnel is more and more determined by the need of controlling smoke in case of fire. The first step of this study focused on full-scale test program development. This included an assessment of the tunnel's condition, identification of possible modifications, design of the ventilation system to be tested during fires and set-up of the test planning. Full-scale experimental runs were carried out utilizing a two-lane tunnel of the Highway A7 Genoa-Milan, in order to simulate the evolving scenarios following an accident with fire development. Firstly, experiments were performed with simulated smoke, so to obtain a complete fluid dynamic characterization of the tunnel, under different atmospheric conditions. The subsequent experimental tests were carried out with several fire loads characterized by different calorific value. Following aspects were deeply analyzed: longitudinal and transversal temperature gradients in presence and in absence of fire-extinguishing automatic systems; effects of different ventilation conditions; evolution of the heuristic pollutants during the fire. The second step was addressed to laboratory-scale experimental runs: design and construction of the laboratory test facilities; experimental runs, data evaluation and preliminary modelling. Combining the results of full testing and theoretical modelling, practical recommendations are drawn concerning, on one side, general measures relating to the tunnel and the traffic (e.g. ventilation design and operation), on the other side specific measures to reduce the consequence of accidents and implement emergency response management.

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INDEX TERMS

Tunnel fire, ventilation, critical velocity, model

INTRODUCTION

Recent calamitous accidents, such as the one at the Mont Blanc, or that of Kaprun (Austria), have focused the attention on the problems of safety in road- and rail-tunnels, enhancing in particular the relevance of prevention and limitation of consequences in case of fire. In the accidents just mentioned, the considerable dimensions of the structures, combined with inadequate safety systems undoubtedly affected the magnitude of disaster. It should be pointed out, however, that even in small- and medium-length road tunnels, such as the ones typically to be found along the Ligurian motorways, the hazards connected with breaking out of fire consequent to a possible accidental event is extremely high, both because of the intense traffic and because of insufficient provision of adequate safety means. It is therefore extremely important to carry out an accurate study of these phenomena to assess their consequences and be thus enabled to design adequate protection systems in order to safeguard the lives of the users, as well as the structures.

METHODS

This work was intended to study the fluid dynamics aspects connected with fires in small- and medium- length tunnels, through an in-depth analysis of this phenomenon under different conditions. The experimental set-up, during full-scale runs, was realized in co-operation with the Genoa Fireman Command and Società Autostrade S.p.A. (Highway Italian Society). Experimental runs were performed in an unused tunnel on the highway A7, from Genoa to Milan: the two-lane tunnel, (reproduced in Figs. 1, 2) is 718 m long, 9.5 m large, with a medium radius of 4.6 m and a maximum height of 6.2 m as follows: chemical smoke; fire load of solid materials; fire load of two cars; fire load of wood stack. The following was measured for each fire and smoke source: air/fire temperature by means of an infrared video camera, air velocity and direction, combustion gases and heuristic pollutant concentrations. Concentration of oxygen, carbon dioxide and carbon monoxide were measured at 1.75 and 5.0 meters over ground level in different sections. Air samples have been analyzed by GC/MS in order to evaluate concentration of polycyclic aromatic hydrocarbons (PAH) at ground level.

The laboratory phase consisted in the simulation of a fire inside a laboratory scale-tunnel (length 6.0 m, height 0.20 m, radius 0.15 m) and in measuring smoke temperature and velocity and investigating its propagation. The first stage was the observation of breaking out of fire in tunnel, under natural ventilation in order to characterize the temperature profiles and the tunnel fluid dynamics. Later on, obstacles were added, to assess how the previously examined phenomena are affected by the presence of vehicles, the final step being an analysis of forced ventilation systems, to determine the optimal configuration with a view to the users' safety.



Figure 1. Real scale tunnel

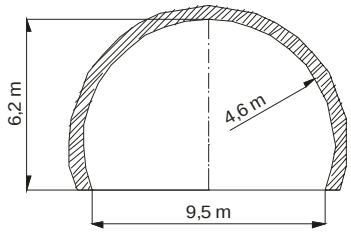

Figure 2. Tunnel cross section

THEORETICAL

In case of fire in a tunnel, a longitudinal ventilation system is often operated in order to create, upstream of the fire, a smokeless area, essential for evacuation and rescue operations. If the ventilation rate is low, the fire smoke may propagate also upstream of the fire, contrary to the ventilation airflow, a phenomenon known as backlayering. The critical velocity, that is the minimum value capable of avoiding backlayering and thus force smoke to move only downstream, is obviously a fundamentally important value when designing ventilation systems. Therefore, the basic scientific problem is to determine the longitudinal ventilation rate necessary to prevent the combustion products from moving upstream of the fire. Current methods for determination of such value are based on semi-empiric equations, obtained by the Froude's number conservation, combined with experimental data. This method is often employed as a scale technique in instances where the Reynolds' number is sufficiently high, and where, therefore, a turbulent regime is established and flotation forces are prevalent.

Starting from the study of Thomas (1968) and the development suggested by Oka and Atkinson (1996), the relation of critical velocity to heat output was studied considering two regions: in the first, the former depends on the latter enhanced to one third, whereas, in the second, it becomes independent from heat output, proving to be constant and equal to 0.40. In the light of the above considerations, the hydraulic radius has been employed as a characteristic dimension in all the various calculations for the case under examination; such value is 10.9 m for the Brasile tunnel and 0.35 m for the experimental apparatus. In the course of the experimental tests, the value of the critical velocity was determined, and it proved to be equal to 1.0 $m \cdot s^{-1}$. By this datum, the Reynolds obtained for the experimental apparatus, is equal to $2.5 \cdot 10^4$, thus sufficiently high to allow this procedure to be used; subsequently, it will have to be calculated for the real tunnel. This similitude criterion employs two equations: eq. 1 (where Q is the heat release rate and R are the tunnel radius), given the geometrical dimensions of both tunnels, provides the ratio between the relevant heat outputs; eq. 2 (where n is inlet velocity) supplies the ratio between the air speed in the two

instances. These considerations may be extended to apply, also in case of forced ventilation, where inertial forces are smaller than flotation forces.

$$\frac{Q_{\text{model}}}{Q_{\text{real}}} = \left(\frac{R_{i\,\text{model}}}{R_{i\,\text{real}}} \right)^{5/2} \quad (1) \qquad \frac{v_{\text{model}}}{v_{\text{real}}} = \left(\frac{R_{i\,\text{model}}}{R_{i\,\text{real}}} \right)^{1/2} \quad (2)$$

Once determined the critical speed in the real instance, the Reynolds and Froude numbers for the Brasile tunnel can be calculated. Here again, Reynolds proves to be rather high, thus confirming this theory's applicability. Finally the latter's entity for the experimental apparatus is also to be worked out: and, thus, verify the conservation of the Froude's number in the real instance and in the model.

EXPERIMENTAL

Real scale tests

The aim of the series of real-scale experiments was to simulate the evolving scenarios following an accident with fire development, so to verify the effectiveness of smoke and fire management strategies and protective technologies. Preliminary tests with chemical smoke allow to conclude that the predominant conditions, corresponding to light constant wind, with variable direction, are to be considered not relevant to the purposes of the investigation.

Fire load of the second test consisted of various solid materials (wood, straw and mattresses), continuously fed in order to have a constant heat flux. The real fire load was not directly measured, but it was estimated as corresponding to 8 MW. Three helical jet fans at the inlet of the tunnel ensured a longitudinal ventilation, so to verify the effectiveness of the prevention of backlayering: they were started after few seconds from the beginning of the fire. During the initial phase of the test, the cloud of smoke rose to the tunnel ceiling and then started to descend slowly to the floor, with a wave-motion: at floor level, at the lee-side of fire, visibility was completely avoided. The longitudinal ventilation was not enough effective in drawing off the smoke gases, but it ensured a reduction of temperature at the floor level, down to 30 °C, during the fire load. During the fire load of two cars (estimated heat flux: 8 MW; smoke flow rate: 30 $m^3 \cdot s^{-1}$), suspended solids (smoke particles) considered as heuristic pollutant, were measured, by means of a sequential dust-sampling device and subsequent gravimetric analysis. PAH concentration, produced by incomplete combustion of organic compounds, has been also measured at ground level. Also in this case, at the lee-side of the fire, the whole cross-section of the tunnel was filled with smoke. On the contrary at the windward side of the fire, visibility was almost complete during fire load. In order to reduce air temperature, a water spray system has been installed: also in this case, temperature at the ground level was under the tolerability limits. Moreover, temperature of air at tunnel ceiling never exceeded 200 °C. The last

test consisted in the combustion of about 260 kg of wood, which yielded a total fire load of 4730 MJ. Also this kind of fuel produced dense smoke, and at the lee-side the tunnel was completely filled with smoke, after the first few minutes of fire. In this case, the water spray system did not start up, causing an average air temperature higher than the previous one: (300°C at the ceiling).
A longitudinal ventilation allowed to remove smoke and cooled the air above the fire at the ceiling of the tunnel, but it affected by smoke the whole tunnel cross section at the lee-side of the fire, increasing as well the temperature at ground level.

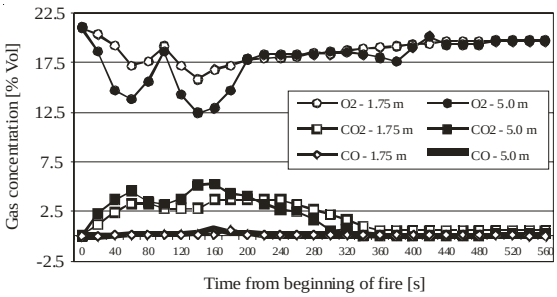

Figure 3. Concentration of combustion gases during test with road cars.

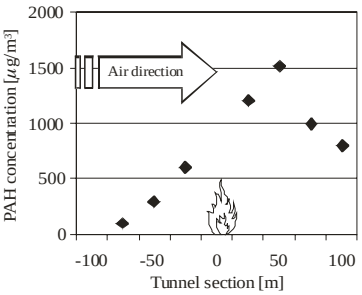

Figure 4. Concentration of PAH during test with road cars.

Laboratory tests

The results were synthesized by the temperature-time curves (Figs. 5 and 6 are two examples) in which they have been defined: the isotherms of the maximum temperatures reached inside the tunnel and the iso-time lines representing the time taken for the temperature to reach the vivibility temperature. On grounds of some data about the vivibility time at different temperatures found in the literature (Ondrus, 1990), the temperature selected was 70°C, which corresponds to a vivibility time of 60 minutes. Last figures represent the fraction of the fire duration in which the temperature, along the longitudinal section of the tunnel, remains above this threshold temperature. In the case of natural ventilation without obstacles, the flame is vertical and the temperature trends downstream and upstream of the fire are symmetrical. In the lowest portion of the gallery, apart from the area around the flames, there is an ample area where the temperature does not exceed 30°C. As regards the time taken to reach 70°C, it should be pointed out that there is an area, both upstream and downstream, where such temperature is never reached. The other curves displaying the times to reach 70°C divide the tunnel into very narrow sections, indicating thus how fast, in time and space, this threshold value is reached. In the case of natural ventilation with obstacles (Fig. 5), the flame is slightly inclined towards them; this implies worsening conditions upstream of the fire, making possible a domino effect. The maximum temperature display is not symmetrical and the area where the temperature does not exceed 30°C is more limited, in respect of the previous

case; therefore less extended is also the portion of the tunnel where the temperature is always less than 70°C. In the central portion, there is an area where the temperature exceeds 400°C, larger upstream (more than 30 cm). In the immediate vicinity of the fire, the temperature remains above such value for a longer time than the duration of the fire itself (1.25). In the case of critical-velocity forced ventilation (Fig. 6), the flame is inclined about 45° in the airflow direction, in respect of the road surface. The pattern of maximum temperatures is not symmetrical in respect of the fire location, as the ones downstream are appreciably higher than in the analogous case under natural ventilation. In the area around the fire, the temperature remains above 70°C for a quite longer time than the duration of the fire (1.5). By comparing with the analogous case under natural ventilation, it may be observed how, downstream the area where the temperature never reaches the threshold value is considerably narrower (below 13 cm), whereas the intervals where the temperatures are reached in increasingly shorter times are much narrower.

In the case of forced ventilation at lower than critical velocity, the flame, after switching on the fan, is inclined about 30° in respect of the road surface.

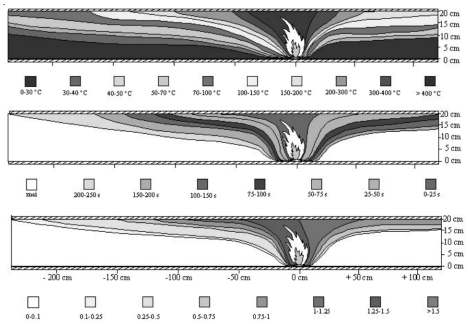

Figure 5. Highest temperature, time to reach 70°C and fire time with t>70°C, without forced ventilation.

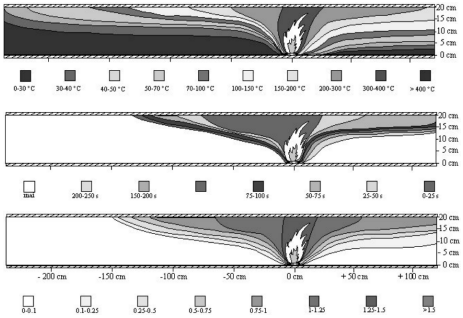

Figure 6. Highest temperature, time to reach 70°C and fire time with t>70°C, under forced ventilation at critical velocity.

As regards the pattern of maximum temperatures, upstream, the areas where maximum temperatures between 200°C and 40°C are recorded may be observed to widen, because of the smoke tendency to stagnate in the upstream portion of the tunnel. In the portion around the flames, there is an area where the temperature exceeds 400°C. Upstream, the temperature exceeds 70°C in a wider area, and for longer time spells than in the cases of natural and critical ventilation, because of the smoke stagnation. Downstream temperatures above 70°C are never recorded and the times taken, in the various sections, to reach such temperatures are lower than in condition of natural ventilation, but higher than in condition of critical ventilation. In the central area, upstream of the fire the temperature remains above 70°C for as long as the duration of the fire, and, close to the ceiling,

along a distance of 90 cm, downstream, it exceeds such value for a time appreciably longer than the fire duration (1.5) throughout a distance of 30 cm.
In the case of forced ventilation at higher than critical velocity, the flame is inclined about 60°. Upstream, the temperature pattern does not change in respect of the basic conditions, whereas, downstream, the situation is considerably worse as the various areas, characterized by different thermal levels, are more spread out; indeed, at 120 cm, the maximum temperature remains always below 30°C, only at levels lower than 2-3 cm. The central area is characterized by maximum temperature in excess of 300°C and this area extends more downstream than upstream. Windward, the temperature of 70°C is never reached beyond 120 cm and there are only two areas where such temperature is reached in less than 50 s. Downstream, the areas where the threshold temperature is reached between 150 s and 250 s are more extended, at 120 cm values exceeding 70°C are never reached below the level of 8 cm. As regards the length of time during which the temperature remains above the limit value, upstream, up to 120 cm from the fire, it is equal to half the fire duration or slightly more.

CONCLUSIONS

As shown in the PIARC recommendations on fire and smoke control during tunnel fires (1997), the aims of preventive and protective actions would be: to save lives by making evacuation possible; to make rescue and fire fighting possible; to avoid explosions; to limit damage to the tunnel structure and equipment. Longitudinal ventilation combined with water spray system, as observed in these tests, allowed the attainment of the last three recommendations, but was not effective in favouring the evacuation of people. In the range of fire load explored during full-scale tests, the use of longitudinal ventilation proved to be useful for an effective removal of smoke in tunnel, allowing as well the fireman to operate at the windward-side of the fire. Making reference to laboratory tests, it should be pointed out that the increase of temperature following a fire in a tunnel, without vehicles and under natural ventilation does not involve danger for users, insofar as, at man's height, the temperatures recorded never exceed 40°C. This is due to the tendency of smoke to stratify below the ceiling and move naturally towards the end of the tunnel, leaving the underlying portion practically free from smoke and, thus, unheated. However, a counter-current motion of lighter smoke is observed under the above mentioned flow, due to drawing of combustion-supporting air towards the combustion point: the air contains smoke particles which, because of gravity, would tend to deposit. The hazard for people may principally derive, in case of a real fire, from toxic substances (typically CO, CO_2, NO, NO_2, SO_2, HCl, HCN and PAH) being produced because of the combustion of the vehicles' materials, or, possibly, of the materials being transported. The thermal increases recorded during the tests carried out at the Brasile tunnel, concerning a fire involving two cars, are of the same order as the ones obtained during the experiment in the scale tunnel: therefore

the observations and the outlines drawn may be extended to real life situations. The presence of a column of motor vehicles involves an increase of temperatures even at ground level, both upstream and downstream. In order to favour the clearing of fumes by eliminating backlayering, forced ventilation systems are installed. From the tests carried out, by impressing to the air a speed equal to the critical velocity a clear positive effect was observed in the area upstream of the fire. Indeed, such area, even though not instantaneously, is freed from the fumes and the temperature recorded becomes stably near the ambient temperature in a relatively short time. In the downstream area, instead, worse conditions are observed at first. An improved combustion, in fact, together with the lowering and accumulation of smoke in the whole section of the tunnel implies a considerable increase of the temperatures, even at low levels. After the extinction of the fire, however, the inflow of fresh air brings about a faster temperature reduction. By employing a lower than critical velocity ventilation, in the area upstream of the fire, conditions become considerably worse as the air speed is not sufficient to counteract the backlayering flow of smoke which, therefore, stagnate and cause a considerable increase in the temperature. Downwind, even though during the fire the temperatures recorded are lower than the ones observed in the critical ventilation tests, the diminished air speed determines a slower temperature decrease after the fire. By a higher than critical velocity ventilation, if, on the one hand, the upstream area is nearly immediately cleared of fumes, the downstream portion, instead, is affected by very high thermal levels even at man's height, thus rendering this area particularly dangerous. It may be inferred, from the above considerations, how important a correct design of the ventilation system is both in connection with the protection of users and with a view to allowing rescue operations to be carried out safely.

ACKNOWLEDGEMENTS

This research was supported in part by the MIUR (Ministry of Instruction, University and Research – Rome) – D.M. n. 235 Uff. VIII/2001.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

CANADA'S INVOLVEMENT WITH POLLUTANT RELEASE AND TRANSFER REGISTERS (PRTRs) IN LATIN AMERICA AND THE CARIBBEAN

GS Hart[1] and J Rosenberger[2]

Executive Summary: At the Rio Conference in 1992, there were a considerable number of commitments made in Chapter 19 Agenda 21 of this conference. Two of these commitments concerned Pollutant Release and Transfer Registers (PRTRs) in developed countries, which committed to: (a) have PRTRs in place by Rio + 10 (The 2002 Johannesburg Conference); and (b) assist developing countries to develop and implement PRTRs in their own countries. Canada has undertaken an extensive and intensive process of awareness raising, concerning PRTRs, in Latin America and the Caribbean. A series of three awareness raising regional workshops (Kingston, Jamaica; Sao Paulo, Brazil and San Jose, Costa Rica) are being undertaken and should be completed by the end of 2003. Early in 2004 a three day conference will be held in Monterey, Mexico. One of the main goals of this conference will be to ascertain how many countries want to go ahead with developing and implementing PRTRs. This paper will describe the methodology used and the progress made in implementing this project.

What is a PRTR? A Pollutant Release and Transfer Register (PRTR) is a database or register of the quantities of potentially harmful chemicals, reported by facilities, which are released (to air, water and land) and/or transferred (for treatment and disposal).

With PRTR programmes in place, government authorities can set priorities for reducing or even eliminating the most potentially damaging releases, and track progress toward meeting environmental objectives. A PRTR also provides an incentive for industry to reduce its releases and transfers.

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Benefits of a PRTR:

(1) Helps Government:
- track progress on emissions
- meet international reporting requirements
- encourage cost-effective approaches to emission reduction and pollution prevention

(2) Helps the Private Sector/Industry:
- identify areas to practice sound environmental and business management
- monitor environmental performance
- engage communities and communicate with the public

(3) Helps the General Public
- understand emissions and make informal decisions on environmental issues and priorities
- become engaged in environmental decision-making

(4) Helps Non-Governmental Organizations
- build capacity for engaging communities
- provide tools for dialogue with communities and stakeholders
- set priorities for action

Why Implement a PRTR? PRTRs are recognized as important tools to raise public awareness about potential chemical risks, and as effective environmental management tools to stimulate chemical risk reduction. PRTRs are always designed to be country-specific, but as mentioned before there are certain basic core elements that are common to all countries. The actual specifics of any country PRTR will depend on their industrial, legislative and policy particularities. Common characteristic of a PRTR include: a listing of pollutants, environmental multi-media and/ or integrated reporting of releases and transfers, reporting of data by source; reporting of data periodically and making data and information available to the public. The whole idea is to be as flexible and simple as possible in each country, so as to add only incrementally to the existing workload. Those countries that have implemented PRTRs such as Canada, the U.S., U.K. and several others, have found that they have resulted in a sometimes dramatic decrease in pollution loadings to the environment.

Background: As part of Chapter 19, Agenda 21 of the 1992 Rio Conference, there was strong support given to the idea of countries developing and implementing PRTRs. Developed countries were all asked to have PRTRs in place by Rio + 10 (2002). In addition developed countries were requested to assist developing countries and countries with economies in transition to implement PRTRs in their countries. The intent was to take stock of progress achieved since Rio, at Rio + 10 in South Africa.

Progress to-date: Since Rio a number of very substantial activities have been undertaken to meet the requirements of the Agenda 21 – PRTR commitment as follows:

a. **The OECD** – developed a guide for governments on how to implement PRTRs and sponsored a number of conferences to raise awareness about PRTRs.

b. **UNITAR** – developed a number of guides to help developing countries and countries with economies in transition to develop PRTRs. This work has usually involved the financial and technical assistance of a developed country. For example, Canada is working with Chile and Ecuador, through UNITAR, to develop and implement a PRTR in those countries.

c. **International Forum on Chemical Safety (IFCS)** – At its third session from 15-20 October, 2000 in Salvador Bahia, Brazil declared "by 2004 at least two additional countries in each IFCS region should have established a PRTR/emission inventory and countries without a PRTR emission inventory should consider initiating a national PRTR/emission inventory design process which involves affected and interested parties and takes into consideration national circumstances and needs". Progress towards this goal, and future PRTR activities, will be discussed at the IFCS Forum IV in November 2003 in Thailand.

d. **United Nations Economic Commission for Europe (UNECE)** – Negotiated a PRTR protocol under the Aarhus Convention (the 1998 Convention on Access to Information, Public Participation in Decision-Making and Access to Justice in Environment Matters). As of September 2003, this protocol has been signed by 36 countries, and the European Community.

Some of the key features of the protocol is that it will:

(i) mandate, for those countries that ratify or accede, the implementation of a PRTR that includes specific requirements for reporting, dissemination of the information, and for public involvement in establishment and modification of the PRTR;

(ii) bring some consistency between the countries of East and West Europe (and other countries that may join) in the development and implementation of their PRTRs;

(iii) provide access to technology and financial assistance for those countries that need it; and

(iv) be open to signature/ratification or accession to non UNECE countries.

e. **Latin America and the Caribbean** – There are approximately 35 countries in this region. There has been quite a lot of activity by various countries,

but in an uncoordinated way. Canada and the U.S. have provided a lot of assistance through the NAFTA/CEC, during the development of a PRTR in Mexico. The Mexican system is expected to come into force by the end of 2003. In addition, Canada has been involved through UNITAR, under the Canada-Chile Agreement on Environmental Cooperation, in helping Chile to move ahead in developing their PRTR. Other countries in the area, such as Brazil, Peru, Jamaica, Ecuador and Trinidad are at various stages of developing a PRTR.

Canada's Role: - Canada has been very active domestically and internationally since the Rio Agenda 21 call to action. Domestically it has put in place a highly successful and internationally recognized PRTR, the National Pollutant Release Inventory (NPRI). NPRI was established in 1992 and is mandated under the Canadian Environmental Protection Act (CEPA) in 1999. The NPRI currently requires companies to report information on releases and transfer of some 300 pollutants to Environment Canada on an annual basis. This information is available to the public in both print and electronic format. One very important aspect of the NPRI's success is the high level of cooperation in the implementation of NPRI between government, industry and ENGOs. Canada has also been very active in the major international activities mentioned before. Indeed it has played a leadership role in several of these activities. In early 2002, Canada, through Environment Canada, initiated a process aimed at organizing and staging a major PRTR Conference of the Americas (COA). This process is now well advanced, and is detailed below:

(i) Environment Canada sponsored a PRTR Workshop for English speaking Caribbean countries in Kingston, Jamaica in March 2002. This Workshop was preceded by information/education visits to 8 English speaking Caribbean countries in order to make them aware of what PRTRs are. Subsequently, delegates from these countries were invited to a two day PRTR Workshop. Approximately 50 delegates attended this Workshop and it was ascertained that at least two countries, Jamaica and Trinidad, would likely go ahead with the development of a national PRTR. Efforts are being made to organize bilateral aid for those two countries to proceed with these projects. In addition, methods of engaging the other countries and encouraging them to proceed are being explored with Caribbean organizations.

(ii) Environment Canada signed a partnership agreement with UNEP Chemicals to develop and stage the COA. This agreement would take advantage of Canada's knowledge of running its own PRTR (NPRI); its desire to help promote PRTRs in the Caribbean and Latin America, as well as UNEP Chemical's vast experience in organizing International Workshops.

(iii) It was decided that the process for South America, Central America and Spanish speaking Caribbean countries would involve the following steps:

a. a triage was carried out of all these countries to ascertain which ones already had a knowledge of PRTRs, as distinct from those which had no knowledge;

b. individual information/education visits would be paid to those countries with no knowledge of PRTRs. This process has been completed;

c. Two educational workshops would be held in Sao Paulo, Brazil for South American countries, and San Jose, Costa Rica for Central America and Spanish speaking Caribbean countries. The Sao Paulo Workshop was held on 24-25/06/03 and the San Jose Workshop will be held in December 2003. Funding for these two Workshops was provided by Canada; and

d. Finally, the COA will be staged in Monterey, Mexico, most likely in April of 2004. Three delegates will be invited from approximately 35 countries, including representatives from government, industry and environmental groups in each country. Funding for delegate participation and running of the conference will be provided largely, if not entirely, by Canada.

Present Status of COA: - The work of planning for the COA is well advanced. The triage of all countries is complete; preliminary visits to appropriate countries has been completed; the Kingston, Jamaica and Sao Paulo, Brazil regional Workshops have been completed; and the San Jose Workshop will be held in December 2003. The organization of the COA itself is well advanced, and it will be held in Monterey Mexico in April 2004.

Objectives of the COA on PRTRs

(1) Provide Canada with an opportunity to demonstrate leadership in helping Latin America and Caribbean countries to understand the value of PRTRs.

(2) Bring together delegates from Latin America and Caribbean countries, so as to develop a common understanding of PRTRs.

(3) Develop an understanding of the core elements of PRTRs, thus encouraging consistency across the region.

(4) Provide an opportunity to develop internet linkage between all countries of the region so as to ensure exchange of information and increase the efficiency of PRTR development in each country.

(5) Try and ascertain which countries would like to initiate a process to develop a national PRTR.

(6) Provide an opportunity for liaison between countries and international funding agencies so as to organize bilateral assistance for those countries that want to move ahead.

(7) Make a preliminary assessment of those countries that think that it would be useful to develop a future multilateral agreement on PRTRs for the Americas.

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DEVELOPMENT OF AIR MONITORING STRATEGY IN LATVIA

N Kadikis*, T Vasiljeva, I Lyulko

ABSTRACT

Systemic approach allows revealing the main direct external factors affecting the organization and functions of monitoring system – relevant legislation together with standards for environmental quality and actual quality of environment. Following, the previously till 1997 implemented manual methods in Latvia were justified by expression of air quality standards as maximum permitted concentrations (MPC) in relation to instantaneously measured and daily averaged concentrations. The planned adoption of the set of air quality standards laid down in European Union's directives required new strategy based on automated observations. So, the ambient air quality monitoring system in Latvia today is established on the basis of relevant European directives incorporated into the environmental legislation of Latvia. Since 1998 the observation system is grounded on automatic measuring devices employing several methods - the method of differential optical absorption spectroscopy (DOAS) for detection of SO_2, NO_2, O_3 and benzene, beta ray attenuation method for detection of PM_{10} as well as infrared spectrophotometer for measurements of CO. The automatic, continuously conducted observations are supplemented by passive sampling methods as well as by investigations on 2 regional GAW / EMEP stations as rural background based on conventional methods mainly. The finalised preliminary assessment and zoning of air quality in Latvia in 2002 – 2003 has served for optimisation of observational network in 2003 manifested as more deep fusion of state and municipal environmental monitoring.

INDEX TERMS

Air monitoring, Air quality, Monitoring system, DOAS, Latvia

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INTRODUCTION

Atmosphere air is one of the most important environmental factors influencing humans, vegetation and historical monuments. Especially the problems of air quality are emerging in big cities and industrial zones. Proper air quality information system is the basic prerequisite for management of air quality. The main elements of the environmental information system are data gathering patterns (monitoring, scientific investigations, statistics, modelling), data processing and storage and reporting (operationally, monthly, annually, etc.) to decision makers and public (Figure 1). Environmental monitoring plays the key role in supplying environmental information.

The first air quality assessment performed in the capital of Latvia - Riga city dates back to 1913 but regular air quality observations as pilot observations in Riga started in 1965. From the time when first regular air monitoring network was established, Latvia has gained rather big experience passing through different stages of overall technical progress in observational techniques and tools for data and information processing as well as development of environmental legislation concerning air quality matters. The ambient air quality monitoring system in Latvia today is established on the basis of relevant European Union's (EU) directives incorporated into the environmental legislation of Latvia. The responsible institution for air quality monitoring in Latvia is the Latvian Hydrometeorological Agency under the Ministry of Environment.

The aim of the report is to reflect the way of development of Latvian air quality monitoring system up to now and to draw some general conclusions with regard to overall organization of environmental monitoring irrespective of the environment to be monitored.

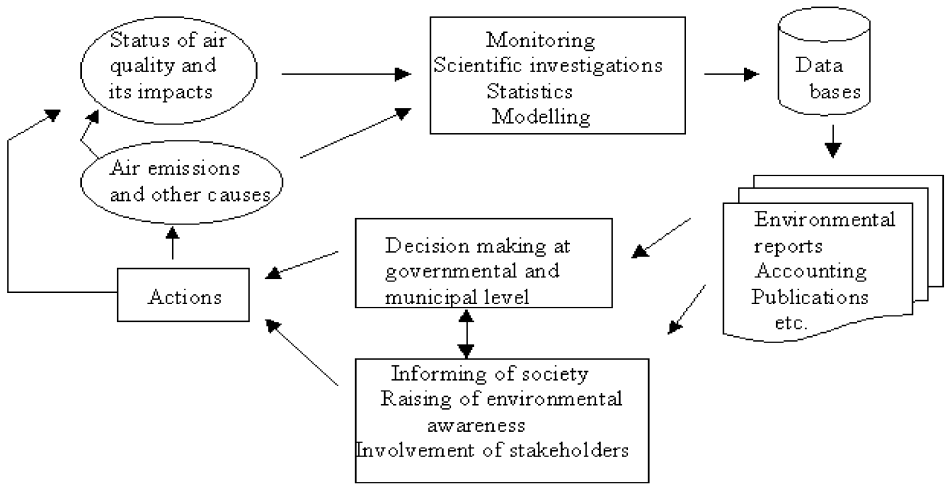

Figure 1. Conceptual air quality management system (Kadikis, Vasiljeva, Jevtushenko et al., 2002).

METHODS

The research is based on analysis on experience of Latvian Hydrometeorological Agency in establishment and performance of air quality observations. Examination of main EU and national legal acts in the field of air quality management is used, as well.

RESULTS

Regular air quality observations in Latvia as pilot observations in Riga started in 1965. Permanent observation's program in Riga was launched in 1969 and until 1974 steady monitoring was carried out only in Riga covering 3 posts. Since 1974 more towns were added gradually (Table 1), but the total number of towns monitored within 1977 - 1997 fluctuates in different years from 6 to 9. The monitoring was founded on manual sampling methods (3-4 times per day for SO_2, NO_2, TSP[1], CO, NH_3, phenol, etc. and 1 time per month for Cd, Cu, Pb, Zn) followed by conventional laboratory analyses and, therefore, often called as wet chemistry methods. Before regaining of independence in 1991, observation's network of Latvia was included in the state observational network of the former Soviet Union and unified methods were implemented summarized in the Guidance on control on atmosphere pollution (Anonymous, 1991). In parallel, observations at natural background level were started since 1985 in Rucava (south-western region of Latvia) and in Zoseni since 1994 (northern region of Latvia). Both stations are working until now within the framework of GAW/EMEP programs as regional sites. Most of observations are carried out applying sophisticated conventional methods based on automated daily or weekly (for heavy metals) sampling and followed by laboratory analyses (Anonymous, 2002a). In its turn, surface O_3 is detected continuously by means of UV spectrophotometer. The turning point in the development of air quality monitoring in Latvia relates to introduction of automated, continuous measurements performed by means of instruments implying differential optical absorption spectroscopy (DOAS) method. From 1998 to 2002 the amount of DOAS stations (OPSIS AB, Sweden) operating within the framework of state monitoring network reached 13. The standard set of parameters included SO_2, NO_2, O_3, benzene, toluene, and xylenes. Entirely 9 towns and 1 rural area located near to Latvian – Lithuanian border and stressed by emissions coming from the oil refinery in Mazheikiai (Lithuania) were covered by continuous measurements (Table 1). Several other important parameters required by European directives, namely, CO and PM_{10} particulate matter are detected on continuously basis applying different from DOAS techniques - infrared spectrophotometer for measurements of CO and beta ray attenuation method for detection of PM_{10}. Additionally Hg fumes were detected by means of atomic absorption mercury vapour analyser. In their turn, the combusted PM_{10} samples

[1] Total suspended particulates

are used for laboratory analyses on heavy metals (Zn, Cu, Cd, Pb, Ni, As, Mn) with atomic absorption flame spectrophotometer. Besides, new possibilities for air quality monitoring have been provided with the development of diffusive sampling methods being some advanced derivation of wet chemistry methods as conventional laboratory analyses are involved. Application of such methods in Latvia started in 2000. During 2001 – 2002 altogether 18 places were covered based on monthly-accumulated SO_2 and NO_2 samples.

Table1. Summary of urban air quality monitoring in Latvia, 1969 – 2003 (stations operating within the basic national monitoring programme in 2003 are given in bold)

Town	*Population, 2000 - 2002*	*Manual methods*		*Continuous automated methods*		
		Started-closed	*Max number of monitoring posts*	*Max number of stations in operation: state (municipal)*	*Pollutants*	*Started-closed*
Riga	816000	1969-1997	5	**3** - 4 **(3)**	DOAS[2] parameters	1994[3]
					PM_{10}	2000
					CO	2002
					Hg fumes	2000-2002
Dau-gavpils	113100	1975-1997	2	1	DOAS parameters	1998-2002
Liepaja	96268	1976-1997	3	**1**	DOAS parameters	1999
					PM_{10}	2000
Jelgava	71004	-	-	**1**	DOAS parameters	2000
Jurmala	58975	1978-1997	2	1	DOAS parameters	1999-2002
Ventspils	46600	1979-1997	3	1 (**1**)	DOAS parameters	1995[4]
					PM_{10}	2002
Rezekne	41069	1991-1995	1	**1**	DOAS parameters	2000
					PM_{10}	2001
					Hg fumes	2001-2002
Valmiera	28732	1974-1997	2	1	DOAS parameters	1998-2002
Jekabpils	26797	1977-1995	2	-	-	-
Olaine	12986	1977-1997	1	1	DOAS parameters	1999
Nigrande community	680	-	-	1	DOAS parameters	1998

[2] Standard parameters of DOAS stations include SO_2, NO_2, O_3, benzene, toluene, xylenes

[3] As municipal monitoring; state monitoring was launched in 1998

[4] As municipal monitoring; state monitoring was launched in 1999

DISCUSSION

Following the classical notions of systemic approach, we can imagine the monitoring as a system surrounded by external environment – elements which directly or indirectly affect functions of the system in question (Figure 2).

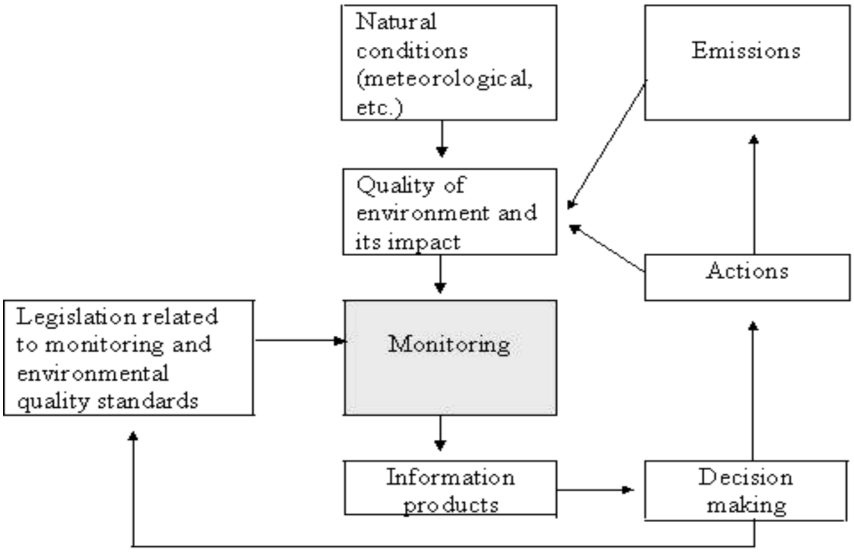

Figure 2. Elements of external environment influencing functions of monitoring system.

Environmental monitoring as a system dedicated to obtaining of data and information with respect to quality of natural environment consists of a number of linked structural and functional units – site selection (*where?*), parameters to be observed (*what?*), observation's or measurement's methods (*how?*), time interval to be covered (*when?*), by whom it will be done, what will be the tactic of observations – with or without early warning function, as basic, synoptic, operational or investigative monitoring (Kadikis, Kolcova and Lyulko, 2002), how the data will be organised in different steps of data flow, how the quality assurance / quality control (QA/QC) and data validation will be carried out, how the data will be stored and, finally, what kind of information must be generated. The main external factor which influences organization of monitoring system is represented by relevant legislation together with standards for environmental quality. The pattern how standards are expressed in terms of time intervals and degree of data aggregation needed governs the strategy of observations. As the former Soviet air quality standards were given as maximum permitted concentrations (MPC) in relation to instantaneously measured and daily averaged concentration (Anonymous, 1991), observation system based on manual sampling 3 or 4 times per day was quite well grounded, in any case from the formal point of view. But changes in air quality are caused by emissions and weather fluctuations within hour,

day, month and year. To this end, it is especially important that methods used in ambient air monitoring could provide steadily information on sometimes rapidly changing situations during short time spans, it means, continuous monitoring in automated mode should be arranged. These considerations are emphasised in the European directives with regard to air quality issued in the 1990-ties and forth. Compared to old Soviet standards, broad range of different standard's expressions is laid down including limit values for one - hour concentrations as well as alert thresholds, which ensure, in fact, early warning function.

Beginning of air quality monitoring in Latvia in the middle of 1960-ties was associated with the wet chemistry methods. In fact, the basic strategy for development of air quality monitoring was quite simple – to establish regular (3 - 4 times per day) manual sampling procedures followed by laboratory analyses in large and/or more industrialized towns of the country. A number of posts in each town were covered usually selected as a frontier zone between industrial and residential areas and the central part of the town influenced by traffic. Actually, Soviet standards were adopted in Latvia in the first years after regaining of independence in 1991. New air quality standards according to European directives were approved in Latvia in 1999. In the light of anticipated standards quite fast reorganization of state air monitoring system was accomplished introducing automatic DOAS stations. To some extent, the reason for such preference was the previously got experience from the first DOAS stations operating within municipal observational network since 1994. The existing historical data from the old observational network were used for specification of new monitoring sites. In reality, automated monitoring was continued in many of the towns already covered by manual methods. In their turn, exhaustive information resulting from automatic observations gave background for preliminary assessment and zoning of air quality in the country performed in 2002 – 2003. One agglomeration (Riga city) as well as two additional zones – western and eastern Latvia have been designated. The monitoring network in 2003 (Table 1) is optimised according to the minimum requirements laid down in the European directives 1999/30/EC, 2000/69/EC and 2002/3/EC (Anonymous, 1999, 2000, 2002b) and taking into account restricted financing from state budget as well as relatively stable and satisfactory air quality status in some of the towns monitored before. The last consideration proves the importance of actual quality of environment as an external factor influencing the organization of monitoring system (Figure 2).

CONCLUSIONS AND IMPLICATIONS

1. Systemic approach to organization and functions of monitoring allows stressing a number of external factors influencing it. Legislation related to monitoring and approved environmental quality standards as well as actual environmental quality status are the main direct factors. The case study on development of Latvian strategy on air monitoring reveals the way of

development from sole manual methods justified by former Soviet Union's air quality standards expressed as MPC for at once measured and daily concentrations to automated DOAS methods as a core of observational system. It ensures generation of data according to European Union's air quality standards, which are adopted in Latvia since the late 1990-ties.

2. Like other small countries Latvia has very limited capacity with respect to testing and certification of new equipment intended for monitoring applications as well as for elaboration of own environmental quality standards. In this case reliance should be put on findings and recommendations of different international organizations and large, economically and scientifically developed countries. For example, conformity assessment in relation to applicability of DOAS stations for ambient air monitoring was made by USA, Sweden, Germany, etc.
3. It is impossible to equip each place of interest with automatic air observation station, therefore, additional methods must be supplemented to automated monitoring – diffusive sampling, operational manual sampling in order to react on complaints about suddenly occurring deterioration of air quality and to identify the reasons, information on emission's statistics as well as information generated by pollution dispersion modelling.
4. All kind of information mentioned above was the background for the preliminary assessment and air quality zoning in Latvia, followed by optimisation of monitoring network in 2003. Practically, it means more deep fusion of state environmental monitoring under the responsibility of the Ministry of Environment and monitoring at municipal level.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

NEW INSIGHTS INTO ATMOSPHERIC HYDROGEN PEROXIDE UNDER POLLUTED AND REMOTE INFLUENCE

D Möller*, M Bierman, W Wieprecht, K Acker, D Kalass, W Hofmeister and X Tian-Kunze

ABSTRACT

H_2O_2 has been attributed as tracer for the oxidation capacity of the atmosphere as well as a toxic species for plants. The dramatic increase of H_2O_2 concentration found in Greenland ice cores has been explained hypothetically by a negative feedback of flue gas desulphurization in Northern America and Western Europe. The idea that SO_2 does play a limiting factor in atmospheric H_2O_2 burden, initiated an one-year highly time resolved monitoring of H_2O_2 in gas and rain water phase suburb of Berlin (summer 2000 till summer 2001). The diurnal and seasonal variation, influences of different air masses (by using back trajectory calculations), correlation with O_3 concentration and other parameters will be presented. Together with polluted air masses H_2O_2 is declined. Evidence is shown that H_2O_2 is chemically produced in aqueous phase.

INDEX TERMS

Hydrogen peroxide, air quality, concentration trend, seasonal variation, wet deposition

INTRODUCTION

Hydrogen peroxide, which is an important atmospheric oxidant, has been found with increasing concentrations in Greenland ice cores over the past 200 years

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(Fig. 1). Most of the increase has occurred over the past 20 years. Being a natural component of the atmosphere (it has been found in rainwater more than 100 years ago, Schöne, 1872), H_2O_2 is one of the species which is to a large extent responsible for sulfur dioxide (SO_2) oxidation in the aqueous phase (cloud and rainwater) in the troposphere (Hoffmann and Edwards, 1975). H_2O_2 is produced in subsequent radical reactions after ozone photolysis:

$$O_3 \xrightarrow{h\nu} O(^1D) \xrightarrow{H_2O} OH \underset{NO,\ O_3}{\overset{VOC,\ CO,\ O_3}{\rightleftarrows}} HO_2 \xrightarrow{HO_2\ (+\ H_2O)} H_2O_2 \quad (1)$$

There is evidence for direct emission from biomass burning (Lee et al., 1997), formation while lightning (Zuo and Deng, 1999) and aqueous-phase chemical formation without consumption of radical precursors (e.g. Faust and Allen, 1992). However, most atmospheric H_2O_2 sources are also linked with precursors having human activities as source. Peroxides (like H_2O_2) have been found to be harmful for living organisms Radicals, subsequent produced after absorption, might impact enzymatic and genetic cell functions, called oxidative stress (e.g. Möller, 1989). Organisms have learned to build up antioxidant systems for repairing structural damages, which however will not completely compensate this stress, following to accelerated alterations and aging, and finally to death. We have to assume a relationship between the oxidant potential of the atmospheric environment and the oxidative stress within biological systems. H_2O_2 already have been suggested 25 years ago by Kok et al. (1978) as a better indicator for the atmospheric oxidation capacity than ozone. However, also due to difficulties in its measurement, H_2O_2 have been measured only at few sites in the world, where longer time series are extremely limited. One of the spectacular findings was the dramatic increase of H_2O_2 in Greenland ice cores (Fig. 1). Möller (1999) proposed to explain the increase by negative feedback of flue gas desulphurization in the Northern hemisphere on the atmospheric H_2O_2 budget, see Fig. 1.

Thus, it is very important to include H_2O_2 in air quality monitoring. Modellers (e.g. Thompson, 1992) calculated a global increased between 22 and 50% for the period 1920-2030, however, without including aqueous phase chemistry. Lelieveld (2001) calculated that the global H_2O_2 production has increased by 60% since pre-industrial time. Already Derwent and Hough (1987) did show by modelling that H_2O_2 concentration will increase stronger than that of O_3. H_2O_2 seems to bery sensitive to the NO concentration, i.e. with decreasing NO it will increase (Gilge et al., 2000). The main boundary layer sink of atmospheric H_2O_2, however, is aqueous phase SO_2 oxidation (Möller, 1995). Consequently, decreasing SO_2 pollution should result in increasing H_2O_2 residence time which lead to higher atmospheric concentrations and, consequently, favorizing long range transportation. Moreover, recently find "new-type" aqueous phase H_2O_2 formation pathways (not yet included in any CT model) may additional influence the H_2O_2 budget positively. We did measure H_2O_2 in gas phase and rain water during one year suburb of Berlin to study influencing factors an H_2O_2 variations at different time scales.

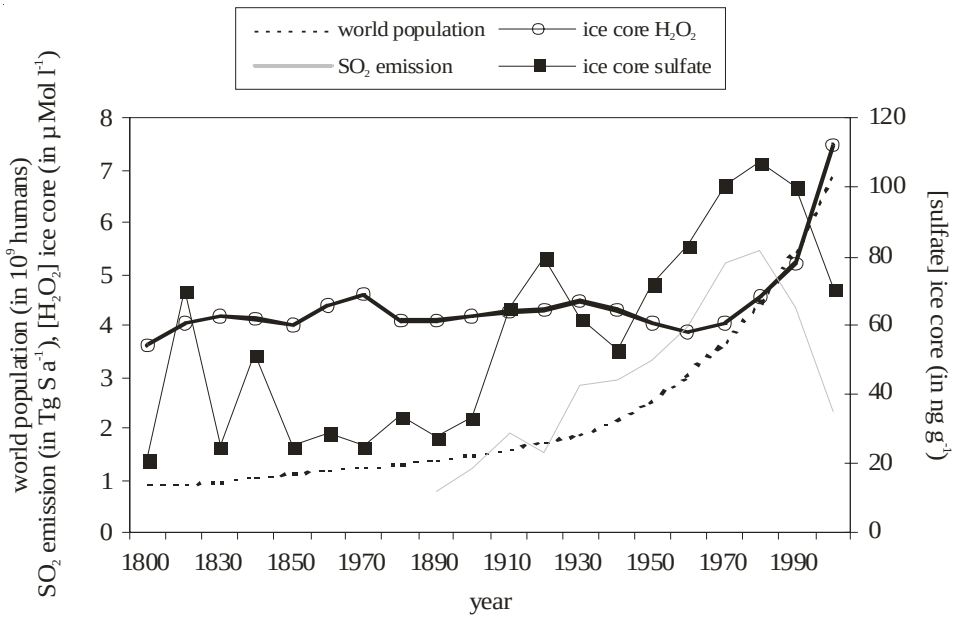

Figure 1. 10-year mean concentrations (in μmol l^{-1}) of Greenland ice core H_2O_2 (Sigg and Neftel, 1991 before 1988, Anklin and Bates, 1997 for 1988-1995) and sulfate (Delmas and Legrand, 1998), world population and total SO_2 emission from Northern America (Gschwandtner et al., 1986) and Western Europe (Molyna, 1996)

METHODS

The monitoring programme have been carried out between May 2000 and July 2001 in Berlin-Adlershof, southern border of Berlin. Gas-phase H_2O_2 was measured by AI 2011CA (Aerolaser), O_3 by Dasibi Model 1108 and SO_2 by TEI Model 43S. Rainwater was collected by a modified Eigenbrodt automatic wet-only collector (including precipitation amount detector) linked with on-line H_2O_2 analysis by an AI 2001 (Aerolaser). Rain water chemical composition was measured by ion chromatography later in our laboratory. Meteorological data were provided by the airport Schönefeld, 5 km more southern. Back trajectory calculation was done by Meteorological Institute of the Free University in Berlin. Quality control for all analytical procedures were done by WMO precipitation chemistry intercomparison and for analysers by intercomparison with them from Institute of Atmospheric Environmental Research (IFU), Garmisch-Partenkirchen. UVA data were provided by Meteorological Observatory Potsdam (DWD).

RESULTS AND DISCUSSION

H_2O_2 concentration does vary in wide range: there is a typical diurnal variation (Fig. 2) and strong seasonal cycle (Fig. 4), beside there are huge fluctuations

depending from meteorological conditions, namely solar radiation and precipitation (Fig. 3).

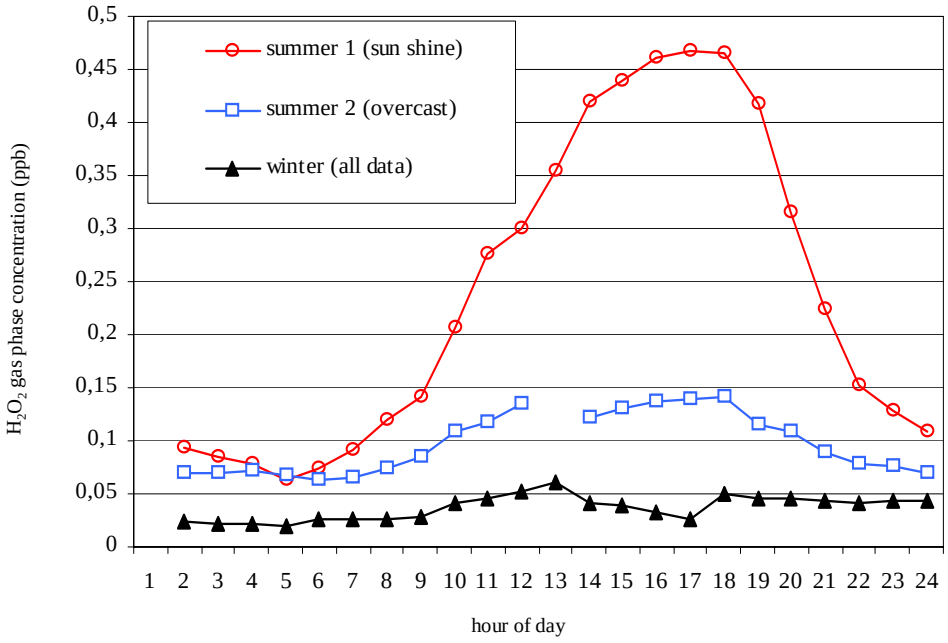

Figure 2. Mean diurnal H_2O_2 variation for selected periodes/situations of the overall measurement periode

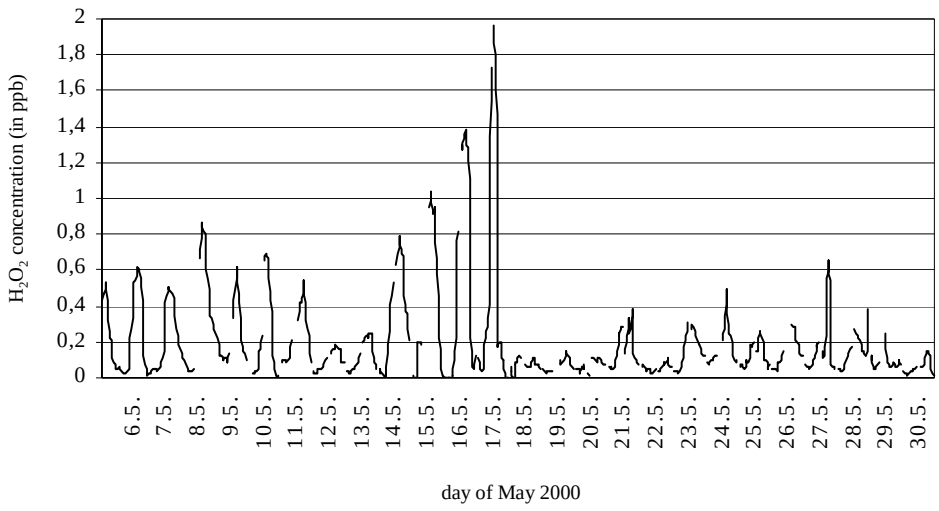

Figure 3. H_2O_2 variation in May 2000 (1 hour averages)

The "typical" diurnal variation, however, is found only at sunny days in summer and being very similar to that one of ozone. It is explained (Möller, 2000) by vertical mixing (downward transport in the morning after broken up the inversion layer) and dry deposition loss in late afternoon when the mixing layer again is established. During daytime photochemical formation is occurring, however, to a small extent. Correlation with ground based ozone have been found to be poor, probably due to ozone loss by NO_x. In contrast, H_2O_2 is chemical stable under dry atmospheric conditions; the only sink near ground is dry deposition. We found, however, a reasonable correlation between daily ground-based H_2O_2 maximum and O_3 measured 323 m abiove ground at a tower, 30 km NW of our site for May 2000

$$[O_3]_{tower} = 47.6 + 70.1[H_2O_2]_{max},\ r^2 = 0{,}59 \text{ (concentrations in ppb)}, \quad (2)$$

suggesting that formation of both species are connected with air masses of enhanced oxidation capacity. Correlation between daily means of H_2O_2 and O_3 are reasonable and also support the similar principial photochemical history of its origin.

H_2O_2 in rain water does show a similar seasonal trend (Fig. 5); it is very probably explained by the solar radiation (Fig. 4). In rainwater seasonal difference are much larger than in gas phase (Table 1). The only "correlation" found between aqueous phase H_2O_2 and another parameter is that with sulfate and nitrate. High sulfate and nitrate in rain water (polluted air) is always combined with low aqueous-phase H_2O_2. However, with low and medium-range sulfate and nitrate also a huge range of aqueous-phase H_2O_2 is occurring. It indicates that H_2O_2 in rain water is influenced by many other parameters in a complex matter not simple reflected by rain water chemical composition.

Subdividing rain events concerning the air mass trajectories (Table 2), seasonal differences may also be explained by different sulfate concentrations. Esp. in summer (when H_2O_2 appears as the main S-IV oxidizing agent in clouds) the anticorrelation between sulfate and H_2O_2 is pronounced.

Considering the H_2O_2 atmospheric budget, we have to take into account three sources of H_2O_2 in rain water: (a) in-cloud scavenging, (b) sub-cloud scavenging and (c) aqueous-phase chemical formation. The only gas-phase production is via HO_2 + HO_2 (+ H_2O), where for HO_2 different formation pathways do exist. $\overline{c_{aq}}\ R_N$ represents the mean wet deposited H_2O_2 mass (expressed in μmol m^{-2}) which can be recalculated into a mean column H_2O_2 concentration (expressed in ppb) according to

$$\left(\overline{c_g}\right)_{column} + \Delta = \overline{c_{aq}}\ R_N\ \frac{1}{h}\frac{\mathbf{R}T}{p}, \quad (3)$$

where Δ = net H_2O_2 production in hydrometeors; **R** gas constant, p air pressure, h column hight (defined being the cloud base). To assess whether there is an aqueous-

phase H_2O_2 net production (i.e. $\Delta > 0$), we now compare $\left(\overline{c_g}\right)_{column} + \Delta$ (= A) with $\left(\overline{c_g}\right)_{daily\ max} \equiv \left(\overline{c_g}\right)_{column}$ (= B) and find the following mean figures:

summer-A	0.70±0,30	winter-A	0.10±0,50
summer-B	0,38±0.11	winter-B	0.07±0.02

Thus, figure A are significant higher than B which means that D is a positive figure. It amounts in summer around 80% of gas-phase H_2O_2 and in winter 40%, resp. This means that the aqueous phase is a net source of H_2O_2, which is stronger in summer than in winter.

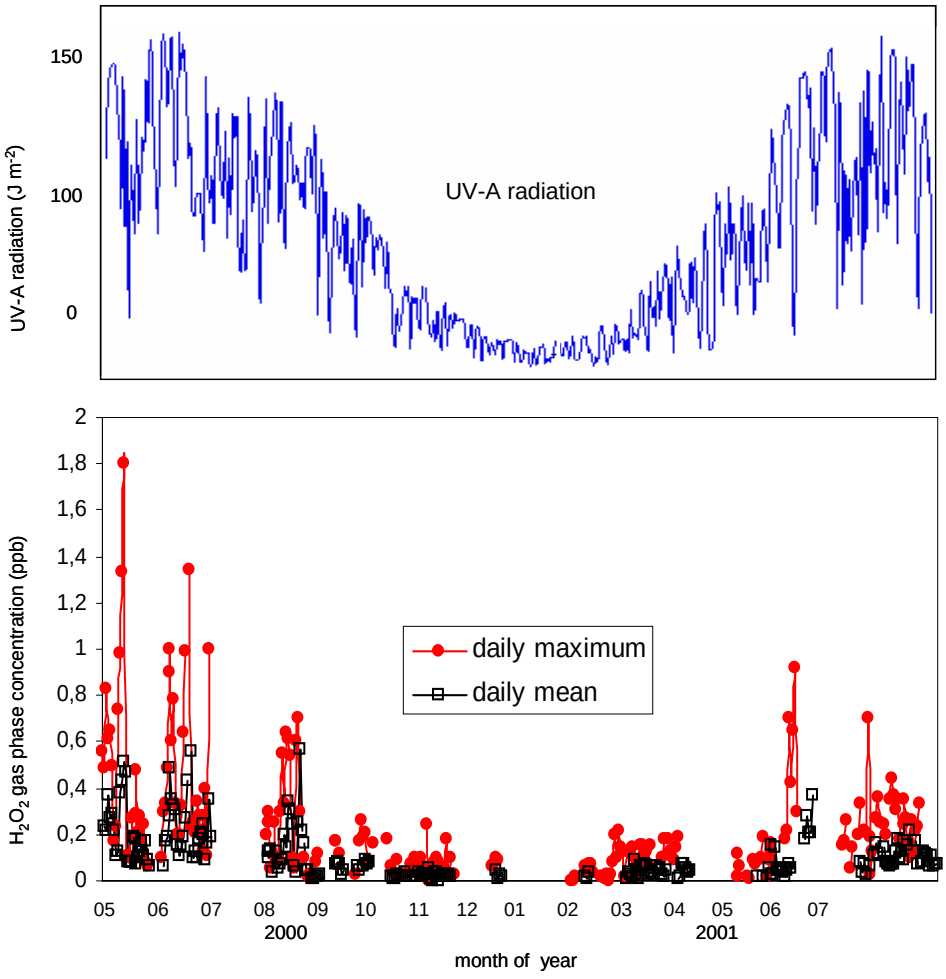

Figure. 4. Variation of H_2O_2 (daily means) in Berlin-Adlershof and UV(A) in Potsdam, May 10, 2000 until July 15, 2001

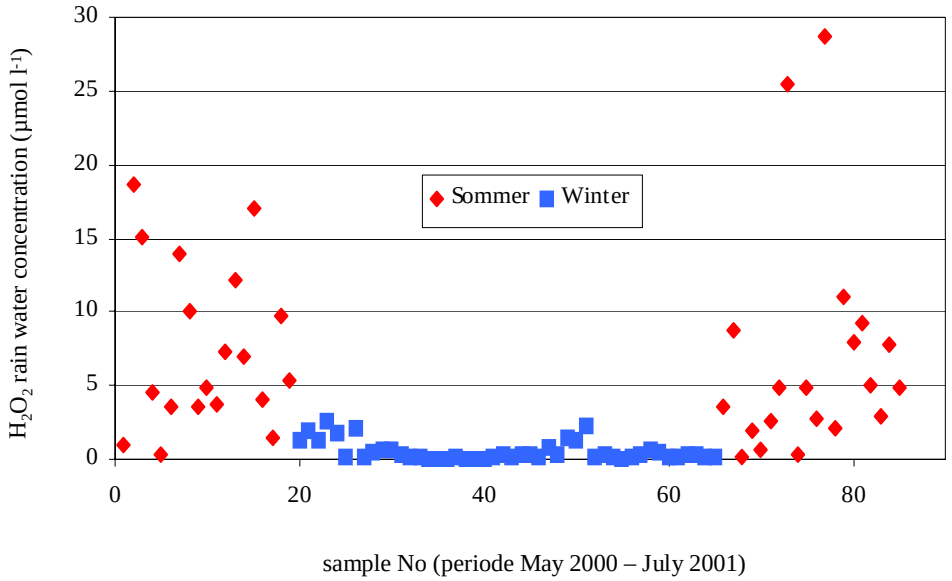

Figure 5. (below) Seasonal variation of H_2O_2 in rain water

Table 1. Averages for summer and winter gas phase (g), precipitation (aq) chemistry and wet deposition (w). n number of rain events, τ_b duration of rain event, R_N precipitation amount, r_N intensity; NO_x concentration from Berlin BLUME network, 9 km SE

	n	R_N (l m^{-2})	τ_b (min)	r_N (l m^{-2} h^{-1})	$[H_2O_2]_{aq}$ (µmol l^{-1})	$[H_2O_2]_w$ µmol m^{-2}	$[H_2O_2]_g$ (ppb)	$[O_3]_g$ (ppb)	$[SO_2]_g$ (ppb)	$[NO_x]_g$ (µg m^{-3})
su	37	5,2±4,5	119±111	2,4±2,1	7,2±6,6	32,0	0,16±0,06	26±11	0,7±0,4	22±14
wi	45	4,1±4,5	271±335	1,0±0,7	0,54±0,68	1,5	0,03±0,02	10±8	1,9±2,0	39±25

Table 2. Mean concentrations of H_2O_2 (in ppb and μmol l^{-1} for gas and aqueous phase, resp.) and sulfate (μmol l^{-1}) for different air mass in summer and winter

	N (NW) - 45° (NE)	W 135° (SE) – 225° (SW)	S 225° (SW) – 270° (W)
aqueous H_2O_2 (summer)	8,1	5,5	11,8
sulfate (summer)	96	117	76
aqueous H_2O_2 (winter)	0,27	0,67	0,54
sulfate (winter)	109	86	135
H_2O_2 ratio summer/winter	30	8	22
gaseous H_2O_2 (summer)	0,17	0,17	0,10
gaseous H_2O_2 (winter)	-	0,03	0,03

CONCLUSION AND IMPLICATIONS

We find evidence for (a) air mass anticorrelation between gas phase H_2O_2 and air pollution and (b) significant H_2O_2 production via hydrometeors (clouds). Air masses burden with more sulfate and nitrate have been characterized with less H_2O_2 comparing with more remote air masses. Thus, the precursors SO_2 and NO will suppress atmospheric H_2O_2. This brings us to conclude that emission abatement will lead to increased atmospheric H_2O_2 concentrations. Consequently, our experimental findings support the hypothetic relationship shown in Fig. 1. With additional future SO_2 and NO emission reduction the peroxide oxidation capacity will further increase. Moreover, there is a strong need to identify (anthropogenic) precursers for H_2O_2 aqueous phase formation and its origin.

ACKNOWLEDGEMENTS

We acknowledge funding of the project by Deutsche Forschungsgemeinschaft (DFG).

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

SHIPBOARD MEASUREMENTS OF LONG-RANGE TRANSPORTED AIR POLLUTANTS OVER THE YELLOW SEA

KC Moon[1, *], YS Ghim[1], GN Bae[1], SB Lee[1] and YP Kim[2]

ABSTRACT

To characterize marine air pollution and long-range transport of air pollutants over the Yellow Sea, the shipboard measurements were conducted on the longitudinal and latitudinal cruising routes from 1999 to 2002. The longitudinal and latitudinal distributions of SO_2, CO, and NO_x did not show a distinct change along the cruising routes. SO_2 concentrations on the cruising routes were lower than those at the background monitoring sites of Deokjeok Island, Gangwha, Taean, and Gosan in Korea, as well as at Qingdao site in China. However, mass and SO_4^{2-} concentrations in $PM_{2.5}$ were higher than those from these monitoring sites. The episodes showing high concentrations of SO_2 or $PM_{2.5}$ both on the shipboard and at the monitoring sites indicate an evidence of the long-range transport of air pollutants by westerlies.

INDEX TERMS

Air pollutants, long-range transport, Yellow sea, sulphur dioxide, carbon monoxide, nitogen oxides, $PM_{2.5}$, sulphates

INTRODUCTION

Due to the rapid industrialization of Northeastern Asia region, significant amount of air pollutants are being released and transported to the neighbor areas. Especially, a quite amount of air pollutants are transported into the Yellow Sea which is located

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between Korean Peninsular and China. Therefore, the long-range transport and deposition of air pollutants over the Yellow Sea should be investigated and quantified. Both long-term monitoring of air pollutants at stationary sites and shipboard measurements over the Yellow Sea are useful. However, there are a few air pollution monitoring sites along the coastlines of Korean Peninsula and China (Figure 1) including Gosan, Jeju known as a super site during the ACE-Asia campaign in 2001.[1] These stationary monitoring sites could give only point measurement data that might be influenced by local sources. On the other hands, the shipboard measurements could provide spatial distributions of long-range transported air pollutants on the sea surface. Previous investigators conducted shipboard measurements of air pollutants over the East China Sea and the Yellow Sea.[2,3] However, they sampled only particulate species for a short intensive period at most once a year. In this study, shipboard measurements of particulate and gaseous species were conducted by using commercial ships on the two interstate longitudinal cruising routes and one domestic latitudinal cruising route on the Yellow Sea. The measurement data were compared with the existing ground monitoring station data. These measurement data could be used to estimate the amount of air pollutants deposition on the Yellow Sea.[4]

METHODS

Three cruising routes of shipboard measurements adopted in this study are shown in Figure 1, together with the locations of existing air pollution monitoring stations.

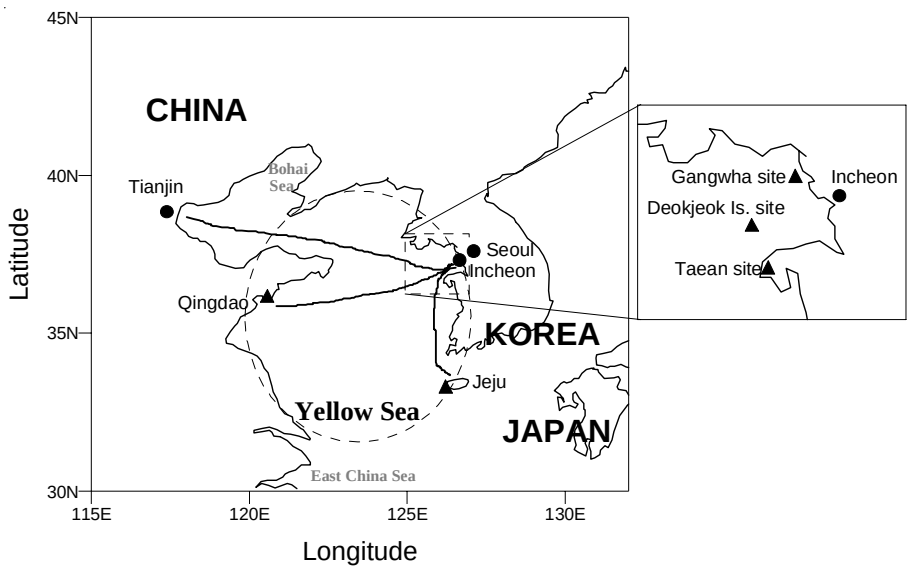

Figure 1. Cruising routes for shipboard measurements together with locations of the air pollution monitoring stations (▲).

To characterize longitudinal air pollution level over the Yellow Sea, we selected two quasi-linear interstate cruising routes across the Yellow Sea between Korean western coast (Incheon) and Chinese eastern coast (Qingdao or Tianjin). The shipboard measurements were made once in spring (April 14-17, 2001), three times in summer (June 12-15, 1999, June 3-6, 2000, and June 3-8, 2002), once in fall (October 23-26, 1999), and twice in winter (December 20-22, 2000, February 28-March 2, 2001) on the cruising route between Incheon, Korea and Qingdao, China (IC-QD route). Only one measurement was carried out on the cruising route between Incheon and Tianjin, China (IC-TJ route) in May 28-31, 2002. The latitudinal air pollution level over the Yellow Sea was investigated on the quasi-linear domestic cruising route along the Korean west coast from Incheon to Jeju (IC-JJ route) once in March 13-15, 2000, and twice in June 12-16, November 15-19, 2000, August 6-12, and November 5-16, 2001.

Shipboard measurements on the longitudinal cruising routes

The cruising route between Incheon, Korea and Qingdao, China was selected because of relatively long cruising time and a quasi-linear path across the mid-Yellow Sea region for investigating the longitudinal variation of air pollutants. To cover the northern part of the Yellow Sea, another cruising route between Incheon, Korea and Tianjin, China was added in 2002. The large regular ferries of a passenger and container carrier were used to sample marine air pollutants. Monitoring equipments were mounted on the upper front deck of the ship to prevent any contamination from own exhaust of the ship such as a stack, and located next to the front rail of the deck to sample fresh marine air. The boundary layer of airflow might be formed on the upper deck, and in a boundary layer the re-circulated air could be contaminated from the stack. The height of sampling position, about 25 m above sea level was likely to avoid the effect of sea salts. The high cruising speed of ferry about 10 m sec^{-1} might result in lower aspiration efficiencies of $PM_{2.5}$ cyclone, and particularly PM_{10} cyclone.

Coarse and fine particles (PM_{10} and $PM_{2.5}$) and gaseous species (HCl, HNO_3, NH_3, SO_2, CO, NO_x) were sampled on shipboard. Two low volume air samplers with a filter holder and a cyclone were used for sampling PM_{10} and $PM_{2.5}$. Water-soluble ions and/or trace elements in PM_{10} and/or $PM_{2.5}$ were analyzed.[5] To avoid the effect of local sources, air sampling was not made within the two-hours cruising distance from the two ports. For the IC-QD route, the marine aerosol sampling lasted overnight for about 14 hours from the evening of the departure day to the next morning. For the IC-TJ route, the marine aerosol was also sampled overnight for about 19 hours. Gaseous species such as SO_2, CO, and NO_x were sampled in a Tedlar bag of 5-10 liters with a personal pump at a flow rate of 1-5 *l* min^{-1} and analyzed at the laboratory within a few weeks. Sea fog was frequently observed except the measurement in October 1999, which might affect the oxidation rates of gaseous species.

Shipboard measurements on the latitudinal cruising route

The small regular ferry of a passenger and container carrier used in this study was operated almost every day between Incheon and Jeju, Korea. The scheduling and installation of equipments on the domestic cruising route were made more easily, comparing with the shipboard measurements on the interstate cruising routes.

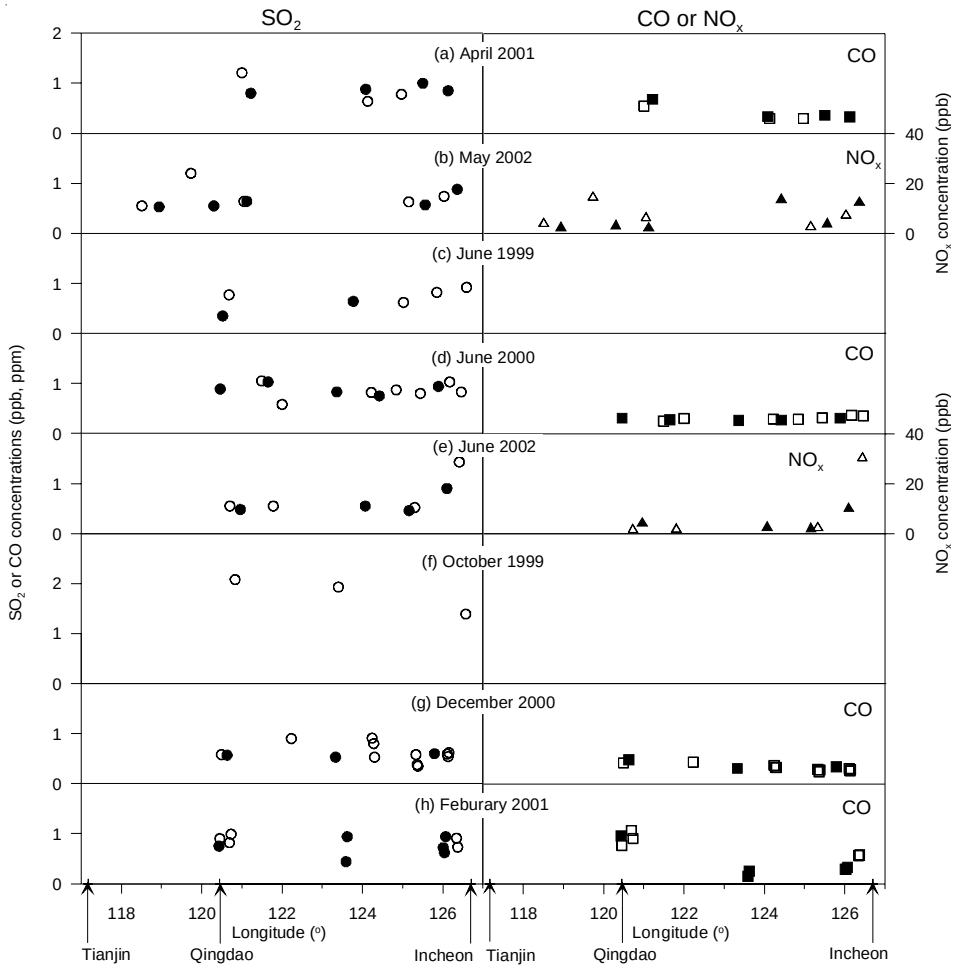

Figure 2. Longitudinal concentration distributions of SO_2, CO, and NO_x over the Yellow Sea. Solid symbols represent the data for forward cruising from Incheon to Qingdao or Tianjin, and open symbols for backward cruising.

The sampling methodology was basically the same as the previous one. At first the sampling equipments were mounted at the rear rail on the upper front deck of the ship. The height of sampling position about 15 m above sea level was a little lower than that on the longitudinal cruising routes. The marine aerosol was sampled continuously for about 11 hours from evening of the departure day to

the next morning. Although the average cruising speed of the ferry was about 10 m sec^{-1}, the relative wind speed that means the vectorial sum of real wind speed and cruising speed, was frequently less than 2 m sec^{-1}, and the relative wind direction that means the vectorial sum of real wind direction and cruising direction, was frequently backward. Therefore, to avoid contamination by the emission from her own stack during the measurement, the aerosol sampling system was equipped with a sector controller operated according to wind speed, wind direction, and particle number concentration since 2001. In the measurement of August 2001, actual sampling time was very short about 4 hours due to frequent operations of the sector controller. So, only one control parameter of wind direction was applied to the sector controller in November 2001. Additionally, the sampling equipments were moved next to the front rail. So, most of the relative wind speed ranged 4-16 m sec^{-1}, and the backward relative wind direction was not observed. The sampling and analysis methods of gaseous species such as SO_2 and CO were also similar to those for the longitudinal cruising routes. In addition to the bag sampling, SO_2 was continuously monitored using a SO_2 analyzer (Thermo Environmental 43C) since August 2001. To protect the analyzer from high relative humidity, a diffusion drier made of silica gel was installed in the sampling inlet, which might underestimate the SO_2 concentration due to gas adsorption.

RESULTS AND DISCUSSION

Marine air pollution level on the longitudinal cruising routes

The longitudinal concentration distributions of gaseous species are shown in Figure 2. Most of concentrations of SO_2, CO, and NO_x were below 1 ppb, 0.4 ppm, and 10 ppb, respectively. The concentrations of gaseous species were not much changed with the longitude on the quasi-linear cruising routes. Also, difference in concentrations of gaseous species between forward and backward cruising directions is not large. The wall loss in a Tedlar bag and sea fog might slightly lower the concentrations of gaseous species.

Since only one aerosol sample was obtained from each way cruising, it is not possible to discuss the longitudinal variation of aerosol concentration. Table 1 summarizes average concentrations of major water-soluble ions in PM_{10} and $PM_{2.5}$ in comparison with the data from the air pollution monitoring stations by the Yellow Sea. Most of PM_{10} mass concentrations were below 50 $\mu g\ m^{-3}$. The average concentration of PM_{10} was 38.2 $\mu g\ m^{-3}$, which is similar to that at Deokjeok site, and is lower than that at Qingdao site. The average concentration of sodium occupied about 1% of the average concentration of PM_{10}, implying that the sampled coarse aerosols were not much influenced from the sea salt. The average concentration of $PM_{2.5}$ was 33.3 $\mu g\ m^{-3}$, which is higher than those at Deokjeok, Gangwha, Taean, and Gosan sites, and is lower than that at Qingdao site. All $PM_{2.5}$ to PM_{10} mass concentration ratios except one sample were greater than 0.7, which is higher than the average ratio of 0.59 at Deokjeok Island.[5] Most of the

ratios of nearly 0.9 implies that long-range transported fine particles were predominant. Under high wind speed conditions the relatively low aspiration efficiency of coarse particles might increase the mass ratio. Mass concentrations of PM_{10} and $PM_{2.5}$ were high in the winter season. SO_4^{2-} was a dominant anthropogenic component in PM_{10} and $PM_{2.5}$. The mass and SO_4^{2-} concentrations in $PM_{2.5}$ on the IC-TJ route are higher than those on the IC-QD route, showing that the northern part of the Yellow Sea is more polluted than the mid region. Shipboard measurements during the cruising a) between Incheon and Qingdao from June 1999 to June 2002, b) between Incheon and Tianjin in May 2002, and c) between Incheon and Jeju from April to August 2001, d) April, June, and November 2000[6], e) TSP for coarse particle; from April 1999 to March 2000[5], f) San Nicolas Island in North Pacific from June to September 1987[7], f-1) Santa Maria Island in Azores in the mid-North Atlantic Ocean during 2-23 June, 1992[8], g) July 1998-June 1999 for particle[5], h) November 1998-July 1999 for particle[5], i) March 1996-December 1997 for particle[5], j) September 1997-November 2000[9], k) January 1999-December 2000 for SO_2[4], l) Annual average in 1999, *XX±YY: average±standard deviation, **A/B: sample number for mass/ for ions.

Table 1. Comparison of mass, water-soluble ions, and gaseous species concentrations in PM_{10} and $PM_{2.5}$.

(a) Coarse particle (PM_{10}) concentration ($\mu g\ m^{-3}$)								
	Mass	SO_4^{2-}	NO_3^-	NH_4^+	Na^+	Ca^{2+}		
IC-QD[a] (11/7**)	38.2±27.0*	11.7±9.3	5.7±4.5	3.9±3.0	0.5±0.3	0.20±0.16		
IC-TJ[b] (2/0)	103.9	-	-	-	-	-		
IC-JJ[c] (10/13)	43.9±28.1	10.5±8.1	5.6±6.2	3.7±2.4	0.9±0.9	0.29±0.28		
Deokjeok[e] (49/36)	37.2±21.8	6.4±3.1	2.5±2.8	1.9±1.4	0.6±0.4	0.45±0.34		
Qingdao[d] (24/24)	77.8±43.2	15.9±10.9	7.2±5.7	7.1±5.4	0.7±0.3	-		
World Oceans[f] (11/11)	17.4	3.57	1.58	0.85	-	-		
(b) Fine particle ($PM_{2.5}$) and gases concentrations ($\mu g\ m^{-3}$ except ppm for CO)								
	Mass	SO_4^{2-}	NO_3^-	NH_4^+	Na^+	Ca^{2+}	SO_2	CO
IC-QD[a] (13/13)	33.3±20.7	9.8±6.1	2.9±3.4	3.0±2.1	0.4±0.2	0.11±0.08	2.2±1.0	0.435
IC-TJ[b] (2/2)	46.0	14.4	5.2	5.1	0.3	0.11	1.8	-
IC-JJ[c] (12/15)	29.8±19.6	7.2±6.1	3.4±3.5	2.6±1.7	0.4±0.3	0.19±0.20	3.4±2.5	0.5±0.2
Deokjeok[e] (50/37)	18.7±10.1	5.4±3.1	1.0±1.3	1.7±1.0	0.3±0.3	0.09±0.06	6.2±6.0	-
Qingdao[d] (24/24)	50.5±29.4	14.0 ±9.9	5.8±5.2	6.8±5.3	0.3±0.1	-	50.8[j]	-
Gangwha[g] (61/60)	29.3±17.7	6.3±6.0	1.4±1.9	2.4±1.8	0.6±0.5	0.57±1.27	11.2±4.8[k]	0.6[l]
Taean[h] (64/64)	20.6±17.9	4.2±3.5	0.7±1.1	1.3±1.4	0.6±0.4	0.14±0.11	5.0±4.2[k]	0.1[l]
Gosan[i] (40/40)	16.6±1.23	5.1±0.5	0.7±0.1	1.5±0.1	0.6±0.1	0.15±0.03	3.9±1.6[k]	-
World Ocean[f] (11/11)	9.7	2.77	0.46	0.68	-	-	0.3±0.2[f-1]	-

Marine air pollution level on the latitudinal cruising route

The latitudinal concentration distributions of SO_2 and CO are shown in Figure 3. SO_2 concentration is sometimes locally high, on the other hands, CO concentration is fairly uniform with the latitude. SO_2 concentrations obtained by a Tedlar bag and from the SO_2 analyzer were compared for the measurements of November 2001, which is not shown in Figure 3. Difference between them was not significant in lower concentration range less than 3 ppb. However, the SO_2 concentrations

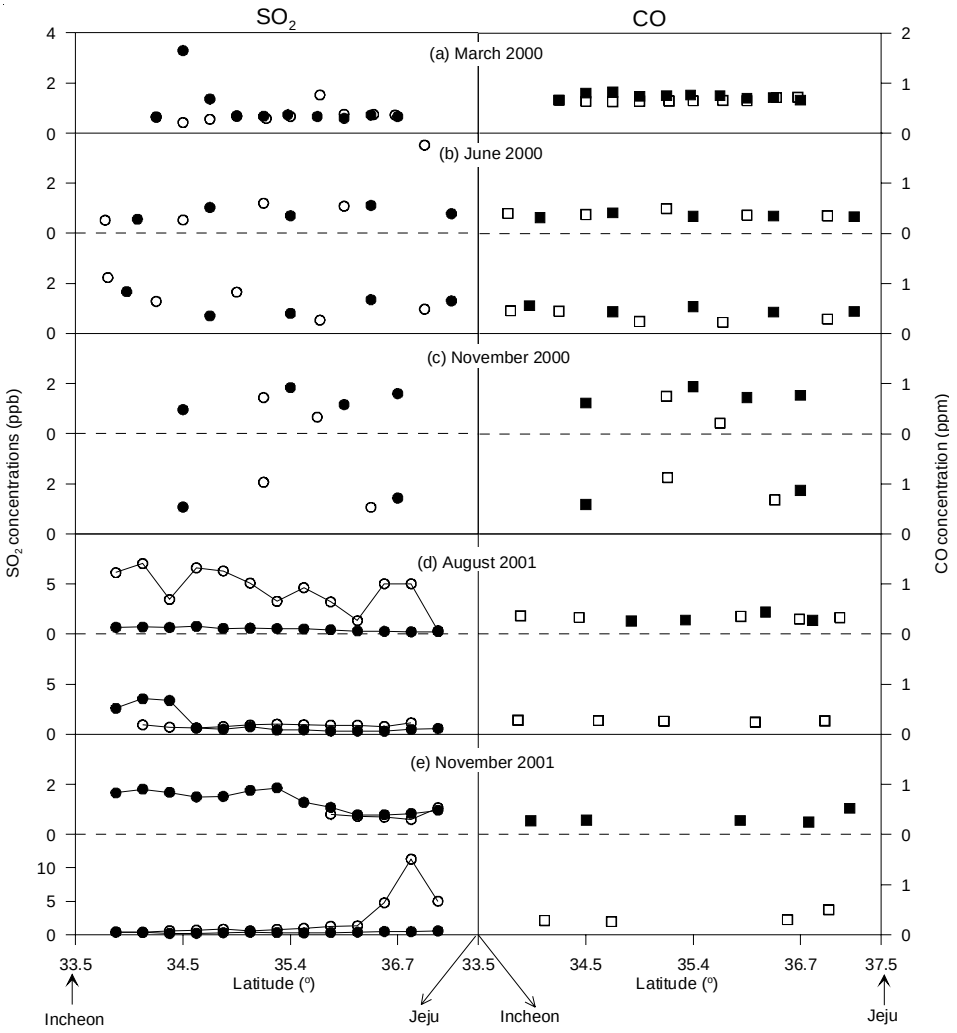

Figure 3. Latitudinal concentration distributions of SO_2 and CO over the Yellow Sea. Solid symbols represent the data obtained for forward cruising from Incheon to Jeju, and open symbols for backward cruising. Symbols with line indicate the data measured by a SO_2 analyzer.

in a Tedlar bag are only about 40% of those with a SO_2 analyzer in higher concentration range above 3 ppb, implying high wall loss in a Tedlar bag. As shown in Figure 3, SO_2 concentration was the highest in the measurement of November 2001, and was also the highest at the urban background site in Qingdao at the same time. Backward trajectory analysis showed that the air mass arrived at the shipboard measurement location was passed over the Qingdao region, supporting the possibility of long-range transport of SO_2 over the Yellow Sea.
As shown in Table 1, average PM_{10} mass concentration measured on the IC-JJ route is slightly higher than that on the IC-QD route. However, average $PM_{2.5}$ mass concentration of the IC-JJ route is slightly lower than that of the IC-QD route. Average SO_4^{2-} concentrations of the IC-JJ route are slightly lower than those of the IC-QD route both for PM_{10} and $PM_{2.5}$. The average concentrations of NO_3^- and NH_4^+ of the IC-JJ route are similar to those for the IC-QD route both PM_{10} and $PM_{2.5}$. The highest mass concentration (84 μg m^{-3}) of $PM_{2.5}$ was observed on the shipboard measurement from Incheon to Jeju on June 14, 2000. This episode was also found at the background monitoring sites on the Korean western coast at the same time. This is considered as an episode of long-range transport of aerosols.

ACKNOWLEGEMENTS

This work was supported by the Ministry of Science and Technology, Korea, for Yellow Sea Research under grant 98-LO-01-01-A-03. We gratefully acknowledge the Korea Telecom for providing the facility at the Deokjeok Island station. Special thanks should be given to Weidong and Jinchon ferry companies for allowing and helping shipboard measurements on their ferries.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

AIR POLLUTION IN ITS SOCIO-ECONOMIC CONTEXT: A PRODUCT FOCUSSED POLICY FOR THE FUTURE

J Murlis*

ABSTRACT

Since the industrial revolution human activity has released materials to the atmosphere. Some are new and many have proved harmful. Air pollutants, arising in particular from energy conversion and manufacturing processes, have become globally distributed and are now to be found in all environmental compartments. The impacts of air pollution are felt at local, regional and global levels. The greatest effects in terms of health and quality of life fall disproportionately on the poorer countries and, within countries, poorer communities and individuals. The pressures that create air pollution arise ultimately from growing demand for goods and services but operate through a long chain of actors, including those involved in production use and eventual disposal. Current control measures have focused mainly on particular parts of the chain, typically directly on emissions through end of pipe and other technological measures. These have proved costly, slow to implement and, without action on other parts of the chain, of limited effectiveness. New ways of controlling pollution, addressing root causes and co-opting socio-economic processes are urgently needed. This paper argues for a more holistic approach with a suite of integrated measures focussed on products and services themselves and involving all the actors involved in their life cycles.

INDEX TERMS

Air pollution, Product Policy, Sustainable Development, social equity, consumer information.

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INTRODUCTION

Evidence of damage from air pollution has been so compelling that societies throughout the world have invested heavily in measures to control sources of harmful atmospheric pollution. This has been mainly through "end of pipe" and other technological measures to reduce emissions. The cost and complexity of these measures has slowed the progress necessary to protect health and the wider environment. Much remains to be done. This paper is about the wider context for air pollution and the socio-economic environment in which new approaches must be developed. It suggests that more effective solutions may lie in approaches that address process of consumption in their entirety.

The 1992 UN Conference on Environment and Development, marked a turning point in framing and managing environmental problems. Increasingly the environment is seen as a whole rather than as compartments that can be managed separately. Increasingly, too, environmental issues themselves are seen in a larger context in which social and economic pressures interact with the environment and in which sustained progress depends on managing them together.

This wider context of sustainable development provides opportunities and challenges for managing air pollution. Understanding how air pollution interacts with other environmental issues, how it arises from patterns of consumption and how these are in turn are effected by social and the economic climates are essential prerequisites for developing and implementing new management regimes. Given the scale of challenge in other dimensions of sustainability, solutions to air quality problems will have to be thoroughly integrated with broader objectives for social and economic progress as well as those for the wider environment.

AIR POLLUTION IMPACTS ON ALL SCALES AND IN ALL COMPARTMENTS

At a local scale, air pollution impacts directly on people and environment, threatening health and the quality of the local environment. The great London smog of 1952 is a good example. Regionally, the products of air pollutants, transformed in the atmosphere, impact on natural ecosystems and on human health, for example through acid rain and photochemical pollution. Globally, air pollution adds to natural greenhouse gas concentrations and creates climate change.

Some air pollutants make their way into other environmental compartments. Toxic micropollutants found in the fat of polar bears in the Canadian Arctic, started life many months earlier as products of incomplete combustion in far lower latitudes: the materials travelled, in several stages of deposition and re-suspension, through the atmosphere, landed on soils, washed into rivers, entered the marine food chain, travelled through fish and seals and finally found their way into the bears' fat where they accumulate and are eventually recycled back through arctic ecosystems (AMAP, 1997).

The effects of air pollutants are not restricted to health and the environment. The smogs of the 1950s created travel chaos, with consequent damage to the UK economy. Acid rain did great economic damage, through impacts on the fabric, for example of historic buildings and on sensitive but prized ecosystems. The South East Asia smog of 1997 was blamed for road accidents, collisions at sea and at least one fatal aircraft accident. The damage was estimated by WWF at $6 billion (Schwela et. al., 1999). Impacts of global warming will be economically highly significant and there will be severe geopolitical consequences, as nations and people react to increased desertification and sea level rise (Pearce et. al., 1996).
Effects of air pollution, then, appear at all scales from local air quality to global warming. They penetrate into all environmental compartments and impact on societies and economies.

AIR POLLUTION: THE UNEVEN BURDEN

Air pollution problems have their origins largely in industrial process and in the conversion of energy. Industrial growth, fuelled by vigorous demand for goods and services, has created considerable wealth for the populations of developing countries and the signs of industry, impressive factory buildings and smoke-filled skies were originally celebrated and welcomed. It was not long, however, before the damaging impacts of industry on society and the environment attracted public concern, rapidly converted, in Britain, into legislation through the Factory acts and the Alkali acts of the 19th century. Since then, development and the creation of wealth have continued, with new an different environmental impacts and with new legislation appearing to manage those that turn out to be politically unacceptable. At a local and regional scale political pressure, responding to impacts that can be readily measured and explained, has ensured that environmental effects of development do not become so harmful that the processes of development themselves are challenged.
In the countries now in transition to a market economy and more open political processes, there was considerable industrial expansion following the end of the 1939-45 war. This was achieved in the context of central planning, without the political expression that would have ensured that environmental impacts were managed effectively. Following the institutional changes in these countries, there has been the urgent need to replace inefficient and polluting industry. Given the regional location of these countries, in proximity to the wealthy countries of Western Europe, there has been considerable interest in ensuring this happens as quickly as possible. International funding has assisted with the necessary investment.
Rapid economic advance in a third group of nations, the developing countries, however, has taken place largely without the stringent controls or investment in clean technology. The social and political imperatives of economic progress have been stronger than concerns about its longer-term impacts on environment or health. With the added burden of high demand for transport, it is now the

developing countries in which urban air pollution problems, for example, are most acute. Effects of ambient air pollution in the most polluted World cities are estimated by the World Health Organisation (WHO, 2000) to effect some 1.5 billion people with 2 billion exposed to high levels of pollution indoors.

The smog over South East Asia of 1997 was an example of the environmental impacts of rapid economic development on developing countries. The problem arose from forest burning for land clearance, combined with pollution from power stations and transport. The problem reoccurred in 2002 and reminded governments in the region that there was now a new balance between narrow economic interests and the broader economic development of the region. Tourism, for example, may turn out to be a more significant economic activity than agriculture but would be deterred by poor air quality. There are consequent signs of a new determination to tackle the air pollution problems: Mexico City authorities are gradually enforcing controls on pollution from transport and the Bangla Desh Government announced a ban on tricycle rickshaws with two-stroke engines (BBC, 24 April 2000).

It seems that in countries of all stages of economic development, there is a growing appreciation of the links between the broad economy, quality of life and environmental quality. Concern about air quality is now high on Governments' agenda. At the same time there are strong aspirations of consumers in all these countries to achieve improved access to goods and services. These will make the task of controlling air pollution hard.

Overshadowing all these local and regional issues, however, is the serious challenge to sustainable development from man-made climate change. Whatever technological means are used to control local and regional pollution, the main energy carriers for economies across the world are fossil fuels. Development on the basis of energy intensity levels enjoyed by the economies of the world's wealthy countries would be a global disaster. Equity between countries in access to energy services and a break in the link between prosperity and per-capita consumption of fossil fuels will be essential components of long-term economic and political stability.

Within countries, and even within urban areas the pollution burden is shared unevenly. A recent UK study (Pye et. al., 2001) shows significant relationships between levels of air pollution and a range of indicators of social disadvantage. Disadvantaged communities tend to lack the political strength needed to resist development, or live on low value land. The California Air Resources Board has an Environmental Justice programme to address inequalities, with its own air monitoring and community outreach budgets (CARB, 2001). The CARB programme recognises the close integration of air quality and quality of life. It spans the many root causes of air pollution, including waste disposal and failure of public transport, and provides support for local communities in tackling them.

The impacts of air pollution on health and quality of life, then, reflect poverty and relative depravation, globally and within countries and conurbations. Yet economic advance achieved through increasing the consumption of those presently

deprived simply increases the overall burden. This attaches air quality agenda firmly to broader agenda of social and economic progress and to issues of equity. The emergence of climate change as a major challenge to future prosperity provides a powerful incentive to address these issues together.

AIR POLLUTION SOURCES: NEW MEANS OF MANAGEMENT

In the main, current means of tackling environmental impacts of consumption focus on manufacture, regulating emissions and other aspects of environmental performance in industry. Much of the effort to control air pollution has been directed towards end of pipe and other technological regulation of industrial processes. These controls have been effective in dealing with immediate problems on a local and regional scale. But they are costly and cumbersome and there are concerns about the rate of progress that can be achieved in the face of rapid growth of consumption.

Consumption patterns of products and the use of energy to secure services (heating and mobility, for example) are the result of decisions made by a long chain of actors. From the time they are conceived, in a corporate environment by marketing departments, to the time they reach the end of their life in service and their remains have to be disposed by waste handlers products go through many hands. At each stage there are opportunities for intervention to reduce their final environmental impacts.

Marketing and design has a considerable influence. There are broad ethical considerations at play in the dialogue between marketing people and the consumers whose requirements they seek to reflect, or to influence. Marketing departments have the potential part to play in the development of markets for alternative products with high environmental performance. Environmental markets exist and are believed to be a growing force in consumerism but there remains much for marketing specialists to do to realise this potential.

Designers can, by taking a life cycle approach, ensure that environmental impacts are minimised throughout manufacturing, use and end of life management. For example, vehicle manufacturer have made considerable progress in designing for minimum emissions and to maximise the proportion of components that can be recycled.

Product manufacture uses many inputs, including minerals, chemicals and energy. To an extent the contribution energy and chemicals make to product environmental performance is folded into the overall performance through industrial regulation. However, it has proved difficult to provide a detailed regulatory framework for each of the many chemicals in volume production and a focus on the products to which they contribute is seen as an alternative to individual risk assessments. In the case of energy, requirements are growing for energy labelling of consumer products such as refrigerators to show their energy efficiency. In some cased, resources are also accounted in the labelling of products, for example where timber from sustainably managed forests has been used.

Consumers play a leading role through the choices they make. Information is essential to inform these choices. For example, prices can signal environmental performance of products if external costs are correctly internalised, but even simple indications from labels support choice in environmental markets. In use, the environmental impacts of products depend to an extent on how consumers behave. For example, the impact of tyres, for example in the contribution they make to airborne particulate matter, depends on driver behaviour. This is linked to the life they achieve in service, which can provide another cost signal to the consumer. This link between good environmental performance and consumer economy exists in many cases but there are others where the manufacturers instructions do not necessarily coincide with immediate economy. In the case of cars, for example, manufacturers recommendations for the calibration of the engine are designed to secure regulated emissions performance, ensuring that emission control equipment is working in optimum conditions. This, however, may not produce best fuel consumption and owners have been know to tamper with the calibration to improve fuel consumption at the cost of higher emissions of regulated pollutants. For such instances, service testing becomes an essential though costly necessity.

The problems of managing the end of life of products have been recognised and are being addressed by governments, largely through waste regulations. These can range from limitations on landfill to control of effluents from sewage works. However, there are also product-focussed approaches, including design for reuse of components and recycling of materials or for rapid and harmless degradation of chemicals. The UK motor industry Automotive Consortium on Recycling and Disposal, ACORD, estimated in 2002 that recycling had reduced the proportion of material from cars withdrawn from service going to disposal to below 20% of the total. There is however, considerable scope for improvements in the management of vehicles at the end of their lives with design to maximise the number of components that can be reused and to minimise the quantity of un-recyclable materials.

An approach to environmental performance based on product offers an attractive alternative both to Governments and to regional authorities such as the European Union. In a recent Communication, (European Commission, 2003) the European Commission has described Integrated Product Policy as a major contribution to sustainable development. It draws attention to the potential gains from a combination of life-cycle analysis and the contribution of a wide range of stakeholders to reduce the environmental impacts of products. Choice matters. A recent report to the European Commission (Labouze and Monier, 2003) suggests that the environmental impacts of equivalent consumer products vary by up to ten times.

However, the work done for the European Commission is based on impacts within Europe alone. Consumer products have far wider impacts (ACCPE, 2002). These will not be limited to the direct environmental impacts but will spread to broader impacts on economies and society. Despite the difficulties in quantifying these, they will inevitably increase external costs and the performance range of options available to consumers.

As the ACCPE report notes, there are many tools that can be used within a product-based approach, including taxes to internalise external costs and education for designers. In particular, it suggests, information for consumers, provided through labelling, ratings or simply descriptions of the life cycle impacts of the products they use is a powerful means of supporting choice for those who wish to incorporate sustainability into buying decisions.

This broad approach to environmental management has much to offer air quality in its socio-economic context. By addressing products as a whole and in particular the services they provide it should be possible to ensure that economic development and progress towards equity in access to goods and services can be achieved without disastrous impacts on the overall air pollution burden.

CONCLUSIONS

The pollutants that create poor air quality are also implicated in a wide range of other detriments to the environment and society. They end up reducing quality of life and prosperity. The damage they cause falls disproportionately on the poor, at national and international scales.

Despite considerable progress and significant investment, air quality problems persist. The proven end of pipe regulatory approaches may have achieved as much as they can and further improvement will depend on a more integrated approach, addressing air quality in the context of the patterns of consumption that are the root cause of emissions of air pollution.

A more integrated approach will involve exploring and understanding the full extent of pollution impacts and the linkages there are between air quality, the wider environment, quality of life and prosperity. This is the challenge we face now.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

UPPER-AIR WIND ROSES FOR THE WESTERN CROATIA

K Pandžić*

ABSTRACT

Synoptic scale upper-air (at the constant pressure surface of 850 hPa; about 1500 m above sea level) wind direction frequency has been considered for one grid point representing the western region of Croatia (especially *Lika* and *Gorski Kotar* region). Wind data sample, from period 1971-1980, has been divided into several classes depending on the season and daily precipitation amounts. The results indicate prevailing south-western upper-air wind directions for wet days (so called precipitation wind roses) and north-western for dry days. Some seasonal variation of wind direction distribution has also been observed. Spacious distribution of average wind vectors for dry and wet days, respectively, has been performed for the Alpine-Adriatic region. A possible correlation among above precipitation wind roses (patterns) and deposition of air pollutants over the region has also been discussed.

INDEX TERMS

Wind roses, Spacious wind patterns, Deposition of air pollution, Croatia.

INTRODUCTION

Croatian part of the Adriatic mountainous hinterland (especially *Lika* and *Gorski Kotar*) is one of the European regions with the highest long-term annual average precipitation amounts. They reach the values of 3000 millimetres per year. Studies indicate a strongly dependence of mentioned precipitation amounts on altitude as well as on exhibition of the area to the "southern" winds blowing over the region (Blumen, 1990; Pandžić, 2000; Ivančan-Picek et al., 2001). These results could also be useful for study of air pollutant deposition into the area.

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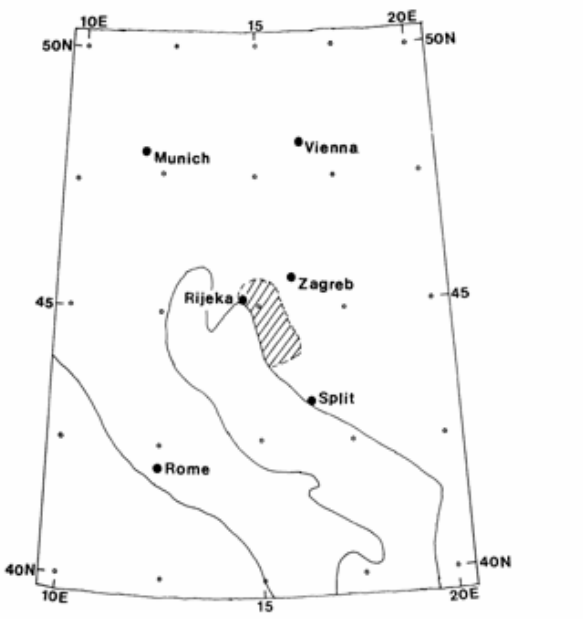

Figure 1. Alpine-Adriatic grid points for which wind field is considered. Western Croatia *Lika* and *Gorski Kotar* region is shaded.

METHODOLOGY AND DATA

Synaptic scale flow, i.e. wind at 850 hPa isobaric surface has been considered (about 1500 metres above sea level what is also level of the highest mountain tops in the area). More precisely, for wind roses' calculation, wind data are taken for a grid point located above *Lika* and *Gorski Kotar* region (Figure 1), which is appropriate reference point for western Croatia. Spacious average wind vectors have been calculated for 5x5 grid points. Daily (00 and 12 UTC) wind data are refereed on period 1971-1980. They are a part of NCEP/NCAR (NCEP - National Centres for Environmental Prediction; Washington; NCAR - National Centre for Atmospheric Research; Boulder) so called *reanalyses* of global weather data.

RESULTS

Wind roses and mean wind vectors to be obtained, days from data period have been classified into three groups: days without precipitation, those with precipitation and with precipitation higher than 10 millimetres, for winter and summer season respectively. Wind rose results indicate that in precipitationless days, north-western wind prevails, while south-western directions are dominant during rainy days especially in the case of relatively heavy precipitation i.e. when daily precipitation is higher than 10 millimetres (Figure 2).

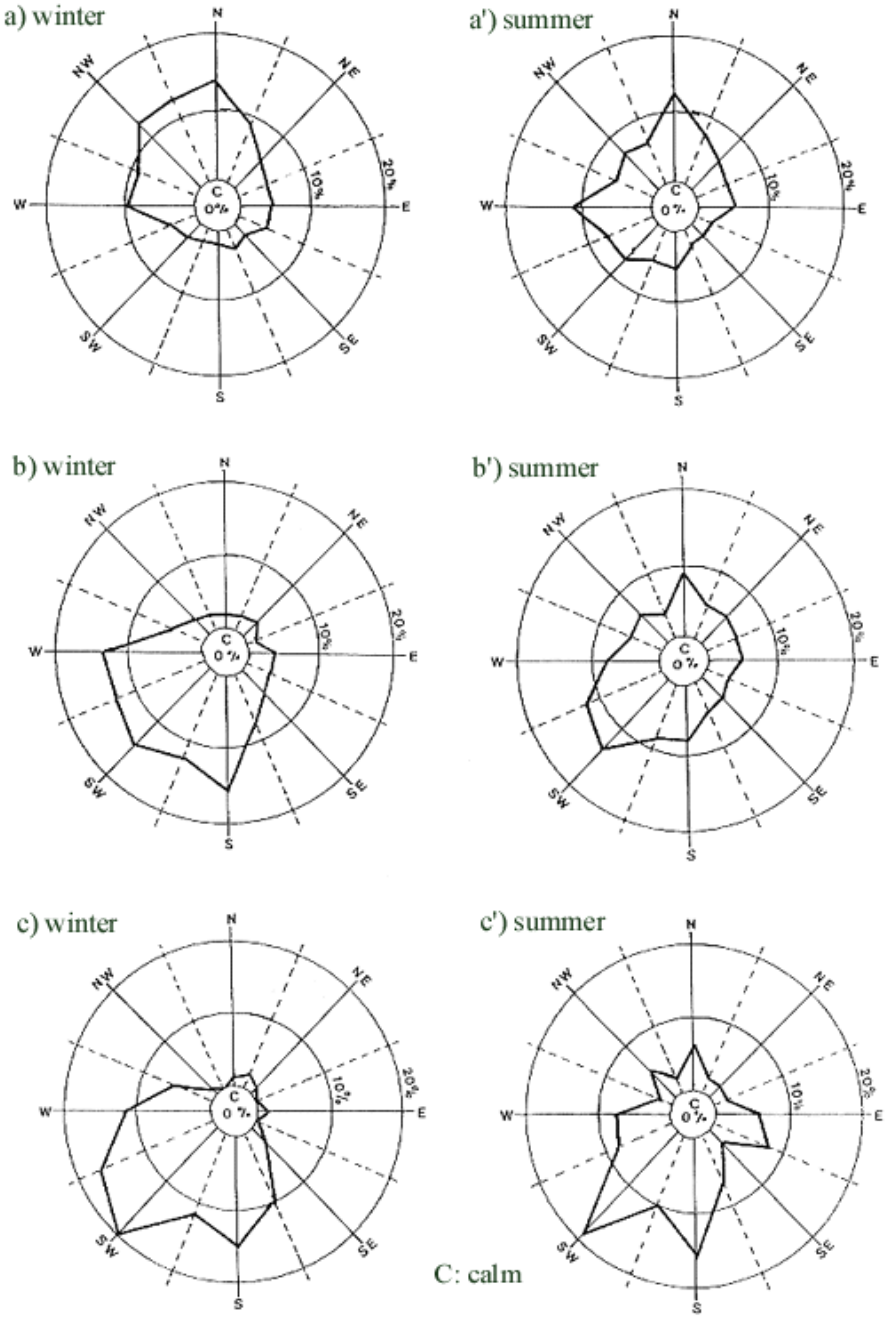

Figure 2. Wind roses for 850 hPa surface above Croatian *Lika* and *Gorski Kotar* region: no precipitation days (a, a'), precipitation days no matter what amount is (b, b') and days with precipitation higher than 10 millimetres.

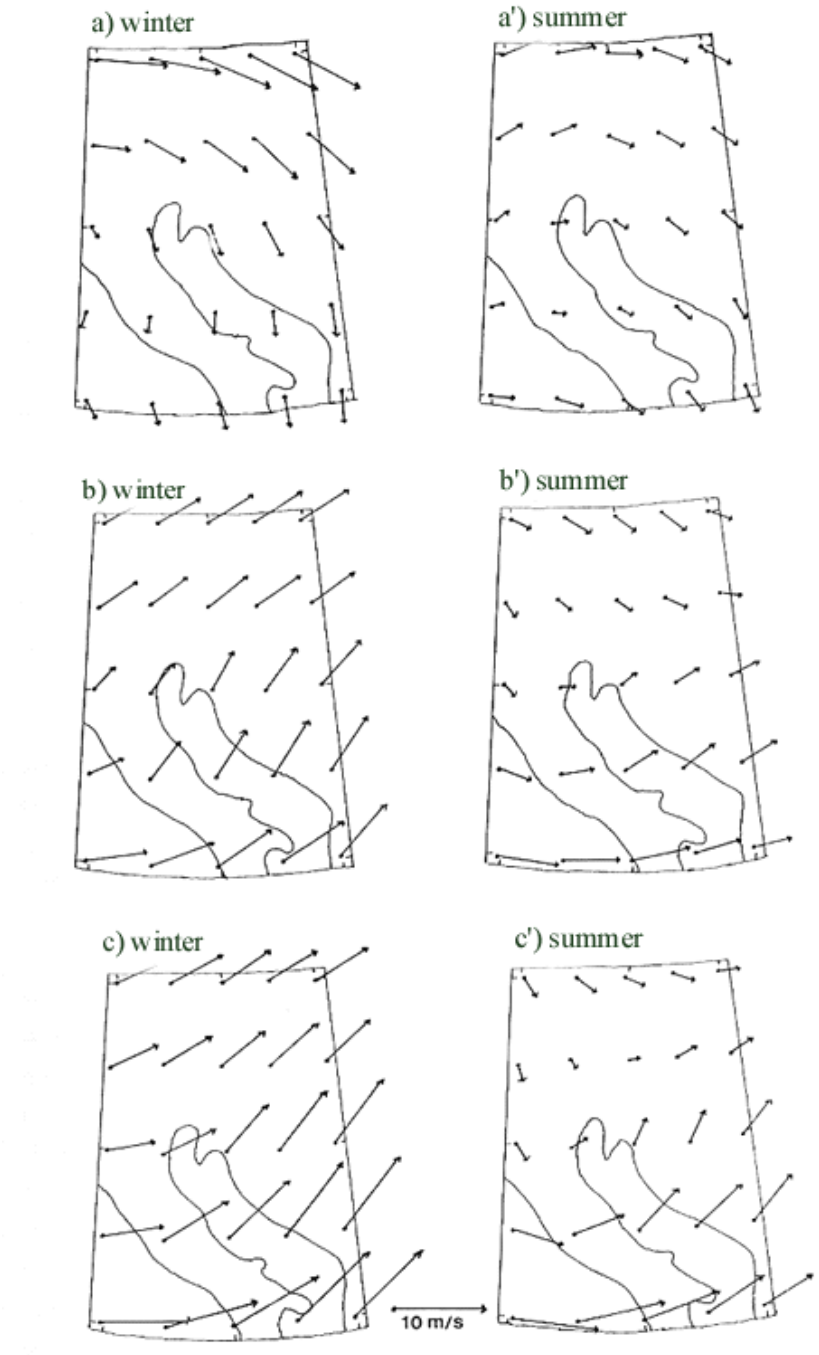

Figure 3. Average wind vectors for 850 hPa surface above Croatian *Lika* and *Gorski Kotar* region. The other is as in Figure 2.

The second part of the wind field analysis, connecting with precipitation over *Lika* and *Gorski Kotar*, includes a space distribution of average wind field over Alpine-Adriatic region (Figure 3). The days are grouped into three categories depending on the precipitation as in the case of the wind roses. Average wind vector over *Lika* and *Gorski Kotar* are from north-western directions for no precipitation case, while they are south-western directions for rainy days. A cyclonic curvature of streamlines for rainy days and anticyclonic for no precipitation days can be imagine what corresponds to the troughs and ridges in the field of absolute topography of 850 hPa surface. Wind speeds are generally higher for winter than summer season. A convergence zone in the summer precipitation case wind field can be observed. This makes association on the frontogenetic zones what is very realistic for the area considered in warm part of the year.

Above considered results cold be powerful tools for study of air pollutant deposition within the area. As first, it could be concluded that dry deposition of air pollutants is prevailing influenced by NW winds while wet deposition (via precipitation) is more under SW wind influences.

CONCLUSIONS

Previous empirical analysis of the average annual precipitation patterns over *Lika* and *Gorski Kotar* has indicated a strong dependence of precipitation amounts on orography of terrain and wind direction. The first, but not independently of the second, causes the higher amounts of precipitation on windward sides of the hills and mountains than in their leewards. The wind roses indicate existence of atmospheric system causing precipitation or no precipitation conditions. Thus, south-westerly winds on the 850 hPa surface indicate existence of cyclonic systems over the area, while north-westerly wind directions mainly indicate anticyclonic system. These results could be useful for study of dry and wet deposition of air pollutants over the area.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

USE, MATERIALS, ENVIRONMENTAL EFFECTS AND PERSPECTIVES OF GEOTHERMAL ENERGY

G Santoprete[1, *], A Tarabella[1]

ABSTRACT

After outlining the contribution given by scientific research, conducted by the Italian industry, to the development of the use of geothermal fluids across the world, the Authors investigate their main applications in industrialised and non-industrialised countries, while highlighting the advantages they offer compared to thermal and electric energy.
Special attention is paid to the main forms of environmental pollution associated with the exploitation of geothermal fluids, such as air, water and soil pollution, noise, subsidence and induced seismicity. Regarding emissions, a comparison is made between pollutants emitted by geothermal power plants and traditional fuel plants (natural gas, oil and coal). Given the importance of the non-condensable gas emissions contained in geothermal fluids, this paper reviews some methods for minimising such emissions. In addition, it considers other substances, such as boron, ammonia, mercury and radon. A distinction is drawn, among pollutants discharged in water bodies, between dominant steam and dominant water fields, since they produce differing environmental impacts. One way to fight pollution could be by reinjecting waste fluids into their original reservoirs by drilling specific wells near the main reservoirs, which would also help them be productive for longer. In order to find a solution to reduce environmental impact, this paper concludes by reviewing the economical advantages involved in the use of geothermal reservoirs.

INDEX TERMS

Geothermal energy, electric and non-electric uses, environmental effects, air quality

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INTRODUCTION

The instability of energy markets that has recently affected the international geopolitical scenario in the last few years has aroused new interest in energy policies aimed at ensuring, first and foremost, safe supplies for industrialised and non-industrialised countries, and secondly the availability of the widest range of local sources.
In particular, this is corroborated by the key role played by some energy sources, for instance geothermal energy, due to the fact it is renewable and can be employed in a wide range of applications. In Italy, geothermal energy is particularly important in Tuscany, where it began to be produced in 1904. Whilst every form of energy production has some negative impact on the environment, by emitting substances that can be harmful for human and animal health, renewable sources are more sustainable than traditional ones, even if their use has not been adequately developed. This paper looks at geothermal energy and describes its main features, applications, pollutants emitted in each environmental medium, and compares it with the most common fossil sources (coal, oil and natural gas), in order to try to determine its potential developments in the national and international energy scenario.

METHODS

After reviewing the possible electric and non-electric uses of geothermal fluids, this paper makes a comparison between the main pollutants produced by the use of geothermal reservoirs and the emissions generated by the use of traditional fossil sources (natural gas, oil and coal). In particular, the review will dwell on those forms of air pollution that are caused by carbon dioxide (CO_2) and hydrogen sulphide (H_2S) emissions. In addition, it also considers other forms of atmospheric pollution, such as nitrogen oxides, boron, ammonia and radon.

DEFINITION OF GEOTHERMAL RESERVOIRS, LOCATIONS, DIRECT AND INDIRECT ECONOMIC USES

Geo- (earth)-thermal (heat) energy is the energy contained as heat inside the Earth and is an enormous, underused heat and power resource that is clean (it emits little or no greenhouse gases), reliable and home-grown, making a country less dependent on foreign oil.
Despite the fact that this heat is present in huge, practically inexhaustible quantities in the Earth's crust, not to mention the deeper parts of our planet, it is evenly distributed, seldom concentrated, and often at depths too great to be exploited industrially. In fact, the thermal energy of the Earth is therefore immense, but only a fraction can be utilised by man.
The geothermal gradient expresses the increases in the temperature of the rock with depth and it is on average at 30 °C/km deep.

The geothermal gradient is not even across the Earth's crust because of the earth's tectonic movements which cause special geological conditions. The shallower layer of the Earth's crust, i.e. the lithosphere, which reaches a depth of 70-100/125 km, has a rigid structure and is composed of blocks or plates, the so-called "lithospheric plates". The aforementioned plates move very slowly on the Earth's surface as they float on the layer underneath, the so-called "mantle", moving apart in some places, and moving closer in some other parts at a speed of a few centimetres per year, in a continuous settlement. Where the plates move towards each other they describe some subduction zones. Sometimes, the lithospheric folds downwards and plunges under the adjacent lithosphere re-descending to the very hot deep zones, where it is dispersed in the mantle and the cycle begins all over again.
Part of the litospheric material returns to a molten state and may rise to the surface again through fractures in the crust. As a consequence, numerous volcanoes are formed parallel to the trenches, on the opposite side to that of ridges.
Geothermal resources are generally confined to areas of the Earth's crust where heat flow is higher than in surrounding areas. This heats the water contained in permeable rocks (called reservoirs) at depth. Naturally, the resources with the highest energy potential are mainly concentrated on the boundaries between plates, where visible geothermal activity frequently exists in different forms: springs, fumaroles, steams vents, geysers end similar.
Concerning usable energy produced inside the Earth, a means for transferring heat to the surface is generally required; this fluid is generally rainwater, which seeps into the earth and reaches the rocks at a high temperature and, because of the geological conformation, forms reservoirs at high temperature and pressure, so that it can be extracted: these elements taken together form the so-called geothermal reservoir.
In most cases the reservoir is covered with impermeable rocks that prevent hot fluids from easily reaching the surface and keep the fluids, under pressure.
Depending on the conformation of the hydrogeological reservoir, three types of products can be obtained for industrial applications: wet, dry and superheated steam. Wells are drilled into the reservoir to extract the hot fluid, and their use depends on the level of temperature and pressure of the fluid. Another division between geothermal systems is that based on the reservoir equilibrium state, considering the circulation of the fluid and the mechanism of heat transfer. We may distinguish the dynamic system and the static system (Nicholson, 1993). In the first one, the reservoir is continuously recharged by water that is heated and is charged from the reservoir either to the surface or into underground permeable formation. Heat is transferred through the system by convection and circulation of the fluid. This geothermal field includes both high-temperature (>150 °C) and low-temperature (<150 °C) systems. In the second one, there is minor or no recharge to the reservoir and heat is transferred only by conduction. The Earth's energy can be converted into electricity or into non-electrical uses.

ELECTRICITY FROM GEOTHERMAL FLUIDS

Energy production from geothermal reservoirs started in Italy between the late XVIII and the early XIX century near today's field of Larderello, not far from Pisa. Steam from fumaroles and shallow wells was at first used to aid the extraction of boric acid from hot wells. In 1904, Piero Conti, the owner of the fields, after falling out with the local energy company, decided to connect a generator to a steam machine fed with this natural fluid. In 1913, this initiative led to the installation of the first geothermal- electric plant, with a capacity of 250 kilowatts. The example set by Larderello inspired other countries; the countries that currently use geothermal energy to produce electricity are listed in Table 1. As can be seen in this Table, the world's energy production from geothermal sources amounts to 7.974 Mwe and has grown by 17 per cent in just 5 years, thus becoming one of the most important renewable sources after hydroelectric sources and biomasses. The United States and the Philippines are the world's leading users

Table 1. Geothermal electric installed capacity in the world in 1995 and 2000 (Huttrer, 2001)

Country	1995 (MWe)	2000 (MWe)	1995-2000 increase in MWe	Increase percentage
Argentina	0.67	---	-0.67	---
Australia	0.17	0.17	---	---
China	28.78	29.17	0.39	135
Costa Rica	55.00	142.50	87.50	159
El Salvador	105.00	161.00	56.00	53.3
Ethiopia	---	8.52	8.52	---
France	4.20	4.20	---	---
Guatemala	---	33.40	33.40	---
Iceland	50.00	170.00	120.00	240
Indonesia	309.75	589.50	279.75	90.3
Italy	631.70	785.00	153.30	24.3
Japan	413.71	546.90	133.19	32.2
Kenya	45.00	45.00	---	---
Mexico	753	755.00	2.00	0.3
New Zealand	286	437.00	151.00	52.8
Nicaragua	70.00	70.00	---	---
Philippines	1.277.00	1.909.00	682.00	55.8
Portugal	5.00	16.00	11.00	220
Russia	11.00	23.00	12.00	109
Thailand	0.30	0.30	---	---
Turkey	20.40	20.40	---	---
USA	2.816.70	2.228.00	-588.00	---
Total	**6833.00**	**7974.00**	**1141.00**	**17**

of electric energy from geothermal sources while the greatest increase has been recorded in Portugal and Iceland.
A mile - deep or even deeper wells are drilled into underground reservoir to tap steam and very hot water that drive turbines that operate electricity generators. At present, three types of plants are operating in the world:

– Dry steam plants, which directly use geothermal steam to drive turbines;
– Flash steam plants, which deliver deep, high pressure hot water to lower-pressure tanks and use the resulting flashed steam to drive turbines;
– Binary-cycle plants, which flow moderately hot geothermal water by a secondary fluid with a much lower boiling point than water. In this case, this causes the secondary fluid to flash to steam, which then drives the turbines.

Geothermal energy plays a very important role in developing countries as shown in Table 2.

Table 2. Electric capacity from geothermal energy versus total electric capacity for some developing countries in 1996 compared with industrial countries in 1996 (Barbier, 1997)

Total electric installed capacity, 1993, Mwe		Geothermal electric installed capacity, 1996, MWe	% of total power installed
Industrialised Countries			
USA	695.120	2816	0.4
Japan	205.140	520	0.2
Italy	61.630	625	1.0
New Zealand	7.520	286	3.8
Developing Countries			
El Salvador	750	110	14.7
Philippines	6.770	1.440	21.3
Nicaragua	460	70	15.2
Kenya	810	45	5.5
Mexico	28.780	753	2.6
Indonesia	12.100	309	2.5
Costa Rica	1.040	60	5.8

The utilisation of natural steam for electricity generation is not the only possible application of geothermal energy. Hot waters, that appear to be present in large parts of all continents, can also be exploited and offer interesting prospects for the future, specially in space heating and industrial processing (Lindal, 1973).

ENVIRONMENTAL IMPACT OF GEOTHERMAL EXPLOITATION: AIR POLLUTION

The environmental impact caused by the use of geothermal fluids depends on the type of rocks these fluids flow through, and remarkably changes from one geothermal reservoir to the next, as can be seen in Table 3.

Table 3. Composition of steam from some geothermal fields

Constituents g/kg	The Geysers USA	Larderello Italy	Matsukawa Japan	Wairakei New Zealand	Cerro Prieto Mexico
H_2O	995.9	953.2	986.3	997.5	984.3
CO_2	3.3	45.2	12.4	2.3	14.1
H_2S	0.2	0.8	1.2	0.1	1.5
NH_3	0.2	0.2			0.1
CH_4+H_2	0.2	0.3			
Others	0.2	0.3	0.1	0.1	

The exploitation of geothermal reservoirs causes some forms of environmental impact, such as: air, water and soil pollution, subsidence, induced seismicity, noise and alterations of the natural landscape.

Air pollution is the most serious environmental problem because it contains non-condensable gases (CO_2, H_2S, NH_3, CH_4, N_2 and H_2) that range from 1.5 to 50 g/kg of steam.The emissions of carbon dioxide (a greenhouse and global climate-changing gas) are high but its emission into the atmosphere is well below the figures for natural gas, oil or coal-fed power stations per kWh generated (Table 4).

Hydrogen sulphide is the air pollutant of major concern in geothermal uses and development. Its emissions generally range between 0.5 and 6.8 g/kWh. Hydrogen sulphide produces a typical odour, often strong near hot springs, and oxidised into sulphur dioxide and then into sulphuric acid and may cause the well-known acid rains.

Unless abated, the specific sulphur emissions from geothermal power plants are about half of those from coal-fed plants (Table 5) and generally the sulphur ones are recycled as feedstock for sulphuric acid production. Future technology will use microbial processes to extract metals contained in the sulphur, allowing further reuse.

As far as water pollution is concerned, a distinction must be made between dominant-steam and water-dominant reservoirs. In the former, most pollution is found in the vapour state and pollution is more prevalent than in liquid water; most pollutants are found in the vapour state and the pollution of water is more easily controlled than in water-dominant reservoirs. Condensed steam generally carries a variety of toxic chemicals in suspension: arsenic, mercury, lead, zinc, boron and sulphur together with significant amounts of carbonates, silica, sulphates and chlorides. In the latter (water-dominant and hot water reservoirs), water and steam

Table 4. CO_2 emissions in g/kWh (Barbier, 1997)

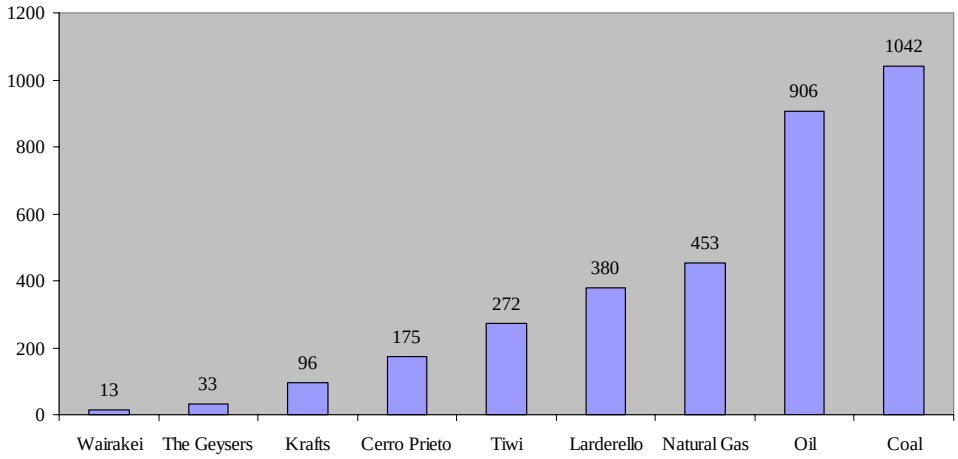
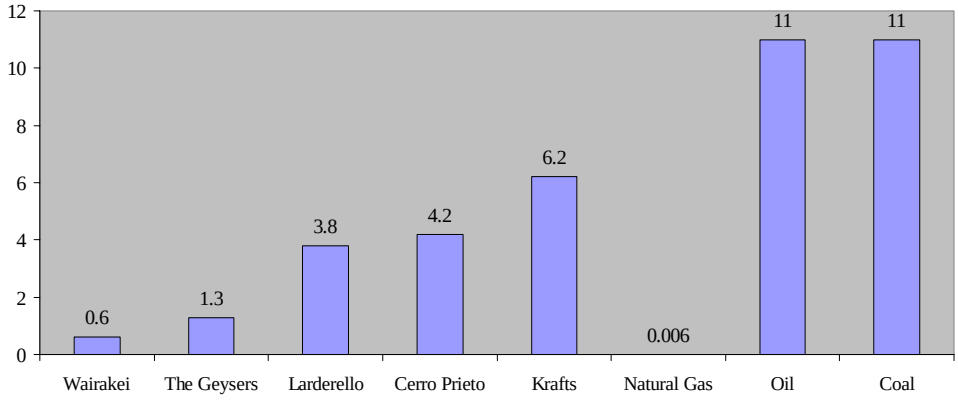


Table 5. Sulphur emissions in g/kWh



are separated at the surface and the volume of water to be disposed of (which may contain large quantities of salts, even above 300 g/kg of extracted fluid) can be as much as 70 kg/kWh, more than four times the steam supply. Reinjection through wells drilled next to geothermal reservoirs is the most common method of disposal. Reinjection may also help to maintain reservoir pressure, to extract additional heat from the rock and to prolong the useful life of the resource. Nitrogen oxides are not emitted from geothermal plants. Boron, ammonia and to a lesser extent mercury are leached from the atmosphere by rain, leading to soil and vegetation contamination. Boron, in particular, can have serious impacts on vegetation. These contaminants can also affect surface waters and impact aquatic life.

Geothermal literature reports that mercury emissions from geothermal power plants range between 45 and 900 micrograms/kWh, and are comparable with mercury emissions from coal-fed power plants. Ammonia is discharged in the air

in concentrations between 57 and 1938 mg/kWh, but due to atmospheric processes it is dispersed rapidly.
Radon (^{222}Rn) is contained in steam and discharged into the atmosphere in concentrations of 3700-78.000 Becquerel/kWh (Layton and Anspaugh and O'Barrion, 1982). There is little evidence that radon concentrations are raised above background level by geothermal emissions.

CONCLUSIONS AND IMPLICATIONS

The production of geothermal energy causes less environmental pollution than the use of traditional fossil fuels. In addition, some economic considerations are in favour of the use of geothermal resources. First of all, it is available in every country (home-grown), thereby reducing the countries' dependency on foreign supplies, it produces employment and boosts the development and sale of technological breakthroughs all over the world, with a positive impact on the balance of trade. Electricity produced by geothermal power plants is becoming cost-competitive with other forms of energy. Another aspect of geothermal power plants allows them to periodically charge premium electricity rates. Availability is the percentage of time the plant can actually produce electricity, and for geothermal plants it is, on average, about 90 per cent.
In conclusion, the use of geothermal energy generally, has clear economic advantages, particularly in developing countries since it can partly replace the import of fossil fuels which have to be paid in hard foreign currency. Geothermal technology is mature and generally well known. The environmental impact of these resources, in particular, regarding air quality, can be controlled through the reinjection of waste fluids into the reservoir from which they were extracted. The problem of pollution can also be satisfactorily addressed.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

MONITORING OF CHINA SAND STORM PARTICLES WITH PETRI DISH AND GLASS SLIDE IN SHELTER

EJ Sun*

ABSTRACT

At present time China sand storm particle was only monitored by an indirect method, the PM_{10} monitoring system in Taiwan. However the PM10 data represent only the total amount of fine particles and is not appropriate for expressing the severity of China sand storm in concerned areas. For this purpose we had developed a microscopic technique during the past two years that can detect and identify the sand particles. A meteorological shelter with two layers of shutter at four directions was designed for monitoring the target sand particles. Within the shelter a 2-liter beaker was placed and a 9-cm petri dish with glass slide was adhered in the beaker. The petri dish with glass slide was replaced with new one each for 2-3 days. Exposed slides were observed under dark field metallurgical light microscope. Results showed that sand particles were differentiable from other anthropogenic particles. Typical sand particles were shiny yellow, yellowish or brown. Those with size 2-10 μm are chosen as indicator particle species for use in counting the deposition. In non-sand storm days the background particle number per field is less than 10. From the results of particle counting in February and March 2003, we have found three and three sand storm episodes at Taipei, respectively. The microscopic approach provides us a direct method for detecting or measuring the severity of sand storm. We therefore recommend this approach to be used in other country or areas for monitoring this transboundary particle pollution.

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INDEX TERMS

Sand storm, Microscopy, Particle, PM_{10}, Taiwan

INTRODUCTION

The sand storm in East Asia is a very important issue as it attacks most of the countries, including China, Japan, and Korea (Kim & Park 2001; Kim et al, 2001; Ma et al., 2001; Zhang, 2003). It also spread over Taiwan and Hong Kong (Fang et al 1999; Lin 2001; Young et al., 1997). After a long-range transport this yellow sand particle can even reach Hawaii and America continent (Perrington et al., 1983). The sand storm not only impairs the sky visibility, contaminates the materials, covers the green plant leaves, but also increases the PM_{10} level, causing human health effects in many urban cities (Kim et al, 2001; Lin 2001; Sabbioni, 1995; Young et al., 1997; Zhang, 2003). For instance the total suspended particulate (TSP) level reached to 3906 $\mu g/m^3$ on April 6, 2000 at Beijing (Zhang, 2003), while the health standard is set at only 250 $\mu g/ m^3$ in Taiwan. It is on this health concern that scientists need to study the pollution event and monitor the pollution severity.

Basically any kinds of particle should have its physical or chemical characteristics that scientist can use to identify and differentiate them from other species of particles (Chen & Sun 1998; Cheng et al., 1976; Farmer& Linton, 1984; Kaufherr & Lichtman, 1984; Ma, 2001; Mamane, 1986; McCrone & Delly, 1973; Rose, 1996; Schure et al., 1985; Sun, 1993a; 1993b; 1993c; 1994a; 1994b; 2001; Sun & Chen, 1998). However since the sand storm particles are originated from Gobi Desert, the soil type particle had great variation in chemical composition, and may have similar composition to those from local emission, making them difficult for chemical speciation and identification (Kim et al, 2001; Rao et al., 2001). Even the enrichment elements are not easy to select as those in modern receptor modeling technique. Right now Taiwan EPA (Environmental Protection Administration of Taiwan) had used PM_{10} data and other meteorological information to predict the occurrence of the sand storm episode around the island. It was a great concern that raised PM10 is only an indirect evidence of the sand storm episode as other pollution sources may also contribute to this parameter. It was based on this concern that we initiated this study since 2000. Part of the results had been published in ASAAQ Conference held in March 2003 at Japan (Sun & Tsau, 2003). Briefly we had developed a direct detection method to monitor the occurrence of sand storm. Under the light microscope, especially the dark-field microscope, we found that the China sand particles showed shiny yellow to brown color, that is differentiable from other anthropogenic particles and salt spray aerosols (Sun, 1994b). Results also showed that the sand particle number per microscope field increased correspondingly, following the EPA's prediction. With this technique we had detected 2, 3, 1 and 1 storm episodes in

February, March, April, and May 2001, at Taipei. In this report we have tried to compare the particle deposition with PM_{10} data and tried to provide more results about monitoring the sand particles using the microscopic technique.

MATERIALS AND METHODS

Collection device for sand storm particle

An anti-rain sampling shelter was designed and established at National Taiwan University (NTU). The shelter is following an early design for collecting air-borne particles as described in a previous report (Sun, 1993c). Principally the shelter is made by four pieces of two-layer plastic shutter (each 36 x 22 cm, consist of an outer frame and 6 pieces of slant board, like those used in bathroom door). They were clamped to each other to form a square fort that can keep the rain droplets from coming into the central petri dish. On the top of the fort is a 60 x 60 x 1 cm square plastic roof. On the bottom is a 40 x 40 x 1 cm square plastic board. The whole shelter is placed at open roof space of a four-floor building with height of 16 m. It is supported by four 1.5 m tall stainless steel poles. One of the four shutters is designed into an openable door with magnetic lock. A 2-liter plastic beaker (19 cm tall, 12.5 cm wide) is adhered at the center of bottom board for further protection from rain or mist interference. A 9-cm plastic petri dish with clean glass slide (7.5 x 2.5 x 0.1 cm, No. 2041 of Assistent Co., Germany) is placed in the center of the open beaker for collecting the sand storm particles.

Generally the 9-cm plastic petri dish with glass slide was replaced with new set in the late afternoon on every Monday, Wednesday, and Friday. The exact collecting time and period were recorded afterward. The new petri dish with glass slide is opened only on site just before use. The exposed one was immediately covered and the whole petri dish with glass slide was taken back to laboratory for particle identification and counting.

Microscopic identification and counting of sand storm particles

For general particle identification, we use a microscopic system that contains a metallurgical light microscope (Olympus BH2-UMA) which use a vertical light source, a polarizing microscope (Olympus BH-2), and a scanning electron microscope (SEM) (JEOL-T330A) installed with an energy-dispersive X-ray (EDX) analyzer (Link QX 2000). The SEM-EDX system was operated under the following conditions: 20-kv accelerating voltage, 60 μA beam, and 15/ 38 cm working distance. Elements heavier than sodium are detectable when a Be window is used, while those heavier than boron are also detectable when a windowless option is applied. However, for the sand particle identification in this study, we found that the SEM-EDX system was not so necessary.

The sand particle collected from Beijing in winter and spring in recent years were used as reference samples for particle identification. The samples were collected with the same set of 9-cm plastic petri dish with glass slide at Beijing City when

the sand storm occurred there. Particle samples collected at NTU in spring and all other seasons were also identified and compared with those from Beijing.
For sand particle counting on each slide, the typical shiny small particles with size 2-10 μm were used as indicator particles, as preliminary study showed that they are adequate indicator for sand storm particles. Totally three observers were trained in recognizing the particles, measuring the size and counting them. Usually ten microscopic fields at 200X magnification were observed and the typical particles were counted. The particle number per field were averaged and compared with PM_{10} data for further analysis.

Correlation between deposited particle number and PM10

The hourly PM_{10} data of the Kutin Air Quality Monitoring Station of Taiwan EPA, located 1 km west from our particle collection site, were obtained from Taiwan EPA. The average PM_{10} concentrations for the period of particle collection were calculated. The correlation between the particle number and PM_{10} data was determined with the equation of correlation coefficient. For this year, the February and March data were analyzed.

RESULTS AND DISCUSSION

Microscopic identification and counting of sand storm particles

The sand particles collected from Beijing were observed and used as reference particles in this study. Generally the Beijing sand storm particles exhibit amorphous shape under light microscopes, although some minor particles have different shape or color. Under a common metallurgical light microscope, typical sand particle showed dark gray to brownish color. Under a polarizing microscope (Olympus BH-2), the sand particles showed various but non-specific colors, depending on the polarizing angle. However, when they were observed in dark field condition under metallurgical light microscope (Olympus BH-2-UMA, with top vertical illumination) at magnification of 200X or 500X, they reflected the light and show shiny colors of bright yellow, yellowish brown or brown.
Under the dark field metallurgical light microscope, the sand particles were differentiable from other anthropogenic particles such as black sphere from heavy oil combustion, carbon black from diesel combustion, color droplets from painting industry, and cement dust from construction site.
Generally the size of Beijing sand particles ranged from 1 to 60 μm. The similar sand particles could be also found in samples collected in non-sand storm days or seasons in Taipei, Taiwan, but the particle number per field was significantly lower than those collected in sand storm days, especially the small shiny ones with size of 2-10 μm. The particle numbers in non-sand storm day or season then could be recognized as a background number or concentration.
For sand particle counting on each exposed slide, only the typical shiny small particles with size 2-10 μm were taken into account. Usually the counting for ten microscopic

fields at 200X magnification was enough for representing each slide sample. In a preliminary study we found that the standard deviation for a ten-field counting was not significantly different from a 20-field counting. Therefore the ten-field counting was adopted for all the samples in this study. For each exposed slide two to three observers were assigned for the observation and counting. The mean of them is adopted for all the values shown in the tables or figures.

Performance of collection device in shelters

The anti-rain collection device was tested for its efficiency in controlling the rain interference. During the 2002 winter season, when it rained heavily, the petri dish with glass slide was carefully examined after the rain. Generally, they performed very well in protecting the petri dish from rain droplets. The salt spray droplets can easily come into the petri dish, but not turning into an interference factor.

When three shelters as described above were installed at the same open roof space at NTU, each was separated for a distance of 2 m, the counted particle numbers were very similar, indicating that they can represent for each other. Therefore only one station was operated after the preliminary study.

Correlation between deposited particle number and PM10

The PM_{10} data of Kutin Air Quality Monitoring Station of Taiwan EPA, located 1 km west from our particle collection site, were compared with the sand particle number data in this study. Since in 2003 the occurrence of sand storm in Taipei is not so frequent as previous years, only the data of February and March 2003 were analyzed.

Since generally background particle number per field at 200X magnification under dark field metallurgical light microscope is less than 10, the samples with particle number equal or greater than ten were recognized as contaminated from the China sand storm.

From the results of particle counting in February 2003, we have found three sand storm deposition episodes at Taipei (Table 1). Two of them are mild as the particle numbers are only 10 and 14 per microscopic field. For March, also three episodes

Table 1. Sand storm particle deposition and its correlation with PM10 at Taipei during Feb 17-28, 2003

Sampling period	Sand particle No./field	Mean PM_{10} ($\mu g/m^3$)	Highest PM_{10}
Feb 10-12	3	23	49
Feb 12-14	2	38	96
Feb 14-17	9	63	144
Feb 17-19	10	59	85
Feb19-21	25	61	104
Feb 26-28	14	57	109

were found (Table 2, Table 3), although two of them are mild with particle number of 12 and 16, respectively. For these three episodes in February the particle number per field ranges from 10 to 25, while the background values are 2-9. For the three episodes in March the range of particle number is 12-27, while the background values are 2-9. The deposition density of the particle however is about ten times lower than those of Beijing samples, collected in November 2002 (Data not shown). The PM_{10} data, however, did not have same changing tendency as those of sand particle number data in this study. For February data, we found that highest PM_{10} occurred mostly on the non-sand storm days (Fig. 1). In March, the situation is about the same (Fig. 2, Fig. 3). These results indicate that local emission sources are more important than the China sand storm in these two months. Taiwan EPA had reported that PM_{10} levels were greatly raised when heavy sand storm occurred in Taiwan. Scientist therefore had tried to adopt the PM_{10} data to track the occurrence of sand storm. In our study we found that this approach is not adequate, as other emission may be larger than the sand storm, especially when the storm is mild. This situation is similar to that reported by Young et al (1997).

The deposited sand particle provided us a direct evidence of the occurrence of China sand storm in Taiwan. We therefore recommend that this approach can be used in other countries or other areas for detection of the sand storm episodes.

Table 2. Sand storm particle deposition and its correlation with PM_{10} at Taipei during March 3-13, 2003

Sampling period	Sand particle No./field	Mean PM_{10} ($\mu g/m^3$)	Highest PM_{10}
March 3-5	3	30	68
March 5-7	2	51	148
March 7-10	27	57	97
March 10-12	4	28	73
March 12-14	4	29	80
March 14-17	7	55	149

Table 3. Sand storm particle deposition and its correlation with PM_{10} at Taipei during March 17-31, 2003.

Sampling period	Sand particle No./field	Mean PM_{10} ($\mu g/m^3$)	Highest PM_{10}
March 17-19	7	26	50
March 19-21	2	23	57
March 21-24	6	48	125
March 24-26	16	48	89
March 26-28	9	58	101
March 28-31	12	54	114

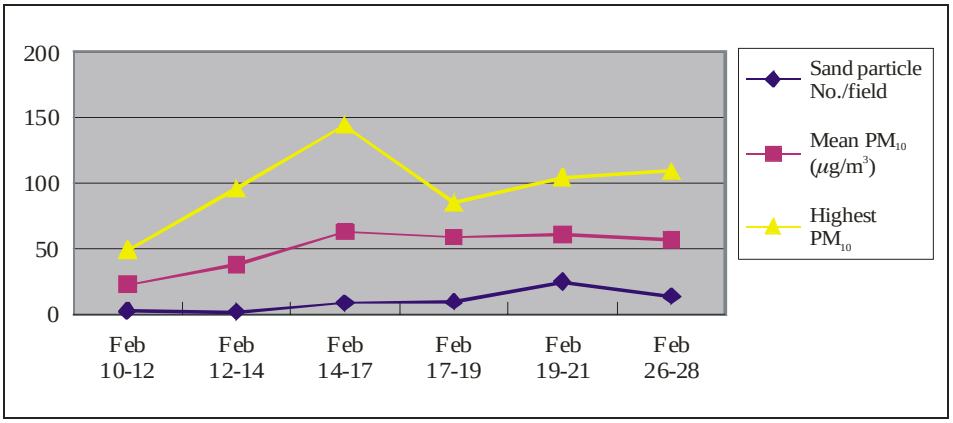

Figure 1. Relation between deposited sand storm particles and mean and highest PM_{10} at Taipei during Feb. 10-28, 2003

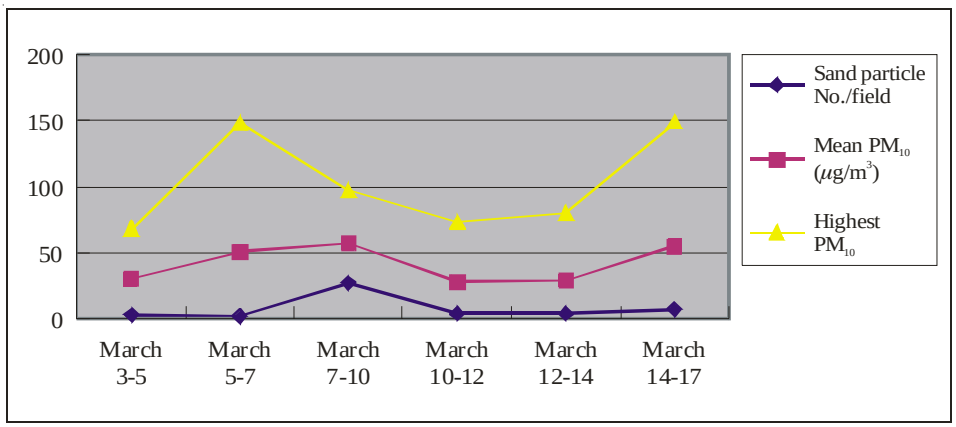

Figure 2. Relation between deposited sand storm particles and mean and highest PM_{10} at Taipei during March 3-17, 2003

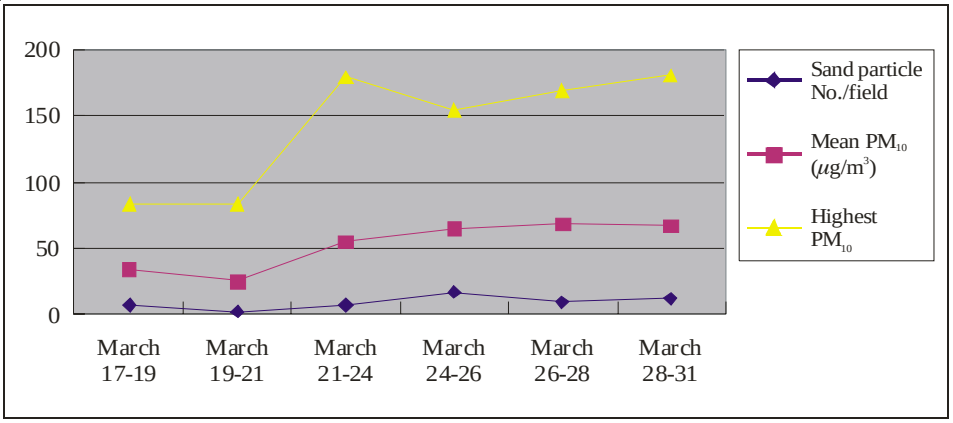

Figure 3. Relation between deposited sand storm particles and mean and highest PM_{10} at Taipei during March 17-31, 2003

CONCLUSION

In this study, we found: (1) The anti-rain shelter performed very well in preventing the rain interference and is adequate for sand particle collection; (2) Under the dark field metallurgical light microscope, the sand particles were differentiable from other anthropogenic particles; (3) The shiny small amorphous particles with size 2-10 μm can be used as indicator particle species for use in counting the deposition, as generally background particle number is less than 10; (4) From the results of particle counting in February and March 2003, we have found three sand storm episodes in each month at Taipei; (5) The microscopic approach provide us a direct method for detecting or monitoring the sand storm; and (6) We recommend this approach can be used in other country or areas to monitoring this transboundary pollution.

ACKNOWLEDGEMENT

This study was supported by grants from National Science Council, ROC (Grant #NSC-91-2313-B-002-356). The author is also grateful to Dr. Reyi Wu, for her help in collecting the sand storm samples in Beijing.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
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REGIONAL STRATEGIES AND CROSS-BORDER CO-OPERATION TO CONTROL OZONE POLLUTION

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ABSTRACT

In many European cities, air pollution is currently perceived as a local problem mainly related to road transport and certain industrial processes. However, some of the air pollution problems that UK local authorities are currently facing are related to air pollutants formed outside their geographical boundaries. For example, ground-level ozone episodes occurring in Sussex and Kent are often attributed to emission sources in continental Europe. Although there are international agreements in place for transboundary pollutants like ozone, relevant regional control strategies are lacking. A number of studies have recently focused on the formation, trends and spatial patterns of ozone pollution in different geographical areas making use of photochemical grid and/or trajectory models, emission inventories and field observations. Some of these tools may be applicable to the Trans Manche region. An analysis of monitoring data from five stations in England showed decreasing numbers of ozone episodes, but persistently high background levels, with some of the highest values observed at rural locations near the south east coast. Ozone concentrations in coastal areas on both sides of the Channel were highly correlated during recent episodes, probably due to the common origin of the sampled air masses. For this reason, co-operation between UK and French authorities is needed in order to optimise strategies for controlling regional ozone pollution.

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INDEX TERMS

Transboundary air pollution, Ozone, VOCs, Photochemical modelling, Regional strategies

INTRODUCTION

In the UK, local authorities are responsible for reviewing and assessing local air quality on a regular basis under the provisions of the Environment Act 1995. In order to facilitate this task, the government's Department for Environment Food and Rural Affairs has issued technical guidance, which prescribes standard methods for assessing compliance with a set of specific objectives for seven pollutants (excluding ozone). This guidance focuses on pollution hotspots in city centres and near major traffic links where population exposure is expected to be relatively high.

Although ozone is one of the pollutants included in the UK National Air Quality Strategy and the French Loi sur l'Air, it is not subject to local air quality control since it is not formed locally. International control agreements exist (UNECE Convention on Long-Range Transboundary Air Pollution Gothenburg Protocol 1979; EU Ozone directive 2002), but regional management strategies are lacking, although local action on ozone precursor emissions (e.g. VOCs and NO_x) is essential in order to mitigate ozone pollution at a local level. To deal with this problem, local authorities need decision-making tools enabling them to assess the potential impacts of existing and future sources of ozone precursors, such as airports, motorways, industrial plants, etc. These tools could be based on existing photochemical models adapted to the regional topographic and meteorological conditions and validated using local emission and monitoring data. This article reviews ozone pollution studies and explores ozone trends in the Trans Manche region.

REVIEW OF OZONE POLUTION STUDIES

The most widely used method for investigating the sensitivity of ozone to precursor emissions is photochemical grid modelling. Mesoscale models like CALGRID and UAM have been extensively used in the past to simulate photochemical pollution in large urban areas (Pilinis et al., 1993; Borrego et al., 2000). However, these complex models require a large amount of input data and computational resources. Furthermore, they are relatively difficult to validate and might be treated as black boxes by the non-experts. Other semi-empirical models based on ambient observations have been derived to assess ozone sensitivity to precursor emissions (Chang and Rudy, 1993; Blanchard, 1999; Ainslie and Steyn, 2002). One such model, the Integrated Empirical Rate (IER) model consists of a simple set of relationships describing the formation of photochemical oxidants collectively termed as Smog Potential (Johnson, 1984). More recently, Derwent and Nelson

(2002) investigated the Integrated Downwind Ozone Production (IDOP) concept with the aim of producing a practical local scheme for assessing the ozone creation potential of each of 120 VOCs that could be emitted by a chemical plant in the UK. A relative index of harm based on the IDOP of each species was produced. Derwent et al. (2003) used a photochemical trajectory model together with the Master Chemical Mechanism (MCM) and a highly speciated emission inventory for organic compounds to describe the formation of ozone in North West Europe. The MCM describes the detailed degradation of a large number of organic compounds and the resultant generation of ozone and other secondary species. The version of MCM used treated the degradation of 123 organic compounds and contained 12692 reactions involving 4342 chemical species. This study identified the most prolific ozone-forming organic compounds and assessed the impact of VOC emission controls.

Vautard et al. (2001) developed an ozone forecasting system for the region of Paris. This is based on a simplified chemistry-transport model (CHIMERE) that simulates the behaviour of approximately 80 gaseous species through nearly 200 chemical reactions. This is coupled with a statistical back-trajectory model that calculates background concentrations of few species. Although balancing well simplicity with accuracy, this forecasting system is adapted to the simple topography of Paris, which means that it does not take into account any complex terrain or coastal effects that may be relevant to other geographical domains.

Jiang et al. (2003) used back trajectories and process analysis to investigate photochemical ozone production in the Puget Sound region (Washington State, USA). A photochemical grid modelling system consisting of MM5, CALMET and CALGRID was modified to include a process analysis scheme and a back trajectory method. This system was used to determine the relative importance of chemical production, advection, diffusion and deposition within the receptor grid cell and also along the air mass transport path from an urban source area (Seattle) to a downwind receptor. In another study, Chen et al. (2003) used a photochemical grid model to assess the sensitivity of ozone concentrations to the emission reductions in VOCs and NO_x in Kaohsiung City, Taiwan. They also examined meteorological conditions during ozone episodes in the area. It was concluded that warm temperature, sufficient sunlight, low wind, and high surface pressure are the parameters that tend to trigger ozone episodes in polluted urban areas. Finally, Ma and Lyons (2003) used a modelling system based on RAMS to show that a thermally induced synoptic scale trough interacted with the local air circulation to enhance the sea breeze flow on the western coast of Australia, allowing pollutant to penetrate further inland and spread over a larger area inducing high ozone events.

Although ozone pollution research relies heavily on modelling, there are certain studies exclusively based on the analysis of field observations. For example, Aneja et al. (1999) used precursor emission maps, meteorological and ozone data to study trends and relationships on high ozone days in three metropolitan areas in

North Caroline, USA. In this study, data from a network of 19-23 continuous monitoring stations were analysed. In another case, Vukovich and Sherwell (2003) examined statistically the relationship between certain meteorological parameters and surface ozone variations in the Baltimore Washington corridor. The results from this study indicated that high temperatures and large concentrations of water vapour were a necessary, but not a sufficient, condition for high ozone to be found in the region. These meteorological conditions were sufficient when significant amounts of solar radiation reached the surface layer and stagnation conditions prevailed at the same time. The above studies provide evidence that topography, synoptic weather conditions and local meteorological effects play an important role in ground-ozone ozone formation and its spatial/temporal distribution.

REGIONAL OZONE TRENDS

Episodes of increased ozone occur during periods of anticyclonic conditions, clear skies and high temperatures over many parts of Europe. These episodic concentrations are added to the background levels, which are subject to a variable but mostly upward trend. On average, summer ozone levels show an increasing gradient from the north west to central Europe (Beck et al., 1999). There are however many areas, e.g. urban, mountainous and coastal regions, that vary substantially from this average pattern. There is evidence that relatively high ozone concentrations tend to occur along the south coast of England and the north coast of France. Ozone levels in Sussex are amongst the highest recorded in the UK in recent years, because of the relatively sunny and warm weather conditions prevailing in the region. Emissions from continental Europe are also thought to contribute significantly to the elevated ozone concentrations observed in South East England. Using ozone measurements made at 20 UK sites, Hayman et al. (2002) showed that episodes of elevated ozone concentrations over the UK were associated with photochemically aged air masses arriving in England from easterly or south-easterly directions, after passing over continental Europe for a period of several days.

In the present study, five ozone monitoring sites were selected from the UK Automatic Urban and Rural Network (AURN). Due to their geographical location (Figure 1), these sites were thought to be affected by ozone formed over continental Europe. Figure 2 (bottom) shows a decreasing number of ozone episodes (i.e. daily maximum 8-hour running mean over 100 $\mu g/m^3$) at three rural sites (Lullington Heath, Harwell and Rochester) during recent years. This trend is consistent with local declines in ozone precursors and in agreement with reported declines in summer ozone in urban areas of West Europe and North America (Vingarzan and Taylor, 2003). By contrast, the annual ozone levels at the same locations have remained relatively stable during the same time period (Figure 2, top), probably due to the hemispheric increase in background ozone levels.



	Monitoring Site	Type
1	Lullington Heath (East Sussex)	Rural
2	Harwell (Oxfordshire)	Rural
3	Rochester (Medway)	Rural
4	London Bloomsbury	Urban
5	Southampton Centre	Urban
6	Rye (East Sussex)	Rural
7	Forêt de Brotonne (Havre)	Rural
8	Phare d'Ailly (Seine-Maritime)	Rural
9	Mesnil Esnard (Rouen)	Sub-urban

Figure 1. Selected stations monitoring ground-level ozone in the Trans Manche region

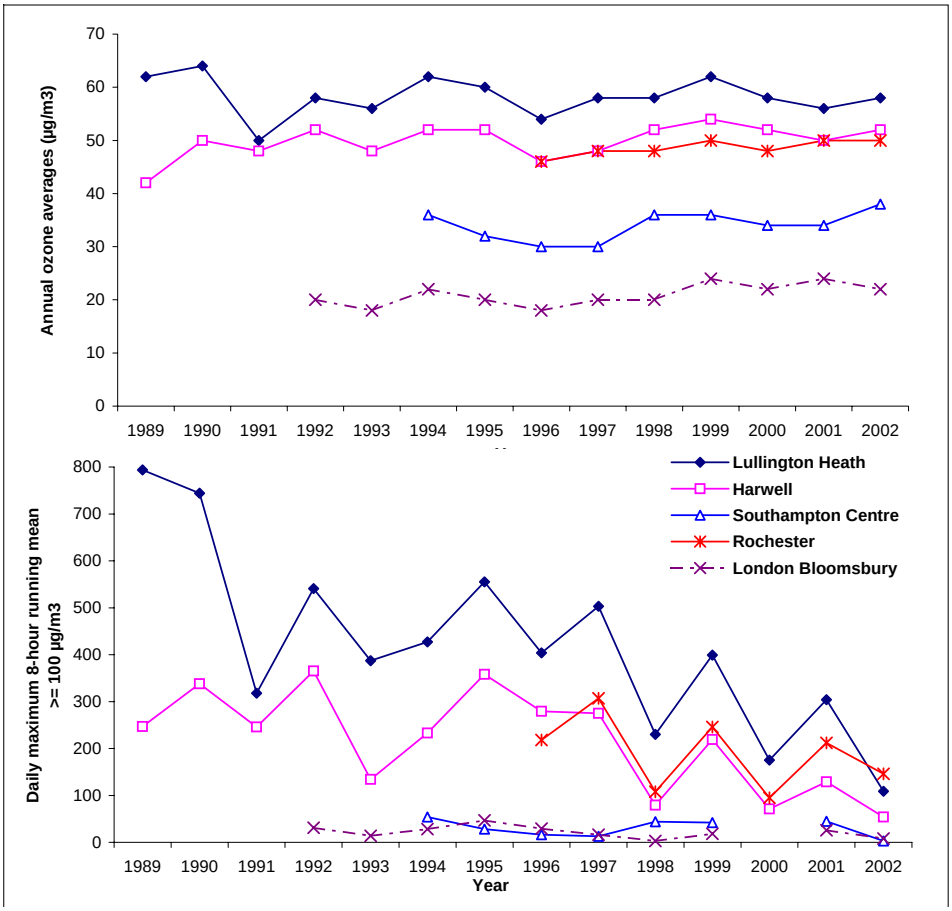

Figure 2. Annual ozone averages (top) and number of daily episodes (bottom) in the UK

Two rural monitoring stations near the coast of Sussex (Lullington Heath and Rye) and two similar stations on the opposite coast of Normandy (Phare d'Ailly and Forêt de Brotonne) were then selected to examine recent ozone episodes. These stations have recorded some of the highest regional concentrations. Daily ozone averages during spring 2003 were plotted in Figure 3, showing high correlation between all four sites. Two ozone peaks were identified on 17th April and 30th May. On these dates, daily ozone levels at one (at least) location on each side of the Channel exceeded 100 $\mu g/m^3$. During both episodes, low south-easterly winds were prevailing over the Channel. This analysis provides some evidence that coastal areas in Sussex and Normandy may be affected by ozone formed over mainland Europe. However, larger monitoring data sets covering adjacent regions need to be analysed in order to strengthen this argument. Finally, The land-sea breeze circulation and coastal topography effects on ozone levels deserve further study.

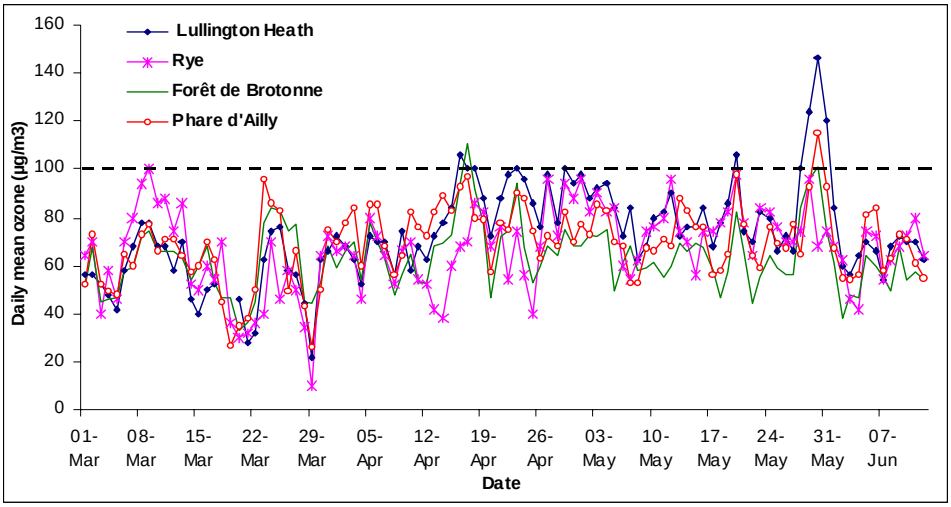

Figure 3. Daily mean ozone concentrations in two UK and two French monitoring sites

DISCUSSION

Photochemical models are generally very complex and it is difficult to perform sensitivity analyses on them. Limited testing of regional relationships has been done in the UK and most policy analyses are based on theoretical chemistry, allowing ozone to develop within a trajectory box. There is thus a policy need to relate ozone production calculations more closely to real situations.

For assessment purposes, the spatial coverage of ozone monitoring in South East England and North France has insufficient density, partly because the EU ozone directive provides no quantitative requirements on network density. Alternative monitoring techniques, such as diffusive sampling and the use of micro-detectors, could help increase the spatial resolution of ozone measurements. Diffusive

samplers were successfully used in a recent study in northern France to reveal the spatial variability of ground-level ozone during summer. This variability may have significant implications in terms of population exposure.

The Trans Manche regions of Sussex and Normandy (and possibly Kent, Picardie and Pas-de-Calais) are facing a common environmental problem, i.e. ozone pollution, which has been very difficult to tackle in other countries. Strategies based on controlling total VOC emissions from road vehicles and industrial sources in USA were in cases ineffective because of ozone formed outside urban areas or ozone transported from one urban area to another (Tanner, 2003). Moussiopoulos et al. (2000) used photochemical models to prove that ozone abatement strategies, which are effective at a regional scale in Europe, may not be effective for a city and its surroundings. Therefore, the control of ozone pollution over adjacent UK and French regions would require concerted cross-border action.

Many local authorities in the UK and France have already formed regional air quality groupings, which aim to optimise resources and co-ordinate action. Local authorities from Sussex, Normandy and Picardie have successfully collaborated in the past within the framework of two interregional EU funded air quality-related projects (*Air Rives-Manche Sensibilisation* and *Santé*). Their main objectives were to investigate the local health impacts of air pollution and raise awareness of this topic amongst professionals and the public. One of the key outcomes was that ozone pollution causes approximately 360 hospital admissions and is a factor in 340 deaths each year in East Sussex, Brighton and Hove. Further co-operation between UK and French authorities is expected to help control regional ozone pollution through information exchange, and sharing of resources and expertise. Such partnerships could be also set up elsewhere in Europe and the world involving local environmental managers with scientists.

CONCLUSIONS AND IMPLICATIONS

There is evidence of an elevated regional background and a decreasing but still significant number of ozone episodes in South East England. Recent ozone measurements on both sides of the Channel (La Manche) are highly correlated. Photochemical modelling is often used in academic research to interpret ozone episodes and study the influence of local topography and meteorological parameters on ozone formation. However, only relatively simple models are likely to find wider application.

Although ozone pollution is a regional problem in Europe, it is mostly tackled at national and international level. It is however essential to develop and implement regional control strategies. Further co-ordinated action is needed in the Trans Manche region to create comprehensive monitoring data sets, harmonise precursor emission inventories, and develop operational modelling tools. Denser ozone monitoring networks would help assess meteorological effects, such as the land-sea breeze circulation, that may induce relatively high ozone concentrations in coastal areas.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge financial support from INTERREG II for the projects *Air Rives-Manche Sensibilisation* and *Santé*.

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Impacts

The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

PUBLIC PERCEPTIONS OF AIR POLLUTION AND ITS EFFECTS IN NORTH LONDON, UK

RJ Day*

ABSTRACT

Understanding public perceptions of air pollution and its effects is clearly important in local policy-making where the public must be consulted. The purpose of this study was to explore perceptions and beliefs regarding the effects of air pollution particularly on health, both in general and personally. The study was carried out in one borough of North London, in four neighbourhoods which were selected to be contrasting in terms of socio-economic status and pollution levels. A combination of in depth interviews and a social survey were used to explore various aspects of perceptions of air pollution and its possible effects including health effects. Beliefs that air pollution in general can cause health problems, particularly respiratory problems and allergies, were prevalent, but not always certain. A significant proportion of people felt their own health was affected by air pollution but this did not differ between sites of high and low pollution, as experience of air pollution in many places such as the area of work was also important. People expressed a desire for more scientific knowledge, but at the same time, public perceptions explored by social science may also contribute to better scientific understanding of effects and better policy making.

INDEX TERMS

Public perceptions, perceived health effects, locality, survey, qualitative interviews.

INTRODUCTION

The 1997 UK National Air Quality Strategy sets out health-based standards for 8 main air pollutants and objectives for their achievement throughout the UK by

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2005. Under the terms of the 1997 Strategy, local authorities are required to identify geographical areas where the health standards for 7 pollutants are unlikely to be met, and draw up action plans in these areas in consultation with local communities. In this context, an understanding of public perceptions of air pollution and its impacts is crucial.

Most work on public perceptions of air pollution dates from the 1960s and 70s and from the US. (e.g. Crowe, 1968, Swan, 1972). These studies were largely by survey and generally arguing for the role of social variables such as socio-economic status, race and the length of time of residence in influencing perceptions of air quality. The most recent interesting studies in the UK which have also given specific attention to perceived health effects are Might, Phillimore, Bhopal and Foy (1995), and Bickerstaff and Walker (1999). Moffatt *et al* (1995) studied a population close to an industrial coking works, and found 40% of adults reported feeling adverse health effects, specifically upper respiratory tract conditions, and raised levels of reported stress due to pollution. They concluded that ignoring self-reported health evidence could result in potentially damaging health effects being overlooked. Bickerstaff and Walker (1999) studied perceptions of air pollution in Birmingham, England where pollution is more from traffic sources. In terms of perceived health effects, they found 45% of people claimed to experience within the family health effects due to air pollution, the most common being asthma, followed by other respiratory complaints, and allergies. They also concluded that overall perceptions of air pollution were formed mainly by local knowledge and experience.

This study took place in the London Borough of Barnet, where over 80% of the air pollution in Barnet is from road traffic, with areas predicted to exceed the NAQS limits of Nitrogen Oxides and particulates (PM_{10}). The study included wider aspects of perceptions including perceived levels of pollution, and ways in which people formed their knowledge, as well as issues of responsibility, trust and preferred policy options. This paper concentrates on the perceived health effects of air pollution both in general, and to themselves personally.

METHODS

The study was carried out in 4 neighbourhoods, which were chosen to be contrasting in terms of modelled pollution levels, and socio-economic status. The neighbourhoods selected were:

Totteridge: High socio-economic status, lower pollution
Hampstead Garden Suburb: high socio-economic status, higher pollution
Grahame Park: low socio-economic status, lower pollution
Brent Cross: low socio-economic status, higher pollution.

The study used both qualitative and quantitative methods. For the first stage, in-depth interviews lasting 45-90 minutes were carried out in each of the four

neighbourhoods with 8-10 residents, covering a broad age and gender balance. Recruitment was by response to a letter. The interviews followed a flexible schedule and covered many aspects of neighbourhood environment and air quality. Transcripts were analysed thematically (Flick, 1998) with the aid of Atlas Ti software. Following the interview stage, a questionnaire was designed, building on the interviews, which was posted to all adults on the electoral role in each neighbourhood. 200 returns were received, and analysed using ANOVA, correlation and regression techniques with SPSS software.

RESULTS

The following results are a selection relating to perceived health effects, both general and personal. Names of interviewees have been changed.

General health effects.

In the interviews, by far the most prevalent theme to emerge in terms of health effects centred around respiratory problems, with asthma being the most referred to. Many people definitely felt that air pollution could cause these conditions.

> R "What kind of illness do you think it might cause?"
> Mrs Chen: "Bronchitis I suppose. I always imagine all those, in the lung, all those spongy, sticky things, anything go in is not good."

> Joan: "bronchitis I would think."
> Brian: "Yes. Asthma."
> R "Do you think causing it, or just making it worse, or?"
> Joan: "Both."

> Paul: "its just not, I think, personally just mainly breathing problems, ... I mean it can give you, bronchitis, it can give you chronic asthma……it can give you cystic fibrosis. Loads of stuff that the pollution does to you."

However causation was often not adamant. Many of the remarks were around making existing conditions worse, again especially in terms of asthma and lung problems – that asthmatics in particular would suffer in poor quality air.

> Julie: "I don't know, probably some people who are asthmatic or, have had you know, damaged lungs.....obviously, put it this way, it doesn't help them,"

Looking at asthma specifically, a recurring theme was the rise in the number of children with asthma in recent times, with people using anecdotal knowledge:

> Mrs D: "And children now, more young children I see with puffers, ... whether its because this is a recent thing, but they do use them more in primary schools now,"

> Brenda: "And the number of children who have puffers... which is a thing that was unknown when I was a child. Now teachers have cupboardfuls."

An association was definitely made between air pollution and increases in asthma, but there was a lot of uncertainty about causality. Often people talked of other possible causes as well, and their unsureness:

> Bob: "I don't know, its, maybe its pollution in general or maybe, maybe its that we no longer have thirty kids, you know, I'm a great believer that when I was a young kid I was allowed to go out and get filthy …… and maybe my immune system is a lot stronger than a lot of kids .."

> Maria: "… in the paper about asthmatics as well, they said it could be linked to some sort of food too early in their diet or something like that, we don't know"

In the survey, the aim was to separate the issues of causality and worsening. Respondents were given a list of health conditions (which arose from the interviews) and asked, **"we would like to know if you think air pollution could CAUSE any of these illnesses to occur IN SOMEONE WHO DID NOT HAVE IT ALREADY."** They were allowed to answer yes, no, or don't know. Responses were as follows:

Table 1. Beliefs in air pollution causing certain conditions.

Condition	Air pollution CAN cause it	Air pollution CANNOT cause it	Don't know
Hayfever / sneezing allergies	89.5%	3%	6%
Other lung / chest problems	89%	4%	6.5%
Asthma	85%	6.5%	8%
Bronchitis	81.5%	10.5%	8%
Skin problems / eczema	63%	14.5%	21%
Cancer	42%	19%	38%
Heart disease	33%	29.5%	36%
Memory problems / Alzheimer's	19.5%	32%	47.5%

The uncertainty expressed in the interviews around causality was not reflected in the survey data. Even though 'don't know' was offered as a response, certainly with respect to the respiratory complaints including asthma, a high proportion of respondents answered a positive belief in the causal potential of air pollution exposure.

As well as specific health conditions, however, something that emerged in the interviews was a strong sense of it being bad for you in a general, systemic, longer

term way, which was often associated with effects being long term and cumulative, and/or additive to other kinds of pollutants. People often rationalised this as 'common sense'.

> Mrs S: "well I'm sure these things are not good for the, your system, er, so some medical people can tell exactly which, but generally definitely not healthy for the... health."
>
> Ali: "I'm sure it does [affect our well-being], but it, this whole, er..... er... well its rate of progression I suppose one wouldn't notice, but how can this help, honestly?"

Personal Health Effects

In the survey, respondents had been asked to rate their neighbourhood air quality on a 7-point scale. Perceptions differed between the four areas, with Totteridge rated 'quite good' and significantly higher than all others, Grahame Park neutral but significantly, and Hampstead and Brent Cross 'quite bad' and significantly lower than the other two areas, though not significantly different from each other. This was broadly in line with the modelled data, at least in relative terms.

In the interviews, there was much less talk of personal health effects than the general. In the main, those who did talk of personal effects were the asthma and allergy sufferers, who felt that air pollution could be a trigger or an extra irritant:

> Barbara (Brent Cross): "it affects me, mainly in summer I'm affected, when it gets, when its very warm, I tend to have, my throat, and my nose gets all blocked up. I think I'm slightly, erm, slight allergy, hayfever type thing, yeah. And you can notice, the symptoms get worse when you're, you know [in a place where there is poor air]."
>
> Ms F (Grahame Park): "Oh, breathing, I mean I have to watch myself anyway 'cause, if I exert myself then I get like short of breath, but, the pollution is a definite, it sort of, aggravates it sort of like immediately, if I'm put in to that, sort of, vicinity"

Other personal health effects that were brought up included irritations of the skin, coughing, eye and ear complaints. Often, though not always, they were talked of with uncertainty as to whether pollution might or might not be a contributing factor.

There was however little difference between the four neighbourhoods in the way that people talked of being personally affected by air pollution, despite the perceived levels being different.

In the survey, people were asked, "**do you, or have you ever, suffered from any illness or health problem you think was *caused* by air pollution?**"

28% of respondents answered 'yes', 53% said 'no', and 16% answered 'don't know'. There was no significant difference in responses between the different areas.

Suffering from certain health complaints was associated with positive responses to this question. Chi squared tests showed that a greater than expected number of positive responses was given by people with asthma (X^2 = 24.70, d.f. = 2, p = 0.000), people with chest problems (X^2 = 9.62, d.f. = 2, p = 0.008), people with hayfever (X^2 = 25.44, d.f. = 2, p = 0.000) and people with eczema (X^2 = 11.08, d.f. = 2, p = 0.004) Those who had answered 'yes' were asked in an open ended question what the health problem was. Multiple answers were allowed and answers were coded post hoc. Responses were as follows:

Table 2. Self reported health conditions believed to be caused by air pollution

Health problem	No. people	% of sample
hayfever, rhinitis or similar	21	10.5
asthma	20	10
other or unspecified chest / breathing problems	16	8
skin problems	4	2
tiredness	2	1
nausea	2	1
throat problems	2	1
eye irritation	1	0.5

People were next asked, "**do you, or have you ever, suffered from any health problem or illness that you think is made worse by air pollution**?" Overall, 36.5% answered 'yes', 47% answered 'no' and 14.5% answered 'don't know'. Again there was no significant difference between the 4 areas.

Asthma sufferers were much more likely to say 'yes' to this question (X^2 =32.83, d.f. = 2, p = 0.000); as were those with chest problems (X^2 = 7.75, d.f. = 2, p = 0.021), hayfever sufferers (X^2 = 45.17, d.f. = 2, p = 0.000) and eczema sufferers (X^2 = 14.57, d.f. = 2, p = 0.001)

Those who answered yes were asked what the problem was, in an open ended question. Responses were as follows:

Table 3. Self reported personal health condition believed to be exacerbated by air pollution.

Health problem	No. people	% of sample
hayfever, rhinitis or similar	29	14.5
asthma	26	13
other or unspecified chest / breathing problems	18	9
skin problems	6	3
cancer	2	1
heart disease	2	1
general allergies	1	0.5
M.E.	1	0.5

DISCUSSION AND CONCLUSIONS

In both the interviews and the survey, it emerged clearly that perceptions of the health effects of air pollution centred around respiratory complaints, allergies and to a lesser extent skin problems. From the survey it was apparent that a high percentage of respondents believed that air pollution can cause these conditions. In the interviews, a little more in depth exploration indicated that although people suspected that air pollution may cause these conditions, particularly asthma, they were less certain and could offer alternative explanations. People seemed to form their beliefs by a mixture of experience and anecdotal knowledge, and scientific explanations acquired largely through the media. This disagrees somewhat with Bickerstaff and Walker (1999) who concluded that the media had a smaller role to play in forming people's knowledge of air pollution.

A significant percentage of respondents felt that they had a health condition either caused or made worse by air pollution. Again, asthma, chest complaints, rhinitis type symptoms and skin problems were the most significant of these. This is similar to the findings of Bickerstaff and Walker (1999) except that allergies were a little higher on the list and skin problems also featured more. The fact that hayfever and rhinitis were at the top of the list may reflect a tendency to class pollen as air pollution; however the interviews showed that this was not the sole explanation as often hayfever sufferers felt that other air pollution made the symptoms worse.

It is very interesting that the perceived effects on personal health did not differ between the areas, despite the measured and the perceived levels of pollution differing widely. It seems that peoples experience of air quality and its effects was not dictated by their residential location, but rather by their general experience which included where they went for work, shopping and leisure activities.

This was a case study with a relatively small sample size and a low response rate and so the actual numerical results in the survey should be extrapolated with caution. However the associations found are robust and the consistency of the results around particular health conditions is notable.

The results of this study point towards the necessity and potential productivity of dialogue between the public, scientists and policy makers. The public on the whole clearly expressed a desire for more research and for more scientific knowledge to be communicated to them. I would also conclude, as Moffat *et. al.* (1995) suggested, that the experience of air pollution and its effects includes 'subjective' aspects which are systematically overlooked by the methodology of epidemiological studies, but which are nevertheless important. Social science approaches are called for in exploring these aspects appropriately, and can thus contribute to better scientific understanding and better management policies.

ACKNOWLEDGEMENTS

This research was funded as a PhD scholarship from the UK Economic and Social Research Council.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

PROFESSIONAL EXPOSURE TO BENZENE: COMPARISON BETWEEN BIOCHEMISTS' INDICES AND FREQUENCIES OF SCE "SISTER CHROMATID EXCHANGES"

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ABSTRACT

Benzene is a leukemic substance utilized in the petrochemical industry and is present, even if at low concentrations, in the air dispersed in urban centres and is therefore a potential risk for all the population. The concentrations which are found in fuel distribution are approximately 5-10 times higher. For this reason it was necessary to set up a correct method to carry out a routine biological control by the monitoring exposure biomarkers. In order to measure the exposure to atmospheric benzene in the working environment it is necessary estimate the feasibility and the validity of several tests. Our survey has looked for both exposure and effect biomarkers. The monitoring was carried out at 10 service-stations sited in several parts of Catania, Sicily, Italy. At the start and the end of each shift blood and urine samples were taken on which we measured benzene and muconic acid (its metabolite) in urine samples and the Sister Chromatid Exchanges (SCE) in blood samples. Moreover, during all the shifts air sampling was carried out to verify the benzene concentration using passive and active samplers directly applied to the workers. The results show that "t,t muconic acid" represents a good chemical index of biological exposure and SCE is an aspecific index of genotoxicity. Thus the complementary use of both the indices seems to be suitable to estimate exposure risk and genotoxic damage.

INDEX TERMS

Benzene, Sister Chromatid Exchanges, professional exposure, exposure biomarkers, effect biomarkers.

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INTRODUCTION

The World Health Organization in 1987 indicated benzene concentrations in air, in city atmosphere, between 3 and 160 $\mu g/m^3$, with values more elevated in proximity to stations of benzine refuelling, fuel deposits and petrochemical industries. Currently, as a result of the incresing spread of green benzines, more than 90% of the benzene emissions in the external air of inhabited centres can be attributed to the emissions of benzine from cars. The WHO has estimated a Unitary Risk of leukaemia (risk per unit of benzene concentration) of 5×10^{-6} of leukaemia cases for every mg of benzene present in the inhaled air.
Objectives: In consideration of elevated exposure to which the population is subject a correct method to carry out a routine biological control by the monitoring of exposure biomarkers (benzene and muconic acid) and of effect biomarkers (Sister Chromatid Exchanges) has been suggested.

METHODS

The monitoring was carried out on 10 service-stations employees from 7 filling stations sited in several parts of Catania. At the start and at the end of shifts blood and urine samples were taken on which we measured benzene and muconic acid (its metabolite) in urine samples and the Sister Cromatid Exchanges (SCE) in blood samples. Moreover, during all the shifts air sampling was carried out to verify the benzene concentration using passive samplers to radial spread (Radiello™) and active samplers (Superchrom SKC), with active carbon vials, directly applied on the workers. The determination of benzene sampled in the air, with passive and active systems, was measured with gas-chromatograph (GC) "Perkin-Elmer 8500" injecting 1 ml of the sample extracted with carbon disulfide. The determination of the benzene in the urine and blood samples, withdrawn and conserved in accordance with the indications of the Italian Society Values of Reference (SIVR), was measured by gas-chromatographic using the technique of Microextraction in the solid phase (SPME: Carboxen/Polidimethilsiloxane 100mm of thickness). The determination of trans, trans-muconic acid (metabolite of benzene) in the urine samples was carried out using the method of high performance liquid chromatography (HPLC) established by "Ducos and coll. 1990" and modified by "Rauscher and coll. 1994". The determination of SCE was carried out using heparined peripheral blood and a fluorimetric method with 5BudR and coloration to fluochrome bisbenzimide (Hoechst 33258) and staining with Giemsa.

RESULTS

The results are reported in table 1. Statistical elaboration of the descriptive type was carried out on these data that showed the reliability of the results (analysis of variance p=0,000). Moreover, the data of benzene, muconic acid and SCE concentration were analyzed using the test of "linear simple regression" (table 2).

Table 1. Results

	Benzene in air μg/m³				***Benzene in urine μg/l*** *V.N. <0,001*		***Muconic Acid in urine μg/l*** *V.N. <200*		***SCE n° exchanges*** *V.N.= 7±3*	
Sample	Cases		Controls		Cases	Controls	Cases	Controls	Cases	Controls
1	147.80	F*	87.50	F	2.73	0.53	569.81	153.19	14.3	8.5
2	157.94	F	134.06	nF	3.97	0.63	485.67	41.48	16.3	7.8
3	127.82	F	88.80	F	1.67	0.84	681.90	212.44	12.9	8.5
4	184.45	NF**	87.19	nF	1.94	1.27	342.91	57.87	17.6	6.6
5	169.74	F	39.90	eF	1.54	0.79	280.00	22.31	12.1	8.2
6	153.04	eF***	83.20	nF	2.51	0.64	431.11	65.54	15.0	10.6
7	152.0	F	93.50	nF	2.58	0.35	615.42	143.61	13.0	7.3
8	149.0	eF	30.40	F	1.30	0.31	398.96	69.82	10.3	7.4
9	149.20	F	16.67	F	1.75	0.89	425.33	97.13	12.4	9.9
10	100.52	F	13.17	F	2.49	0.66	607.92	84.45	17.3	10.9
Legend: *F = smoker **nF = non smoker ***eF = ex smoker										

Table 2. Linear simple regression into various determinations in the cases

	MA/BA	**SCE/BA**	**SCE/MA**	**MA/BU**	**BU/BA**
n	10	10	10	10	10
r	-0,727	-0,05651	0,1146	-0,699	0,8478
t	-2,995	-0,1601	0,3262	-2,765	4,521
g.d.l	8	8	8	8	8
p	0,0172	0,8768	0,7526	0,0245	0,0019

MA=muconic acid
BA=benzene air
SCE= Sister Cromatid Exchanges
BU=benzene urine

DISCUSSION

As can be seen from the results reported above the concentrations found in the cases are all higher with respect to those of the controls. From the statistical elaboration such differences were all found to be statistically significant. This result was expected as the controls were taken from the general population who are not the particularly exposed and the cases, instead, were exposed to higher more continuous concentrations. From the statistical analyses of the data in our possession we can see that muconic acid in the urine of the exposed cases increases after extended exposure to low doses (diminishing benzene concentration in the air), while the urinary benzene increases in a significant way with the increase the benzene concentration in the air. Moreover, exposure to high benzene concentrations corresponds to an elevated frequency of SCE. We can conclude that muconic acid and SCE can be considered valid risk indicators of exposure rather than effect.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

METILTERBUTILETHER: AN EMERGENT PROBLEM IN ATMOSPHERIC POLLUTION

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ABSTRACT

In automobile and aeroplane engines, in place of benzines with the addition of organic metals to prevent knocking, mixtures of petrol with alcohol, ethers and benzene can be used that are able to tolerate high compression and therefore give high efficiency. Gasoline with the addition of MetilTerButilEther, a compound deriving from methanol, is today the most used among gasoline oxygenate additives. MTBE and its derived aldehydes are considered in literature substances that have been demonstrated to be toxic and potentiality cancerogenous. Because of the elevated degree of leaching and the insufficient biodegradability possessed by this compound it is found unchanged in subsoils, leakages from storage tanks, with the highest risk for contaminating ground waters. Indeed, such a substance has been found in the drinking water of several pools in proximity to tanks in variable concentrations from 20 mg/l to 200 mg/l.
EPA is carrying out studies on the possible effects to health, and the presence and distribution of MTBE in the atmosphere. Until the real danger of MTBE on environmental equilibrium and on human health has been established a surveillance program has been started for risk assessment on the environmental matrices and on human exposure in urban and extra-urban areas. The monitoring has been carried out on 10 service-station employees in 7 filling stations sited in several zones of the city of Catania, Sicily, Italy from the centre to the periphery. The study has provided a method for standardized methodical sampling, determination and verification of the levels of MTBE concentrations in the air and in human tissue.

INDEX TERMS

MetilTerButilEther, cancerogenous potentiality, work exposure, monitoring, pollution.

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INTRODUCTION

For the atmospheric environment we intend “every modification of the normal composition of atmospheric air, the presence of one or more substances that in any quantity or under any conditions alter normal health and constitute a direct or indirect danger for the health of the citizens or for private or public assets ”. Polluting substances can be distinguished by the physician if they carry out their toxic action without transformation (Benzene and MetilTerButilEtere), and secondary when such pollutants carry out their toxic action only after their transformation.

The main source of primary polluting substances is vehicular traffic, i.e. automobiles, in place of propellent benzines with the addition of organic metals to prevent knocking, mixtures of petrol with alcohol, ethers and benzene can be used that are able to tolerate high compression and therefore give high efficiency. Gasoline with the addition of MetilTerButilEther, a compound deriving from methanol, is today the most used gasoline oxygenate additive. MTBE and derived aldehydes are considered in literature to be toxic and potentiality cancerogenous. Because of the elevated degree of leaching and the insufficient biodegradability possessed by this compound it is found unchanged in subsoils, leakages from storage tanks, with the highest risk for contaminating ground waters. Indeed, such a substance has been found in the drinking water of several pools in proximity to tanks in variable concentrations from 20 mg/l to 200 mg/l. EPA is carrying out studies on the possible effects to health, and the presence and distribution of MTBE in the atmosphere.

Until the real danger of MTBE on environmental equilibrium and on human health has been established a surveillance program has been started for risk assessment on the environmental matrices and on human exposure in urban and extra-urban areas.

METHODS

The monitoring has been carried out on 10 service-station employees in 7 filling stations sited in several zones of the city of Catania, Sicily, Italy from the centre to the periphery. Each worker was supplied for his shift (8 hours) with an active auto-sampler with an active carbon tube for MTBE sampling. Moreover, at the end of each shift each worker gave 5 cc of venouse blood and 150 cc of urine for sampling to identify the eventual presence of MTBE. The determination was carried out by a gas-chromatograph “Perkin-Elmer 8500” under the operating conditions shown in table 1, for the air samples active carbon tubes were extracted with methyl alcohol, they were then injected with CG 5 ml, instead, for the biological samples the method of the head space comparing SPME system with the Gas-TIGHT system was used.

Table 1. Operating conditions of Perkin-Elmer GC.

Column	BB WAX 30m x 0.53 mm x 1.0 μm
Gas	He
Flow	4 ml/ min
Temperature	40 °C x 10 min
Injector	250 °C
Detector	FID 275 °C

DISCUSSION

This study has provided a standardized method with a protocol for sampling, determing and verifying the levels of MTBE concentrations in the air and in humans. For the biological samples (blood and urine) the best method is GAS-TIGHT. Results are reported in table 2 and are comparable with those reported in literature.

Table 2. Concentrations of MTBE

Samples	*MTBE $\mu g/m^3$ Air*	*MTBE $\mu g/l$ Blood*	*MTBE $\mu g/l$ Urine*
1	20.06	156.0	13.5
2	35.15	210.0	7.23
3	34.47	77.0	29.56
4	13.75	190.0	26.37
5	20.35	96.0	19.68
6	1.28	182.0	21.39
7	87.56	229.0	18.05
8	81.84	159.0	18.51
9	55.50	100.0	16.59
10	85.40	126.0	18.72
Average	43.53	152.5	18.96

CONCLUSION

From our results it can be seen that the Gas-Chromatographic method with FID detector for the determination of MTBE is satisfactory. Obviously the head-space method for the biological samples is indispensable.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

DUSTS AND NOISE MEASUREMENT IN A HOUSEHOLD WASTE SORTING PLANT AND CORRECTIVE MEASURES: A REAL-SCALE STUDY

L Galtier, C Békaert, V Decottignies and E Senante*

ABSTRACT

This article deals with a real-scale study on dusts and noise measurements in a sorting plant for household wastes (10 000 tons/year of recyclable material).
Dusts concentrations have been measured using a portable Personal Data Ram apparatus ($PM_{2.5}$, PM_5 and PM_{10}). Ambient noise has been measured using a portable Sound-meter (maximum and average data). The experimental approach and the description of the site are detailed in the article. Measurement points have been determined from the study of workers tasks and frequency.
Results show that, except from exceptional tasks, such as sweeping, average ambient concentrations of dusts ($< 0{,}15$ mg/m^3) are in agreement with regulatory specifications (PM 10 < 10 mg/m^3). As a result, dust management is not of major concern for the workers and, consequently, for surrounding populations. On the other hand, noise measurements show that average values may exceed regulatory specifications (from 60 to 95 dBA $>$ 85 dBA for 8 hours of exposure). Sources of noises have been identified (explosion of plastic bottles under engines tires, chock of metallic or plastic material against metallic receptors) and simple modifications were performed to improve noise management. Such a study illustrates that the use of simple methods to determine dusts and noise levels can induce a significant improvement of workers comfort.

INDEX TERMS

Risk assessment, dust, noise, on-site measurements

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INTRODUCTION

Dust emission in a waste sorting plant may have an impact on both workers health and the environment due to two aspects of the particles: their size (linked with their concentration) and their nature (heavy metals or organic compounds such as Polycyclic Aromatic Hydrocarbons). Due to their size, particles are responsible for chronic respiratory pathologies (ISO 7708 standard; Lazaridis, 2001). Particles can be defined as a function of their diameter and the stage at which they deposit in the human respiratory system. There are three types of fractions (Figure 1): thoracic fraction (PM_{10}), alveolar fraction (PM_5) and breathable fraction ($PM_{2.5}$).
In addition to dust, excess noise can cause a significant discomfort among plant workers.

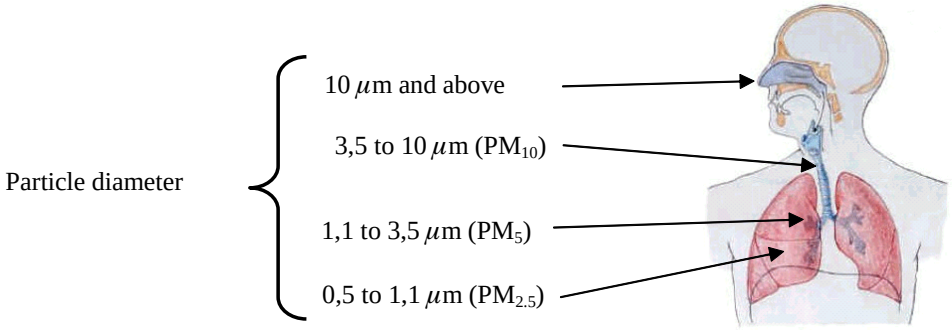

Figure 1. Definition of the different fractions of particulate matter on the Human Respiratory System.

The following paper reports dusts and noise measurements carried out at a sorting plant for household wastes (10-000 tons/year of recyclable material) located in the North West of France. Since 2000, the sorting plant is equipped with a trommel for the automatic sorting, a baler, floor sorting and one sorting belt conveyor. The types of wastes treated on this site are:

– glass (4 500 tons/year)which goes to a specific treatment channel,
– metals, plastics, cardboards, papers and aluminium briquets (2 500 tons/year),
– paper in separated flow (2 500 tons/years).

The objective of the study was to assess dusts and noise levels in the workers ambiance in order to perform corrective actions which turn out to be a priority at such sites.

METHODS

Dusts measurements:

In order to measure dust concentration, the widely used reference method is based on gravimetry for stationary source emissions (EN 13284-1) and for

workplace atmospheres (EN 13205). This technique is based on the aspiration and filtration of a certain volume of gas and a measurement of the filter weight before and after the filtration step. For the determination of particle size in ambient air, a cascade impactor from ESM Andersen Instruments can be used. It enables the granulometric determination with particles' diameter from 0.5 μm to 10 μm and its principle is similar to gravimetry adapted to all the filters used in the different stages in the impactor. For the measurement of dust concentration and particle size at the sorting plant, an optical monitor, the personal DataRAM 1200 from MIE company, has been used. It was validated by comparing it to the reference method (gravimetry). This apparatus is designed with a pump module to perform particle size selective measurements ($PM_{2.5}$ to PM_{10}) and to combine them with the particles concentration (Figure 2). The detection system is based on nephelometry which provides a measurement range from 0.001 to 400 mg/m^3. The personal DataRAM 1200 is also used for continuous emissions monitoring in ambient air, for extractive sampling and measurements from conducts at landfill sites, for estimating particles concentration at landfill gas or at sorting sites.



Figure 2. Optical real time monitor – personal DataRAM 1200 from MIE.

The measurement campaign was carried out using both techniques: the Andersen impactor and the optical monitor. During a first step, measurements with the optical monitor have allowed to assess the concentration of particles and to adapt the sampling time for the collection of particles on filters. During a second step, the Andersen impactor was used to check the concentration of total dust and to measure precisely the particle size. Finally, in a third step, the determination of the nature of particles was carried out with the following protocol: particles extraction by washing the filters with specific solutions depending on the target compounds or elements. Heavy metals or organic compounds can be adsorbed on dust particles or can constitute the particles themselves.

For the analysis of heavy metals, the preparation step consists in a wash of the filter and an acid digestion of the metallic particles with a mixture of three acids (HNO_3, HCl and HF). The analysis is performed with an Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) instrument as described in the EN ISO 11885 standard. For the analysis of Polycyclic Aromatic Hydrocarbons, the preparation step consists in a wash of the filter followed by a solvent extraction with acetonitrile or dichloromethane. The compounds are analysed by gas chromatography coupled with mass spectrometry.

Noise measurements:

Noise measurements were performed with a sound level meter Extech Instruments using a range between 30 dBA to 130 dBA and a resolution at 0,1 dBA.

RESULTS AND DISCUSSION

Dusts measurements

Dust concentrations were obtained for the three fractions ($PM_{2.5}$, PM_5 and PM_{10}) on four measurement points : in the sorting belt conveyor, at the truck unloading hall, at the baler and at the storage of recyclable material. All the concentrations obtained on the sorting plant were under the TWA (Time Weighted Average) values of exposure imposed by the regulation and based on a period of eight hours: 10 mg/m^3 for PM_{10} and 5 mg/m^3 for PM_5. Some exceptional tasks, for example, sweeping, can occasionally cause a significant exposure to dust but this exposure is less important when it is calculated relative to eight hours of work. So, average ambient concentrations were in agreement with regulatory specifications. As a result, dust management is not of major concern for workers and consequently, for surrounding populations of this sorting plant.
Concerning the nature of particles, ambient concentrations were not high enough to enable the collection of particles on filters; therefore their mineral and organic composition could not be determined.

Noise measurements

A cartography of noise on the sorting plant was established in relation with the regulatory specifications for industrial activities. These specifications are: 85 dBA for eight hours of exposure and 135 dBA for occasional exposure. Above these thresholds preventive actions need to be implemented. Measurements show that some average values may exceed the specifications; the following sources of noise have been identified: 90-100 dBA due to explosion of plastic bottles under engine tires in the truck unloading hall, 95-100 dBA due to shock of metallic or plastic material against metallic receptors in the sorting belt conveyor. Noise appeared to be a point to take into account for workers comfort. Some simple recommendations were proposed to improve noise management on the sorting plant : driving engines should be more careful to avoid shocks against the floor

and consequently noise, a plastic protection inside the metal collector should improve the reduction of noise in the sorting belt conveyor.

CONCLUSION AND IMPLICATIONS

This study shows that simple on-site measurements and further recommendations can be a great help for the operators to improve facility management in order to comply with health and environment requirements. Following this study, some modifications were implemented at the site and they have contributed to improve noise management.

ACKNOWLEDGEMENTS

The authors would like to thank the manager and the operators of the sorting plant for their cooperation during the measurements.

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Dubrovnik, CROATIA 6-10 October 2003

TOXICITY OF DIBUTYLTIN DICHLORIDE (DBTC) IN RATS

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ABSTRACT

Organotin compounds are of particular toxicological interest, because they are used as stabilizers in polyvinylchloride (PVC) manufacturing and as biocides in agriculture and in antifouling paints. DBTC is a product of PVC-stabilisation and a metabolite of tributyltin biocides.
In studies of the acute toxic effects of DBTC (6 and 8 mg/kg b.w. i.v.) in rats an acute interstitial pancreatitis, bile duct and liver lesions and a depression of the immune system were observed. After i.v. treatment with 6 and 8 mg/kg DBTC high concentrations of DBTC (10^{-5} – 10^{-6} M) excreted in bile caused cytotoxic effects on the bile duct epithelium. A total necrosis of the surface epithelium of the duct after 24 h led to adhesion and obstruction of the duct followed by cholestasis. In dependence on time (4 weeks to 1 year) the acute lesions on pancreas and liver developed to a pancreatic fibrosis and liver cirrhosis. A single i.v. administration of 4 mg/kg DBTC induces mild lesions on pancreas and liver after 2 to 4 days followed by a restitutio ad integrum after 14 to 21 days. Repeated treatment of rats with DBTC (4mg/kg i.v. in intervals of 3 weeks) induced an acute pancreatitis, after 9 to 12 weeks a pancreatic fibrosis and after 1 year a chronical pancreatitis and liver cirrhosis. The minimal toxic dose of DBTC on pancreas and liver is 1 mg /kg DBTC i.v.
In rats, DBTC (6 and 8 mg/kg i.v.) induced thymus atrophy and depression of thymus-dependent immune reactions. The mechanisms of the toxic effects of DBTC are discussed in relation to the mode of action of DBTC on the bile duct, pancreas, liver and immune system.

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INDEX TERMS

Dibutyltin dichloride; pancreatitis; liver lesions; fibrosis; thymus atrophy

INTRODUCTION

Organotin compounds have been widely used as biocides in agriculture and in antifouling paints, catalysts and plast stabilizers (Kimmel et al. 1976, Merkord 1994). Dibutyltin dichloride (DBTC) is the final product of the stabilization reaction of PVC and it has been used as a catalyst for formation of polyurethane foam. In biotransformation, dibutyltin compounds may be formed as metabolites of tributyltin biocides (Kimmel et al. 1976).

In studies focused on the toxic effects of DBTC on the bile duct, liver, and pancreas and on the biliary excretion of tin in rats, it was shown that DBTC [6 or 8 mg/kg body weight intravenous (i.v.)] induces an acute interstitial pancreatitis and liver lesions in rats (Merkord et al. 1982, 1989, 1991 und 1995).The pathogenesis and the natural course of this pancreatitis has been described in detail (Merkord et al. 1997). Depending on the dose (6 and 8 mg/kg DBTC i.v.) and time (1-24 weeks), the lesions developed into pancreatic fibrosis and liver cirrhosis (Sparmann et al. 1997, Merkord et al. 1999).

Additional intake of ethanol (15% in drinking water ad libitum; concentrations of ethanol in the blood 0.5-0.7 g/l) increases the toxic effects of DBTC on pancreas and liver during the acute and chronic course (Merkord et al. 1998).

In previous studies, we found that a single dose of 4 mg/kg DBTC i.v. induces a mild interstitial pancreatitis after 2-4 days followed by a *restitutio ad integrum* after 21-28 days.

In the present study, the lesions of rat thymus, rat pancreas and rat liver after single administration of 1, 4 and 8 mg/kg DBTC i. v. and after administration of 1 and 4 mg/kg DBTC i.v. at intervals of 3 weeks have been investigated for the period of one year. The pathohistological changes of the thymus, pancreas and liver were examined by lightmicroscopy 1, 4, 7 days and 2, 3, 4, 6, 9, 12, 24 and 56 weeks after administration of DBTC. Furthermore, pathobiochemical parameters of pancreatitis (amylase and lipase activity in serum), liver lesions (alkaline phosphatase and bilirubin in serum) and of fibrosis (hyaluronic acid in serum) were studied. These studies are of toxicological interest with regard to comparison between toxic effects after a single high dose of DBTC or effects after repeated treatment with lower doses of DBTC in long intervals, which induce mild and reversible lesions on thymus, pancreas and liver after single administration.

METHODS

Male inbred rats (LEW-1W, Karlsburg) weighing 150 ± 20 g body weight were used in this study. For intravenous administration DBTC (Sigma-Aldrich Chemie GmbH, Steinheim) was dissolved first in 100% ethanol. Two parts of this solution were mixed with three parts glycerol. The animals (7 per group) treated with a single dose of

DBTC (1, 4 or 8 mg/kg body weight) were sacrificed 1, 4, 7 days and 2, 3, 4, 6, 9, 12, 24 and 56 weeks after treatment. In the group treated with repeated doses of DBTC (1 or 4 mg/kg body weight) at intervals of 3 weeks, the animals were sacrificed four hours after the last administration on day 21, 42, 63, 84, 168 and 392 after the first treatment. The control group received the solvent only at intervals of 3 weeks and the animals were sacrificed at the same time as the repeated DBTC-group.

Morphology

Tissue samples of thymus, pancreas, liver and biliopancreatic duct were fixed in calcium formalin and processed for histopathological examination. Paraffin sections were stained with hematoxylin and eosin.

Analytical methods

The amylase and lipase activities in serum of rats were measured with test kits of Roche Diagnostics GmbH (Germany) using the analyzer EPOS 5060 (Eppendorf, Hamburg, Germany).
Bilirubin was determined by the DPD method (37° C).
Alkaline phosphatase was measured by an optimized method of the German Society of Clinical Chemistry (37° C) with p-nitrophenylphosphate as substrate.
All these parameters were measured on the analyzer Hitachi 717 with test kits from Roche Diagnostics GmbH (Germany).
Hyaluronic acid was assayed by the RIA technique using a test system purchased from Pharmacia (Freiburg, Germany).
The concentrations of tin in pancreas and liver were estimated by atomic absorption spectrophotometry after microwave-induced digestion. For electrothermal determination of tin at 286,5 nm, an AAS GGC 908 was used.

Statistical analysis and evaluation

Means of normally distributed data with similar variances were compared by Student's t-test. $P < 0.05$ was considered as significant (Sachs, 1992).

RESULTS

Morphology

Control-group: No changes in thymus, pancreas, liver or biliopancreatic duct morphology were noted in samples taken from control animals up to 56 weeks.

DBTC-group (single dose of 8 mg/kg i.v.): One day after DBTC treatment an acute interstitial pancreatitis had developed with inflammatory cells, dilated acinar lumina and scattered acinar cell necrosis. The biliopancreatic duct was dilated and a partial necrosis of the surface epithelium was observed. In the liver, edema of the portal tracts was the only sign of damage. One week after DBTC treatment acute interstitial pancreatitis with infiltrates of eosinophilic granulocytes, histiocytes, lymphocytes, macrophages and plasma cells were observed (Figure 1a). The biliopancreatic duct

showed an extreme dilation and the total necrosis of the surface epithelium of the duct lead to adhesion and obstruction of the duct followed by cholestasis. In the liver, an acute inflammation of portal tracts and parenchymal necrosis in the perivenular zone were present. Two to 4 weeks after DBTC treatment fibrotic areas and tubular complexes around the biliopancreatic duct were present. Intrahepatic bile duct hyperplasia and parenchymal necrosis were observed in the liver. Nine to 12 weeks after DBTC treatment pancreatic fibrosis and early signs of liver cirrhosis were present. Twent-four to 56 weeks after treatment chronical pancreatitis and liver cirrhosis were observed (Figure 1b). The time course of the effects of a single i.v. dose of DBTC revealed that thymus atrophy, as determined by thymus weigth and total cell count, was maximal 4 to 7 days after treatment and reversed to normal within 9 to 14 days.

DBTC-group (single dose of 4 mg/kg i.v.): One day after DBTC treatment interstitial edema was seen in the pancreas in the form of an enlarged space between the pancreatic acini, filled by some granulocytes and histiocytes. Four to 7 days after administration of a single dose of 4 mg/kg DBTC i.v. mild interstitial pancreatitis developed. The changes in acinar cells were vacuolisation, cystic degeneration and single-cell necrosis. The biliopancreatic duct was minimally dilated and the biliopancreatic duct epithelium showed swollen epithelial cells and partial necrosis in some segments. In the liver, mild inflammation of portal tracts was present . No changes in the thymus were found. Four weeks after administration of DBTC the pancreas and liver showed no changes and the biliopancreatic duct was normal.

DBTC-group (single dose of 1 mg/kg i.v.): One day after DBTC treatment no changes on thymus, pancreas and liver were observed. Four to 7 days after administration of a single dose of 1 mg/kg DBTC i.v. mild inflammation and interstitial edema in rat pancreas were seen. No changes on liver and thymus were observed. After two weeks all organs have a normal structure.

DBTC-group (repeated dose of 4 mg/kg i.v.): In the first 3 weeks we found the same result as in the DBTC-group with single dose of 4 mg/kg DBTC i.v.. Six weeks after repeated administration of 4 mg/kg DBTC i.v. the biliopancreatic duct was thicker than normal, and there was fibrosis in its wall and in the adjacent pancreas. In the liver, after repeated doses, the inflammation of the portal tracts was stronger and, at times, accompanied by some bile duct proliferation. Twelve weeks after repeated administration of 4 mg/kg DBTC i.v. the biliopancreatic duct was extremly dilated and the pancreas showed an interstitial and periductal fibrosis. In the liver, signs of inflammation, isolate necrosis and intrahepatic bile duct hyperplasia were present. Twenty-four weeks after repeated administration of 4 mg/kg DBTC i.v. chronic pancreatitis and liver cirrhosis were seen (Figure 2a and b). The thymus was normal. When comparing these effects to the toxic effects after single administration of 8 mg/kg DBTC i.v., the lesions on repeated administration of 4 mg/kg DBTC were milder.

DBTC-group (repeated dose of 1 mg/kg i.v.): After 7 repeated doses of 1 mg/kg DBTC i.v. mild inflammations in pancreas and liver were observed. The thymus

was normal. After 14 repeated doses of DBTC a mild pancreatitis and inflammation around the portal tract in the liver were seen, but no changes on biliopancreatic duct and thymus.

Pathobiochemistry

Acute pancreatitis was indicated by significantly elevated levels of amylase and lipase. The activities of both enzymes were significantly increased from the basal level 1 day after treatment with DBTC and returned to normal values for amylase on day 4 and for lipase on day 7 after DBTC application. The significant increase in serum lipase activity within the first days after DBTC administration (4 or 8 mg/kg i.v.) is a pathobiochemical indicator of acute pancreatitis.
The significant increase of alkaline phosphatase activity and bilirubin concentration in serum 6 to 56 weeks after repeated treatment with DBTC (4 mg/kg i.v.) is a sign of cholestasis.
Elevated serum levels of hyaluronic acid were found 9 to 56 weeks after repeated treatment with 4 mg/kg DBTC i.v. (Figure 3). In comparison to single administration of 8 mg/kg b.w. DBTC the levels were lower on repeated treatment.
After repeated treatment with DBTC (1 mg/kg i.v.) no increase of lipase activity, alkaline phosphatase activity and bilirubin concentration in serum after 6 to 56 weeks were observed.

DISCUSSION

The toxic effects of DBTC on thymus, pancreas and liver in rats are dose dependent. The minimal toxic dose of DBTC on pancreas and liver in rats is 1 mg/kg b.w. i.v., on thymus 6 mg/kg b.w. i.v. After treatment of rats with a single dose of 8 mg/kg DBTC b.w. i.v. acute interstitial pancreatitis and biliopancreatic duct lesions with necrosis and obstruction developed. In dependence on time, the acute lesions had a tendency to chronic course, when the obstruction of the duct and the cholestasis persisted (Merkord et al. 1999). It is of particular toxicological interest whether lower doses of DBTC, which induce mild and reversible lesions after single treatment, may lead to pancreatitis, pancreatic fibrosis and liver cirrhosis when give repeatedly in long intervals.
The repeated administration of 4 mg/kg DBTC b.w. i.v. to rats at intervals of 3 weeks induced acute pancreatitis and biliopancreatic lesions after 6 and pancreatic fibrosis and liver lesions (inflammation of portal tracts, intrahepatic bile duct hyperplasia and necrosis) after 9 to 12 weeks. Fifty-six weeks after repeated administration of 4 mg/kg DBTC b.w. i.v. chronic pancreatitis and liver cirrhosis were seen. The thymus was normal. The repeated administration of 1 mg/kg DBTC b.w. i.v. (14 times) induced mild pancreatitis and inflammation around the portal tract in the liver. No changes on biliopancreatic duct and thymus were seen.
The induction of organotoxic effects with repeated administration of low doses of DBTC (4 mg/kg b.w. i.v.) could be due either to accumulation of organotin or

to an addition of the single cytotoxic effect of the compound. Accumulation of organotin or tin can not be assumed. The half-life of about 2 days can be estimated for the elimination of organotin in rats after administration of DBTC. This half-life is longer than the half-life of bis (tri-n-butyltin)oxide (TBTO) in the blood of rats (20 hours) and shorter than half-life of di-n-octyltin dichloride in rats (8 days) after single i.v. administration (Pennings et al. 1987; Hümpel et al. 1987). In rats treated with single dose of 8 mg/kg DBTC i.v. the highest concentrations of tin were measured in liver (13.7 ± 1.1 μg/g wet weight) and in pancreas (2.4 ± 1.2 μg/g wet weight) 24 hours after administration. However, 10 - 14 days after treatment the tin concentrations were not higher than those in the control group (Merkord et al. 2000).

An addition of the single cytotoxic effect of DBTC administered at intervals of 3 weeks could lead to the strong organotoxic effects on pancreas and liver observed in our study. The regeneration of the epithelial cells in the biliopancreatic duct of the rat may not be complete during the intervals of application and inflammatory cells may react stronger during repeated treatment.

In most subchronic or chronic toxicity studies the animals are treated daily. The risk of toxic effects after intake of substances at intervals of weeks seems to be rarely investigated. Our findings demonstrate that the organotin compound DBTC induces toxic effects on pancreas and liver by repeated treatment of rats at long intervals. The risk of exposure to organotin at long intervals should be considered.

ACKNOWLEDGEMENTS

This study was supported by Grant FKZ 0122101 from the Ministry of Research and Technology of the Federal Republic of Germany. The autors wish to thank Mrs. Ingeborg Neumann and Mrs. Rita Kleinfeldt for their expert technical assistance.

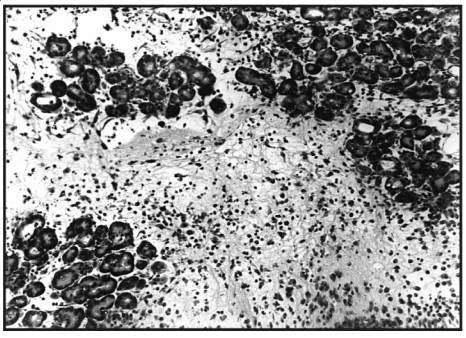

Figure 1a. Rat pancreas 1 week after i.v. administration of 8 mg/kg DBTC. Acute interstitial pancreatitis. HE x 120

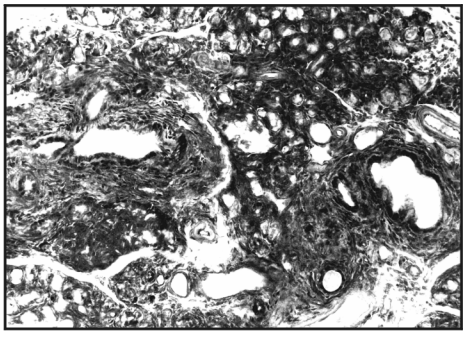

Figure 1b. Rat pancreas 1 year after i.v. administration of 8 mg/kg DBTC. Chronical pancreatitis. HE x 120

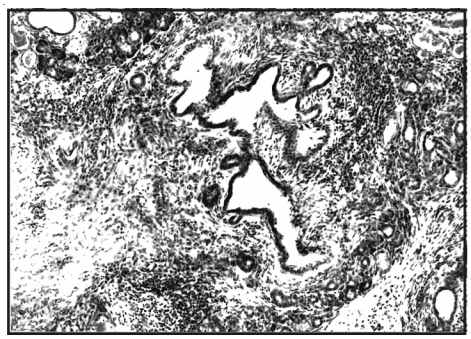

Figure 2a. Rat pancreas 6 month after repeated admi-nistration of 4 mg/kg DBTC i.v.. Chronical pancreatitis. HE x 120

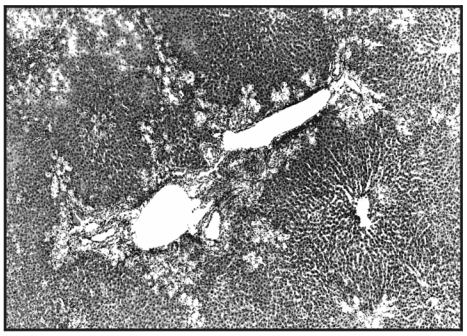

Figure 2b. Rat liver 6 month after repeated administration of 4 mg/kg DBTC i.v.. Intrahepatic bile duct hyperplasia and liver cirrhosis. HE x 120

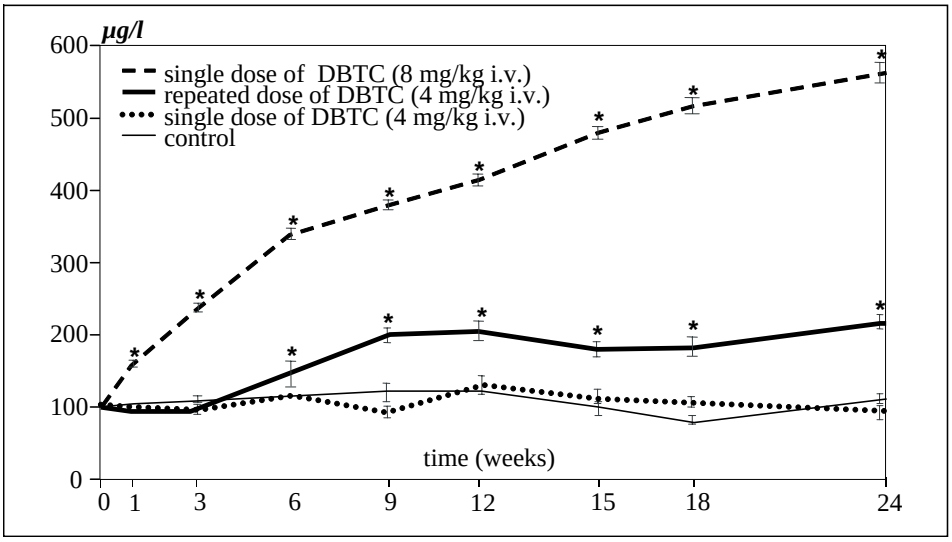

Figure 3. Hyaluronic acid in serum of rats up to 24 weeks after i.v. administration of DBTC (single or repeated dose of 4 mg/kg b.w. and single dose of 8 mg/kg b.w.) and repeated dose of the solvent (control). Repeated treatment on week 3, 6, 9, 12, 15, 18, 21 and 24. Mean values ± SD, n = 7, *p< 0.05.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

DOSE-RESPONSE-FUNCTIONS FOR POLYMER WEATHERING: A CONTRIBUTION FOR THE MAPPING OF AIR POLLUTION EFFECTS

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ABSTRACT

The mapping of air pollution effects on materials shall depict on a ***national level*** the deterioration potential of air pollution and the resulting economic damage. In an ***international*** frame programme of the UN/ECE clean air act and on the basis of the mapping results effective and cost efficient decreasing and diminishing strategies could be developed and concluded.
In this paper the principal methodology of the mapping of air pollution effects on materials by the example of economical relevant polymers will be declared (e.g. PVC and PUR). Therefore at Fraunhofer-ICT dose-response-functions for the polymer ageing depending on air pollution and environmental parameters were calculated from natural weathering investigations.
At the Institut für Navigationssysteme INS, Universität Stuttgart with these data the maps of corrosion rates for these polymers was generated and at the Institut für Energiewirtschaft und Rationelle Energieanwendung IER, Universität Stuttgart the resulting economic damage was calculated. With the comparison of corrosion rates for the different materials the results for polymers will be declared.

INDEX TERMS

mapping, air pollution effects, UV-radiation effects, environmental simulation, modelling of air pollution effects, material damage, economical effects

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INTRODUCTION

Within the UN/ECE-clean air act the deterioration of materials including historical buildings and cultural heritage is a main goal. For the realisation of the sulphur- (Helsinki 1985 and Oslo 1994), nitrogen- (Sofia 1988), VOC- (Genf 1991), heavy metal- (Aarhus 1998) and POPs-protocols (Aarhus 1998) as well as the multi-pollutant-protocol (Göteborg 1999) and the started diminishing tasks quantitative data for air pollution effects on materials are necessary.
With the aid of national maps, which depict the different effects on materials, climatic data and air pollution concentration and deposition in relation to tolerable corrosion rates in their regional distribution, regional deterioration potentials will be determined and economic damages calculated in their geographic distribution. Then the necessity of passive and active protection plans for buildings and cultural heritage could be negotiated or defined.
Basis for the mapping work are the conditions in the "Manual on Methodologies and Criteria for Mapping Critical Loads & Levels and Geographical Areas where they are exceeded" (UBA, 1996), as well as the adoptions and actualisation generated during the methodological development from the UN ECE Task Force on Mapping (UN/ECE Workshops in Berlin 1998 and Stockholm 2000). The scientific basis of some dose-response-functions were developed during an „International Co-operative Programme on Effects on Materials, including Historic and Cultural Monuments (ICP-Materials)". With the results of the this programme from the 8-years exposure of different materials on 38 locations (35 in Europe and 3 in North America) with different climatic and air pollution conditions following rates were determined:

- ***Back ground corrosion rates*** (the 10. percentile - K_{10} – of all detected corrosion rates for the different materials)
- ***acceptable corrosion rates*** as a multiples of the back ground corrosion rates ($n * K_{10}$, n=1.2 to 2) and
- ***dose-response-functions***

In this UN-ECE-programme the investigated materials were some metals, natural stones, paintings and glass in different exposition conditions against climatic and air pollution. But for other polymers, excepted paintings, there was a lack of dose-response-functions. For this reason some investigations from ICT on polymers were incorporated to these results.
The main influencing parameters concerning metal corrosion are:

The ***pollutants***

- SO_2 - Immission (average value in $\mu g/m^3$)
- NO_2 - Immission (average value in $\mu g/m^3$)
- O_3 - Immission (average value $\mu g/m^3$)
- H^+ - Concentration in the precipitation (average value in mg/l)
- Cl^- - Concentration in the precipitation (average value in mg/l)

As well as ***climatic parameters***

- relative humidity (average value in %)
- Amount of precipitation (average value in mm)
- temperature (average value in °C)
- and additional the global radiation (average value W/m²) for polymers.

On this basis state-wide and area-related

- the relevant ***pollutants and climatic conditions*** were measured,
- the ***actual corrosion rates*** for the different materials were estimated
- ***and the degree for overflowing the acceptable corrosion rates*** for the different materials calculated.

With the aid of the determined material loss rates (corrosions- or deterioration rates) the estimation ***of the economic damage*** is possible.

Description of the material deterioration with models

A dose-response-functions describes the mathematical dependency between air pollutants, measured as concentrations and the other environmental parameters like temperature, global radiation, and relative humidity. For non-protected, free weathering of materials the dose-response-functions will be divided in two parts. One part is for dry deposition and another part for wet deposition /Tidblad/. The wet deposition includes the transport of water and ingredients from precipitation and the dry deposition all other processes. For the mathematical models of the corrosion rate of metals therefore a partition of the dose-response-function in the following way has been established:

$$K = \text{dry}\,(T, Rh, [SO_2], [NO_2], [O_3], t) + \text{wet}\,(\text{Rain}[H^+], t) \qquad (1)$$

with K as the corrosion rate, T is the temperature in degree C, Rh is the relative humidity in %, [ ] is the concentration in $\mu g/m^3$ (SO_2, NO_2 and O_3), t is the exposition time in years, rain is the amount of precipitation in mm and $[H^+]$ is the acid rain in mg/l. Dependent from the material the corrosion rate describes the mass loss (ML, g/m^2), the surface resistance (R), ASTM D 1150-55 1987 (ASTM, 1-10), the decrease of the layer thickness (LL, μm) or the gain in mass (WI, $\mu g/cm^2$).

Examples for dose-response-functions are /Tidblad et al 2002/:

Unsheltered Exposure:

Weathering steel ($N=148$, $R^2=0.68$)

$ML = 34[SO_2]^{0.33}\exp\{0.020Rh + f(T)\}t^{0.33}$

$f(T) = 0.059(T-10)$ when $T<10°C$, otherwise $-0.036(T-10)$

Aluminium ($N=106$, $R^2=0.74$)

$ML = 0.0021[SO_2]^{0.23}Rh\cdot\exp\{f(T)\}t^{1.2} + 0.000023\text{Rain}[Cl^-]t$

$f(T) = 0.031(T-10)$ when $T<10°C$, otherwise $-0.061(T-10)$

Exposure under a sheltering roof:

Weathering steel (N=148, R^2=0.76)
$ML = 8.2[SO_2]^{0.24}\exp\{0.025Rh + f(T)\}t^{0.66}$
f(T) = 0.048(T-10) when T<10°C, otherwise -0.047(T-10)

Zinc (N=91, R^2=0.80)
$ML = 0.058[SO_2]^{0.16}Rh\cdot\exp\{f(T)\}t^{0.49}$
f(T) = 0.039(T-10) when T<10°C, otherwise -0.034(T-10)

In all dose-response-functions it is obvious, that the global radiation is not directly included. But the radiation is essential for the polymer ageing, creating chain scission and micro cracking of the surface, hardening and brittle the polymer. Therefore ICT involved the global radiation as a dominant environmental parameter in the dose-response-function.
For the ageing of polymers the global radiation has a strong influence. Not only the UV-radiation leads to chain scission, also the heating IR-radiation accelerates the ageing process in the natural environment. Gases and water vapour penetrate into the polymeric material and lead to a deterioration also in the interior parts of the polymer. Opposite to metals there is no build up of a corrosion layer but a deterioration of the matrix and an mass loss of polymer material. For example for glass-fibre-reinforced materials the fibres will be visible at the surface. The often occurring change in surface tension by drying and wetting the polymer surface leads to micro cracks and material damage or function loss of the system. According Guillet et. al. (Rabek 1995) it is possible to assume for the surface material properties of a polymer a proportional effect to the incoming global radiation, cause the possibility of a chain scission is proportional to the amount of incoming photons. The possible chain scission leads then to the change of the material property. The material property ME has therefore the dependency from the global radiation G and the exposition time t in the form:

$$ME \sim P1\ G\cdot t^{P2} \qquad (2)$$

with P1 and P2 as parametric factors for the investigated material property. Is this material property also depending from the oxygen content of the atmosphere, the P2 lays between 0,5 and 1 with the tendency to 0,5 when the photo-oxidative damage is dominant and a tendency to P2=1 when the photo-oxidative process plays no role. The irradiation of the global radiation is depending on the location of the exposition, the radiation was measured during the exposition time, on the other hand it is also possible to calculate the irradiation with a computer model (VDI 3789 Blatt 3).
Additional to the photo-inducted ageing the influence of the humidity, precipitation and air pollution lead to a damage of the polymer. During the life cycle of the polymer product takes up water vapour and gases till the saturation level is reached. According to the in the region of $10^{-8}cm^2/s$ laying diffusion coefficients D of most polymers, this saturation phase needs at room temperature

some days if the wall thickness is small (1mm). Because of the square dependency of the diffusion process for thicker parts weeks and months are necessary till saturation is reached. After the saturation phase the concentration of the incorporated gases changes with the periodicity of the surrounding air pollution concentration. The penetration depth of the periodic change of the air pollution till a value of 1/e of the amplitude at the surface is depending from the period T_p and the diffusion coefficient D for the gas.
In this case the diffusion coefficient is dependent from the temperature of the material and increases by a factor of 10 when the temperature rises 40°C. For the penetration depth ET of a gas therefore it could be written:

$$ET \sim P_i \, (D_i(T) \, T_p/\pi)^{1/2} \tag{3}$$

With P_i as parametric factor and D(T) as temperature dependent diffusion coefficient (Saechtling 1998). The amount of gas and water vapour, incorporated in the polymer surface therefore could be estimated as the product of the air pollution concentration and the penetration depth with a period duration of one year for gases with summer and winter smog conditions. The penetration depths are several hundred microns up to 2 mm.
If the periodical changes are shorter the yearly, for example daily, the penetration depth of a gas into the polymer is only up to 200 μm. The penetration depth of the gas is additional reduced by possible photo-inducted chemical processes in the polymer. Therefore it is possible to describe the mathematical dependency of the penetration depth in the form:

$$ME \sim P_1[Gas1](D_1(T)T_1/\pi)^{1/2} + P_2[Gas2](D_2(T)T_2/\pi)^{1/2} + ... + \\ + P_N[GasN](D_N(T)T_N/\pi)^{1/2} \tag{4}$$

with:
[Gas#] is the concentration of the gas or the water vapour,
$D_i(T)$ is the temperature dependent diffusion coefficient of the gas,
T the temperature of the material surface during exposition,
P_i are parametric factors for the damage reactions in the material.

With these parts of the formula the modeling of the change of the material property in a aged surface layer of a polymer after natural weathering could be written in the form:

$$ME = \text{const.} + P1G \cdot t^{P2} + P_1[Gas1](D_1(T)T_1/\pi)^{1/2} + \\ + P_2[Gas2](D_2(T)T_2/\pi)^{1/2} + ... + P_N[GasN](D_N(T)T_N/\pi)^{1/2} \tag{5}$$

In the following chapter these dose-response-function was proofed for the material properties of polymers, natural weathered for 8 years at different locations in Germany (Reichert et. al. 2002). Dose-response-functions for polyurethane (PUR), for polyvinylchloride (PVC), fibre reinforced polyester (PES) and alkyd resin based lacquer were developed. As a scale for the damage the penetration

depth of a dye (PUR, PVC), the colour change (PES, PUR) or the reduced layer thickness (Alkyd resin based lacquer) of the material was used. Only two examples are given in this paper:

DAMAGE DEPTH OF THE POLYURETHANE LACQUER (PUR)

In this chapter the results for the modelling of the penetration depth of a dye as a scale for the damage depth of the polymer is depicted. These colouring test deliver a quantitative value for the damage depth of the polymer starting from the surface. The calculated material properties with the model will be compared with the measured values from the natural weathering investigations.

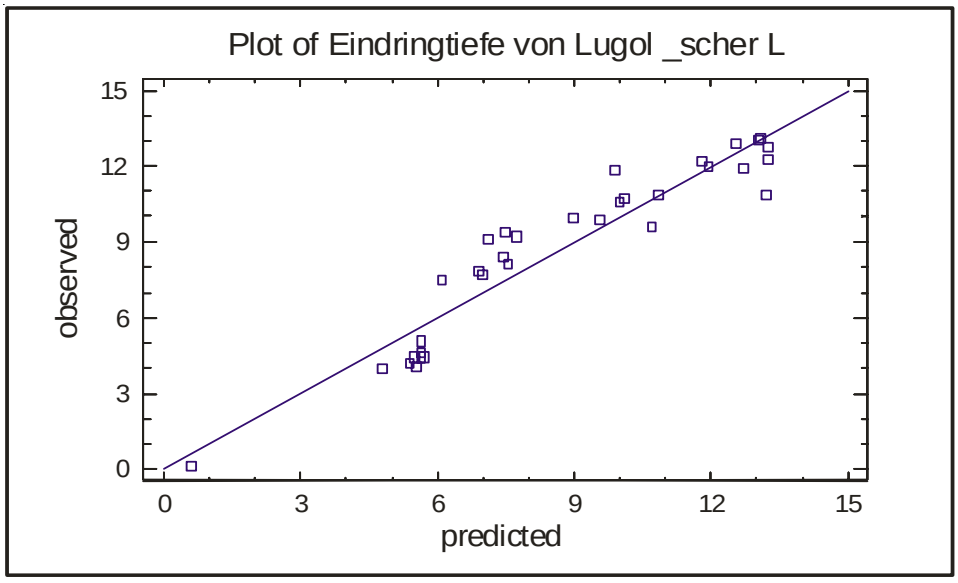

Figure 1. Comparison of calculated values with the model (predicted) and the measured values (observed) for the penetration depth of a dye after the natural weathering of a polymer

The dose response functions then will be described in the form:

$$\begin{aligned}\text{Penetration depth in PUR} &= 0{,}5777 + 0{,}4900 \bullet (G \bullet t)^{1/2} \\ &+ 0{,}0253 \bullet (10^{-9} \bullet T \bullet 10^{8}/3{,}141)^{1/2} \bullet rH \bullet t \\ &+ 0{,}0184 \bullet (10^{-9} \bullet T \bullet 10^{8}/3{,}141)^{1/2} \bullet NO_2 \bullet t \\ &+ 0{,}0122 \bullet (10^{-9} \bullet T \bullet 10^{8}/3{,}141)^{1/2} \bullet O_3 \bullet t\end{aligned} \quad (6)$$

With:
Penetration depth in PUR in μm
G = global radiation (radiance, annual average in W/m^2)
t = exposition time in years
T = averaged air temperature at exposition (annual average in °C)

rH = averaged relative humidity at exposition (annual average in %)
NO_2 = averaged concentration for NO_2 in $\mu g/m^3$
O_3 = averaged concentration for ozone in $\mu g/m^3$

This model has the following regression values:
R^2 = 89,60 %
R^2 (adjusted, dependent on the amount of variables) = 88,12 %, Standard Deviation = 1,17
With this physical and chemical based model the prediction of the change in the material properties works very well. Sulphur dioxide is not involved in the model because of a very small, but negative correlation, which might be a result of the strong decreasing concentration of this air pollutant during the last years.

COLOUR CHANGE OF FIBRE REINFORCED POLYESTER (PES)

In this chapter the results for the modelling of the colour change of fibre reinforced polyester (PES) is depicted. The calculated colour changes from the model will be compared with the measured values from the natural weathering investigations.

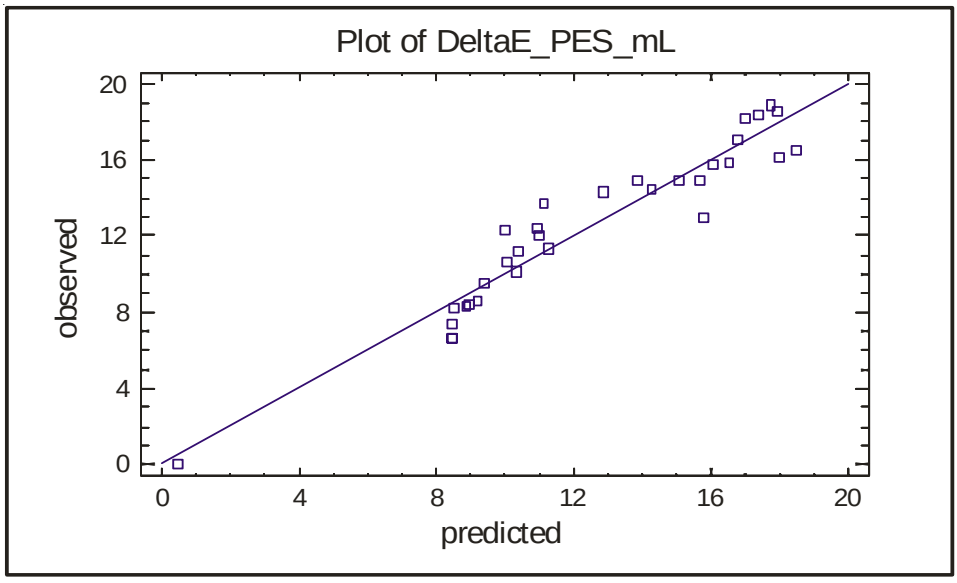

Figure 2. Comparison of calculated values with the model (predicted) and the measured values (observed) for the colour change of the polymer PES.

The dose-response-function then could be described as:

$$\begin{aligned}\text{Delta E} = {} & 0{,}4383 + 0{,}5979 \bullet (G \bullet t^{0{,}4})^{1/2} \\ & + 0{,}0354 \bullet (10^{-9} \bullet T \bullet 10^{8}/3{,}141)^{1/2} \bullet rH \bullet t^{0{,}65} \\ & + 0{,}0064 \bullet (10^{-9} \bullet T \bullet 10^{8}/3{,}141)^{1/2} \bullet SO_2 \bullet t^{0{,}65} \\ & + 0{,}0195 \bullet (10^{-9} \bullet T \bullet 10^{8}/3{,}141)^{1/2} \bullet O_3 \bullet t^{0{,}65}\end{aligned} \quad (7)$$

With:
Delta E = Colour change of PES (Lab*-system)
G = global radiation (radiance, annual average in W/m^2)
t = exposition time in years
T = averaged air temperature at exposition (annual average in °C)
rH = averaged relative humidity at exposition (annual average in %)
O_3 = averaged concentration for ozone in $\mu g/m^3$
SO_2 = averaged concentration for SO_2 in $\mu g/m^3$

This model has the following regression values:
R^2 = 91,68 %
R^2 (adjusted) = 90,45 %
Standard Deviation = 1,33
In this equation the correlation show no influence of NO2 for the colour change of PES. Therefore it is not included in the model.

MAPPING

The research project "Mapping material damages in Germany" (UBA/BMU FE-No. 201 43 205) was integrated into German research activities under the UN/ECE Convention on Long-Range Transboundary Air Pollution (LRTAP), which are co-ordinated by the German Federal Environmental Agency. Within the scope of these research activities the project is connected to two UN/ECE International Co-operative Programmes (ICP's) – the ICP on Modelling and Mapping of Critical Loads and Levels and their Air Pollution Effects, Risks and Trends (ICP Modelling and Mapping) and the ICP on Effects of Air Pollution on Materials, Including Historic and Cultural Monuments (ICP Materials).
For calculation of the damage depth in all places in Germany the state-wide and area-like data for the global radiation is necessary. The averaged radiance (W/m^2) at one place can calculated from the integrated radiation (kWh/m^2) for one year. The Institute of Navigation, Stuttgart University has prepared the auxiliary maps also on temperature, rainfall, relative humidity, concentration of SO_2, concentration of O_3, concentration of NO_2, deposition loads of protons and deposition loads of chloride. Calculating these auxiliary maps is a precondition for mapping material damages in Germany. Furthermore, the mapping of material damages demands implementing dose-response-functions into GIS (Geographical Information System). Mapping material damages implies availability of high resolution raster data on climate and air pollutants.
The following data on climate and air pollutants have used for mapping:

- climate (annual mean or annual sum):
  relative humidity (%)
  rain fall (mm)
  temperature (°C)
  irradiance (W/m^2)

- air pollutants (annual mean or annual sum):
  concentration of SO_2 ($\mu g/m^3$)
  concentration of O_3 ($\mu g/m^3$)
  concentration of NO_2 ($\mu g/m^3$)
  deposition loads of chloride (wet only, mg/l)
  deposition loads of protons (wet only, mg/l)

In previous research projects at Institute of Navigation, Stuttgart University (INS) a database on air pollutant concentrations and deposition loads has been established (ANSHELM ET AL. 1998, GAUGER ET AL. 1997, GAUGER ET AL. 1999, GAUGER ET AL. 2002). This database has been updated and extended during this research project. This data pool and the dose-response-functions are the basis mapping of material damages in Germany is based upon. Mapping of material damages has been carried out for 1990, 1995 and 1999. For the economic assessment of material damages a longer exposure period is more suitable. It has been decided within the group to use an eight year exposure period ($t = 8$) to calculate the maps, which are intended to be used for economic assessment of material damages.
Mapping results indicate, that the changes in deposition loads and concentrations of air pollutants, which happened during the 1990ies had some effects on material damages. The majority of materials shows, that material damages due to air pollutants have receded during the 1990ies. In particular, this is the case for those materials, whose damages are caused predominantly by the concentration of SO_2 (weathering steel, zinc, aluminium, copper, bronze, Portland Limestone, Mansfield Sandstone, paint coatings, glass M1). Damages to glass M3 (sheltered exposure) is excluded from this trend, because for materials in sheltered position the concentration of SO_2 is less important.
To assess damages to polyurethane lacquer (PUR) two dose-response-functions have been available. The first function uses the infiltration depth of Lugol's solution to describe damage depth, the second one uses changes in colour as a criteria for damage. Looking at the infiltration depth of Lugol's solution no trend is detectable. The decline of SO_2 seems to have no effect on damage depth of polyurethane, whereas, change in colour seems to be influenced by SO_2 concentration. High concentration of SO_2 correlates with low Delta e values, which is equivalent to a whitening of the material. Damage depth of polyvinyl chloride (PVC), too, is influenced by the concentration of SO_2. In Saxony, Thuringia and Saxony-Anhalt there have been high air concentrations of SO_2 in the beginning of the 1990ies, which entailed high infiltration depths of acridine orange staining into PVC. In 1999 SO_2 concentration has diminished to very low concentrations all over Germany. Highest damage depth of PVC is no longer bound to regions of highest SO_2 concentrations, but to region with high values of annual mean temperature.
In 1990, changes in colour of polyester have been very intensive in those regions with exceptionally high concentrations of SO_2. At the end of the 1990ies SO_2

concentrations have declined. Most intensive changes in colour, now occur in some regions with high ozone concentrations and high values of relative humidity. Mapping results for damages to alkyd resin lacquer cannot be assigned to spatial patterns of any air pollutant or climatic parameter.

ECONOMIC DAMAGES FROM AIR POLLUTION

The tasks of the Institute of Energy Economics and the Rational Use of Energy (IER) Stuttgart University include the assessment of the economic costs of the deterioration of building materials due to effects of air pollutants. The work contained the extension and update of the methodology for the assessment of economic damages at residential buildings in Germany on the basis of measured data, developed within the previous project. Particularly, material inventories were derived for the years 1990, 1995, and 1999 and used for the calculations of material damages. In order to carry out calculations for such a large area like Germany, the so-called damage function approach was used. Beside its applicability on large areas of investigation, a further advantage is that the results can easily be updated. Because of the availability of data, the study is restricted to the estimation of maintenance costs of residential buildings. The loss of cultural heritage and the damage on further economic goods could not be considered. Furthermore, other cost components like e.g. the loss of cultural and aesthetical value were not taken into account.

Starting from the area specific corrosion rates calculated by the Institute of Navigation, first, the material surface which had to be repaired because of the damage in the different years was calculated by applying the derived material inventories and maintenance criteria. Afterwards, using the area specific maintenance costs the invested maintenance costs due to damages caused by air pollution in the years 1990, 1995, and 1999 were assessed. Galvanised steel, zinc, aluminium, sandstone, limestone, other natural stones, and rendering were considered. Additionally, rough estimates were assessed for alkyd melamine and alkyd paintings, windows made of PVC and copper.

A major part of the work contained the calculation of material inventories for the years in focus. Updating and extending the maintenance criteria and specific maintenance costs by literature review and expert questioning was a further task. In the first step of the calculations a stock of residential buildings was derived from the data of the building censuses of 1987 and 1995 derived by the Federal Statistical Office of Germany and respective updates together with data for the new Laender in 1990. Simultaneously, the data were categorised by age, number of floors, number of apartments, and type of construction. The calculated values were in a next step attributed to specific types of buildings before they were assigned to specific settlement types. For the used settlement types, a census of material surfaces at representative buildings had been published for Cologne and Dortmund. Thus, by using those data finally maps of material surfaces on

the level of districts for the years 1990, 1995, and 1999 were estimated. Furthermore, within the district areas, the data on material surfaces were distributed to areas of settlement. For comparison, both sets of maps were used in the calculations of economic costs.

The estimation of the maintained surface area resulted in the highest estimates at about 3.2 km^2 for galvanised steel in 1990. It could be seen that the estimates become smaller for 1995 and 1999 with 2.9 and 2.6 km^2. Similarly the shares of damaged materials compared to the total surface area decreased from 4 to 3.5 to 3.1 percent. The second largest material surface area which is to be maintained was calculated for rendering with 1.8, 1.3, and 0.96 km^2. Aluminium is following at 1.2, 1.1, and 0.97 km^2 (calculations on district area). The results of the estimations on the settlement areas show only a small discrepancy to those results.

For the calculation of maintenance costs considering the material surfaces which can be calculated with a comparable low uncertainty, the largest values were estimated at 81, 74, and 66 million Euro for galvanised steel, followed by aluminium (55, 49, 44 million Euro), rendering (55, 39, and 29 million Euro), and the natural stones. The total costs were estimated to 310, 250, and 210 million Euro in 1990, 1995, and 1999 respectively. Referred to the population of Germany, per capita costs of 4.9, 3.2, and 2.6 Euro per person were derived. The largest contribution was assessed for galvanised steel. The highest cost values with about 29000 €/km^2a were observed for 1990 in the Ruhr area. Further high costs were calculated at about 10000 to 15000 €/km^2 a for the regions Cologne-Bonn, Berlin, Frankfurt, Bremen, and Hamburg. For 1999, estimates higher than 10000 €/km^2a were only assessed for the Ruhr area (up to about 18000 €/km^2a) and for Stuttgart (about 11000 €/km^2a).

Important surface materials like concrete and typical facade paintings could not be considered in the analysis due to a lack of dose-response functions. At least for a part of the painted surface area, a rough estimation could be carried out by making assumptions about the share of the painted area which represents paintings on which the UN ECE functions on alkyd-melamine and alkyd paintings for steel can be applied. Furthermore, rough estimates were derived for windows of PVC and copper surfaces.

The calculated repaired surface areas for paintings and windows of PVC are with about 10 and 30, and 19 km^2 much larger than for the other materials. For copper the value represents 2 km^2. The total sum of the roughly estimated costs for the paintings, windows of PVC, and copper exceeds the assessed values for the remaining materials. Thus, although the estimates are uncertain they show that damage estimates for those materials could represent a large share of the total damage costs. Further high contributions are to be expected from the consideration of typical facade paintings, concrete, and soiling effects. Damages in those areas can still not be assessed, because no dose-response functions are available.

Additionally to the fact that damages of some important material surfaces are not or only roughly assessable, for the quantifiable material surfaces only maintenance costs for residential buildings were taken into account. Furthermore, other economic goods and cost components like e.g. aesthetical costs and the loss of the cultural value are not included in the results. Thus, the sum of the relatively certain assessable maintenance costs represents a lower estimate for the real material damage caused by air pollution in Germany.

ACKNOWLEDGEMENT

We thank the Umweltbundesamt, UBA Berlin for the support and funding of this project.
Further Information: Institut für Navigation, INS http://www.nav.uni-stuttgart.de; Institut für Energiewirtschaft und Rationelle Energieanwendung IER http://www.ier.uni-stuttgart.de; Fraunhofer-Institut für Chemische Technologie http://www.ict.fhg.de

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

AIR POLLUTION IN AN AREA OF SÃO PAULO, BRAZIL: HEALTH EFFECTS ON CHIDREN

H Ribeiro*

ABSTRACT

In 1960´s and 1970´s air quality in the metropolitan area of S. Paulo, Brazil, was largely influenced by industrial sources. Industrial air pollution control programs started in 1976, focusing on particulate matter and SO_2 from stationary sources, and were very successful. The new vehicle emission reduction program, based on emission levels established in 1986 for carbon monoxide, hydrocarbons and nitrogen oxides, started in 1989. The Program to Control Vehicle Pollution had good results, since it managed to reduce the levels of nearly all air contaminants, in spite of the amazing 750% increase of the region's vehicle fleet in the period. Between 1977 and 2000 CO levels dropped 3.1%; SO_2 levels dropped 88.1% and particulate levels 58.4%. Currently, ozone is the pollutant that causes the greatest concern and vehicles are the main source of contaminants in S. Paulo.
Control programs were not equally effective in the city' s different regions. This study assessed air pollution data, in a historical perspective, of a residential area of the city (Cerqueira César) that was never influenced by industrial sources, in order to evaluate the results of the Program to Control Vehicle Pollution. The study verified the prevalence of symptoms of respiratory diseases in children that live in the area, as compared to prevalence of symptoms in children that live in control area of low pollution.

INDEX TERMS

Air pollution control, vehicles, Sao Paulo, respiratory symptoms, children health

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INTRODUCTION

Air quality has been a constant worry in the city of Sao Paulo, during the last 3 decades, since it became very contaminated by industrial and mobile sources and it resulted in negative health impacts on the population. Air quality, in S. Paulo, has been monitored by CETESB, through a network of 11 non-automatic stations since 1973 and a network of 25 automatic stations since 1981.

Air quality, in the Metropolitan area of Sao Paulo, is the result of a complex system formed by mobile (vehicles) and fixed (mostly industries) emission sources, by topography and by meteorological conditions of the region. Nowadays, atmospheric pollution is directly associated to vehicle emissions as industrial emissions are under control (EMPLASA, 2000).

In 1986, a program of emission reductions for new vehicles was adopted through the enactement of the Federal Automotive Pollution Control Law- PROCONVE- which set emission standards for carbon monoxide, hydrocarbons and nitrogen oxides in regard to Otto vehicles, and smoke for Diesel-powered vehicles. The program started to be effective in 1989.

In 1990, air quality standards were revised. The new standards included the concept of primary standards for the protection of public health and secondary standards for the protection of the environment and human well-being in regard to suspended particulates, inhalable particulates (PM_{10}), smoke, carbon monoxide, sulfur dioxide, nitrogen dioxide and ozone (Table 1).

Table 1. Brazilian national air quality standards ($\mu g/m^3$)

Pollutant	Primary Standard	Secondary Standard
Total Suspended Particles	240 (24 hours average) 80 (annual geometric mean)	150 (24 hours average) 60 (annual geometric mean)
Inhalable Particles (PM_{10})	150 (24 hours average) 50 (annual arithmetic mean)	Same as primary
Smoke	150 (24 hours average) 60 (annual arithmetic mean)	100 (24 hours average) 40 (annual arithmetic mean)
Sulfur Dioxide	365 (24 hours average) 80 (annual geometric mean)	100 (24 hours average) 40 (annual geometric mean)
Carbon Monoxide	40,000 (1-hour average) 10,000 (8-hours average)	Same as primary
Nitrogen Dioxide	320 (1 hour average) 100 (annual arithmetic mean)	190 (1 hour average) 100 (annual arithmetic mean)
Ozone	160 (1 hour average)	Same as primary

Source: CETESB, 2000.

A program to reduce the number of cars on the streets started in 1996. Each week day, according to the final number of the plates, 20% of the cars are prohibited to circulate. When the program started, the schedule was from 7 a.m. to 8 p.m. and only during winter season when atmospheric conditions favor concentration of pollutants because of shortage of rainfall. From 1998 on, the schedule was reduced to rush hours (7 a.m. to 10 a.m. and 5 p.m. to 8 p.m.) but for the whole year. The prohibition is meant more to improve traffic conditions than to decrease air pollution, which is partially under control.

A comparison between emissions at the beginning of the air pollution control program developed by CETESB- Companhia de Tecnologia de Saneamento Ambiental (the Sao Paulo State Environmental Protection Agency)- in the mid-1970s and in 2000 shows that sulfur oxide emissions decreased 88% and particulate emissions decreased 58.4%. Carbon monoxide emissions, however, decreased only 3.1% and hydrocarbon emissions increased 46.6%. The worst case is nitrogen oxides emissions, which increased 208.1%. Mobile sources substantially increased their contribution to the air emissions in the region in terms of HC, NO_x, SO_x and particulate matter. Most carbon monoxide emissions stem from mobile sources (Table 2).

Table 2. Comparison of emissions in 1977 and 2000

Parameter	CO	HC	NO_x	SO_x	PM*
Total emission in 1977	1,715	257	124	321	154
Total emission in 2000	1,661.8	376.7	382	38.3	64.1
Alteration in the period (%)	-3.1	+46.6	+208.1	-88.1	-58.4
Contribution of mobile sources (%) in 1977	94.2	75.3	74.3	10.0	7.8
Contribution of mobile sources (%) in 2000	97.7	96.8	96.3	55.4	50.7

* Particulate matter

Total vehicle fleet of the Metropolitan Region of Sao Paulo, in 2003, is 5,497,633. It is composed of 4,294,272 cars; 39,905 buses; 168,792 trucks; 476,597 vans; 439,599 motorcycles and 80,000 others. Those dramatic numbers show why vehicles became the main sources of air pollution in the city.

Parallel to the air quality evaluation program was the installation of a system to measure vehicle emissions (CO, HC and NOx) using, as reference, the "Constant Volume Sampling System" adopted in the US. This system was the basis of PROCONVE- the federal air pollution control program for motor vehicles.

PROCONVE established a gradual reduction of vehicle emissions. For example: in 1989, 24 grams per kilometer was set as the emission standard for carbon monoxide for new light-duty vehicles. In 1992 the target was 12 grams per kilometer, and after January 1997 all new cars had to observe a maximum carbon monoxide emission rate of 2 grams per kilometer. Also, from 1997 onwards the

emission standards adopted for HC and NO_x have been almost the same as those in the U.S. and other developed countries (0.3 gram per kilometer for HC and 0.6 gram per kilometer for NO_x).
Although the vehicle fleet has increased more than 750% in the city of Sao Paulo since 1970, air quality in the region did not worsen in the same proportion. In fact, for some pollutants, it improved. At present, major air pollution problems are related to fine particles (PM_{10}), carbon monoxide and ozone. It must be noted that in regard to the situation in the 1970s air pollution now covers a much broader area both in the city of Sao Paulo and in the metropolitan region.

METHODS

This study analyzed air pollution data from a residential neighborhood with upper middle class income, close to downtown - Cerqueira Cesar-that was never influenced by industrial sources and where there is larger proportion of newer cars, in order to evaluate the results of the air pollution control program for motor vehicles. Data was collected by CETESB automatic monitoring station. The selected period was 1992 to 2000 because it covers the 1992 and the 1997 targets mentioned above. Pollutants measured were SO_2, Smoke, Total suspended particles, NO_2, NO, Inhalable particles.
The prevalence of symptoms of respiratory diseases of 100 children 11 to 13 years old that live and study in the area was verified through a questionnaire developed by The Epidemiology Standardization Project (Ferris,1978) and applied in a government school located within 2 km distance from the monitoring station. Results were compared to the prevalence of symptoms of children, from the same age group, that live in a control area with very low pollution level.

RESULTS

Air pollution levels have been decreasing in the area as result of the pollution control program. As can be observed on table 3, below, there was a drop in the concentration of most pollutants. Smoke, TSP, Inhalable particles, NO_2 and NO concentrations that were above the annual standards, now are below but close to the primary standards (Table 1). Levels of CO that exceeded the standard in 64 days/year in 1992, have not exceeded it on a single day in the last 3 years.
However, secondary standards for Smoke and Total suspended particles are still surpassed.
The results obtained from the survey are shown on table 4. As a general trend, the prevalence rates of symptoms of respiratory diseases are higher in Cerqueira Cesar. In 25 out of 32 symptoms analyzed, the prevalence rate was higher than in the control area.

Table 3. Levels of Pollutants at Cerqueira César Monitoring Station-São Paulo Annual Mean $\mu g/m^3$

							Number exceedances of 8h CO air quality standard
Year	SO_2	Smoke	TSP	NO_2	NO	IP (**)	CO
1992	19	_		75	70	92	64
1993	18	_		62	131	90	54
1994	12	_		_	_	65	44
1995	16	_		_	_	61	24
1996	21	83	87	83	117	46	5
1997	15	72	88	79	114	43	3
1998	12	61	85	67	86	40	0
1999	15	55	72	64	68	44	0
2000	16	49	78	70	79	48	0

(*) = Station Cerqueira César - Faculdade de Saúde Pública da Universidade de São Paulo
Av. Dr. Arnaldo, 725 - São Paulo - SP
(**) = Arithmetic mean
Source: CETESB - Companhia de Tecnologia de Saneamento Ambiental - Relatórios de Qualidade do Ar no Estado

DISCUSSION

The results of this survey confirmed the hypothesis that air pollution affects the respiratory function of children living in more polluted districts of Sao Paulo Metropolitan areas. In spite of successful pollution control measures, present day pollution levels seem to be an important etiological factor of respiratory diseases in children. The results also indicate that primary standards might not protect children from health impacts. Children are more vulnerable to air pollution because they may receive an increased delivered dose of outdoor pollutants, compared to adults, because they have a higher minute ventilation per unit body mass than adults, are generally more physically active, and spend more time outdoors.

CONCLUSION

The data emphasized the need to reinforce pollution control programs and investments in clean technology public transportation in order to reduce the number of cars on the streets so that all areas comply with secondary standards of all pollutants year round to protect children's health.

ACKNOWLEDGEMENTS

CNPq- Conselho Nacional de Desenvolvimento Científico e Tecnológico for financial aid Schools and students for participation in the survey.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

A MULTICENTRIC STUDY OF PERSONAL EXPOSURE: WHAT LESSON?

I Roussel*, J Dechenaux, C Shadkowski and E Muls

ABSTRACT

This paper presents an experimentation that took place in four French towns. About 30 volunteers where involved in each town. The experiments relating to NO, NO_2 and BTEX, proceeded, for each volunteer, over two seasons, one in Spring 2001 and the other in Fall and Winter.
2001-2002. This variation shows that air pollution has a seasonal character impossible to circumvent of the air pollution. This experiment shows clearly the weight of "indoor" pollution, but there is no precise data for the transfer of outdoor pollution inside the houses. Indeed external measurements used in this experiment are those of the of measurements networks which do not correspond directly to the pollution level measured in the volunteer's residence immediate surroundings. The influence of "indoor" pollution stresses the importance of personal choices carried out at the time of the choice of the housing and on its mode of use, (garage communicating with the house, gas cooking….).
The choices concerning the means of transportation also exert an influence on the personal exposure. However the time spent in transportation is shorter than the time spent at home (2 hours on average against 12). Commuting has thus a lesser weight than housing.
The interpretation of the results obtained with oxides of nitrogen are not always congruent with that obtained for the BTEX, which corroborates the complexity of the phenomenon of the air pollution and the difficulty of its exploration based on measuring indicators.

INDEX TERMS

Personal exposure, indoor pollution, determinant of the exposure.

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APPA

INTRODUCTION

This study proposed to take direct measurements of exposure on a certain number of adult volunteers (approximately about thirty per site) and non smokers living in the agglomerations of Marseilles, Dunkirk, Lille and Grenoble. This experimentation complements some others already done in France (Dusseaux 2001, Gonzales-Flesca N, 2000).
The experiments relating to NO, NO_2 and BTEX, proceeded, for each volunteer, over two seasons, one in Spring 2001 and the other in Fall and Winter 2001-2002. This study contributes to identify the determinants of personal exposure. The aim of this study is to facilitate the right choise of housing and way of life for reducing the sources contributing to personal exposure. In fact, benzene induces health risk (Cicolella A. 1997, Cocheo 2000, Mosqueron L, 2002, Rotko T, 2001)

METHODS

For each sentinel, the experiment consists of (except technical hitch):

- of a "measurement" of the exposure cumulated over 48 h. for N0x and the BTEX, (badges Ogawa and Radiello)
- of a measurement of indoor pollution (N0x and BTEX) laid out in the living room throughout the experimentation, (Ogawa badge and radiello)
- answers to a questionnaire on the housing characteristics and their space time activity budget (BETA) filled according to a step of time quarter-schedule. BETA was filled for 5 days to test the occurrence of a possible modification of the timetable because of the constraint posed by the port of the badges.
- Of an evaluation of calculated outdoor pollution based on the "measurements" taken by the AASQA (Approved Association of Monitoring of the Quality of the Air) of the concerned agglomeration (average of the entire data obtained by the network on the background sites and proximity sites as well). The quality tests carried out for N0 show that the response of the analyzers used by the networks and the passive sensors used during this experimentation do not have a stable answer.

The sentinels were recruited on a volunteer basis. They, therefore, do not constitute a representative sample of the population of the four agglomerations. For example, executives and higher professions categories are over-represented in this study. According to indications provided by the Investigation-households, the intellectual professions category to which belong the sentinels, is a population who is less at home and who spends more time in their car.
The type of housing occupied by the sentinels reveals a cleavage between Northern and Southern cities. For instance, in Lille and Dunkirk, the houses are strongly represented in accordance with the cultural characteristics in Northern France

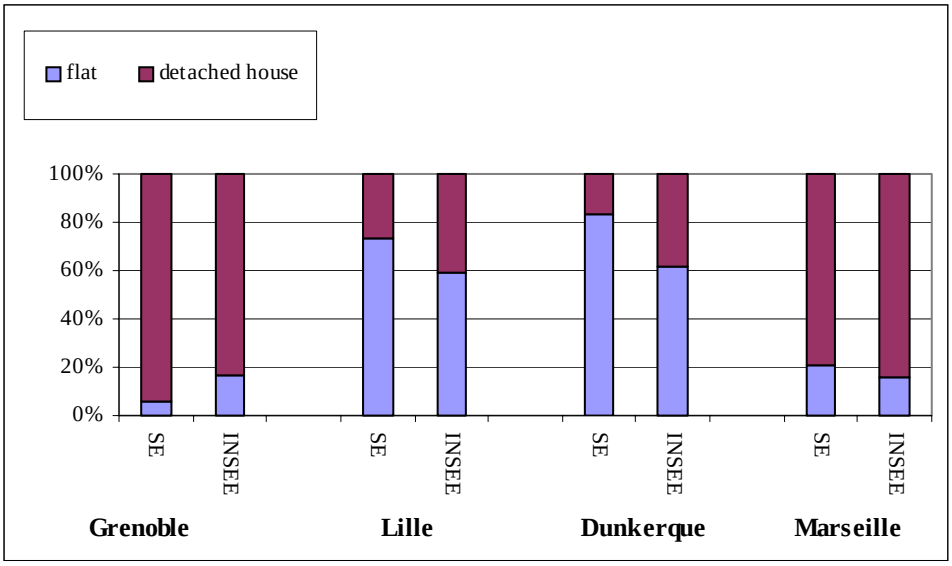

Figure 1. Type of housing represented in the sample of sentinels (SE) compared to the total population for the 4 cities (INSEE)

(Figure 1). The practices of do-it-yourself and gardening strongly follow this cleavage as well as the presence of a garage communicating with housing. However, in spite of these cultural characteristics, a multicentric study is justified since, over the totality of the sentinels, the variables representing the towns of membership, do not appear with a strong weight. The individual choices of the sentinels in term of housing, activities, and ways of life appear more significant than the collective characteristics of each agglomeration.

RESULTS

Over the totality of measured pollutants, the level of the personal exposure is higher than the level of indoor pollution, which is higher than the level of outdoor pollution. (Derbez 2001). The spatial heterogeneity of a primary compound such

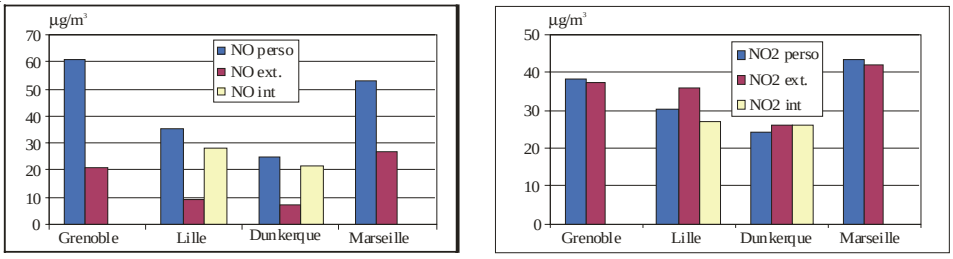

Figure 2. Mean levels of NO and NO_2 measured in the four agglomerations

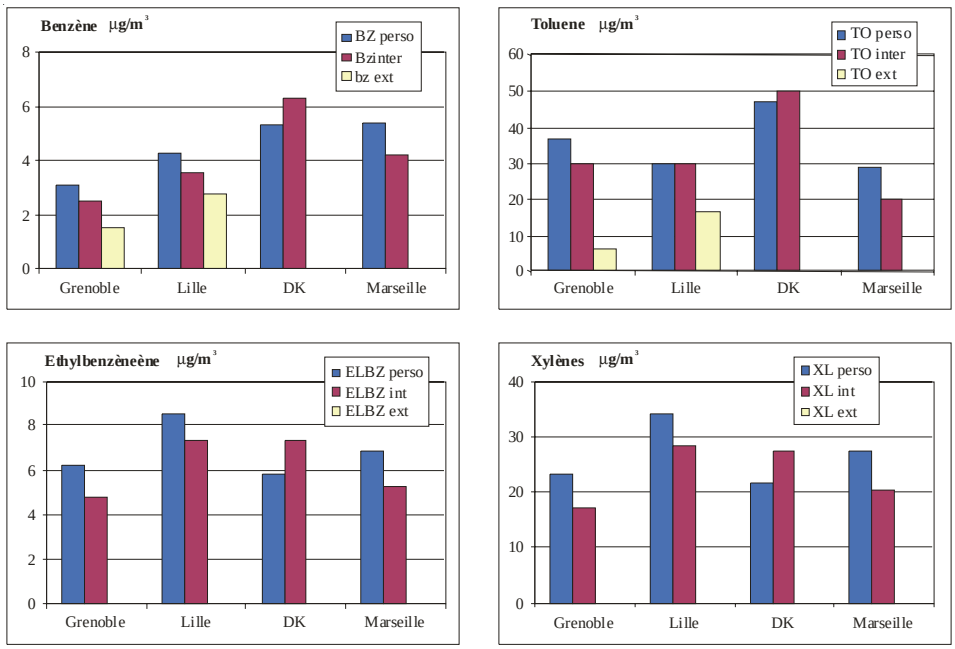

Figure 3. Levels of BTEX measured in the four agglomerations

N0 is much stronger than for a secondary compound such NO_2. In Dunkirk, the indoor concentration of NO_2 is even higher than the other measured concentrations.

The NO_x level is higher in southern cities while for the BTEX this geographical correspondence is less clear. It should be noted that in Dunkirk, whatever the pollutant, the indoor concentrations are higher than those of the personal exposure and, a fortiori, with external measurements.

Taking into account the measurement integrated over 48 h., the search for determinants raises more questions than demonstrating causal relationships.

Table 4. Principal determinants of the individual exposure to benzene (multiple linear regression (n=60))

Variables selected	**R^2 (%)**
Benzene – indoor exposure	61,3
(time spent in car) Ln	3,5
Type of activities	1,7

Table 5. Principal determinants of the individual exposure to benzene (multiple linear regression n=60).

	Coefficient of regression	**Standard deviation**	**P**
Constant	0.373	0.111	0.001
Benzene – indoor exposure	0.04605E	0.004	0.000
(time spent in car) Ln	0.209	0.065	0.002
type of activities	0.236	0.111	0.037

DISCUSSION

These results can be used for the specification of a relevant prevention policy. Admittedly, the levels observed, with the exception of two Dunkirk people, are not medically alarming. However, taking into account current knowledge on public health, even if, at the individual level, it is illusory to try defining a medical risk, the determinants observed make it possible to drive choices after weighting the level of exposure of the inhabitants for various pollutants.

The research of a specificity related to the agglomeration is skewed by the volunteers mode of recruitment. In Grenoble, taking into account urban transport problems, the volunteers mode of recruitment was emphasized towards urban habitat. On the other hand, the Marseilles sample is preferentially formed by students who were motivated by this experimentation, which explains a Marseilles specificity concerning the age and the way of life.

These results underline the weight of the way of life, the weight of housing choices, the number of displacements and the means of transportation used, which, in accordance with the results of other studies, underlines the importance of individual behavior in the measured of personal exposure levels (Noy D, 1986, Rijnders E, 2001). However, a true prevention policy cannot be based only on individual choices. The impact of the individual way of life on pollution levels points back to choices of public policies: The individual choices concerning housing return to social aspects and standards of construction.

It is possible to wonder about adhesives, paintings, materials resulting from process of recycling generating benzene sources. Standardization must also affect the principles of ventilation. Cooking must be carried out under good conditions.

The negative impact of the garage contiguous to housing is clear. The architects should be more sensitive with this question.

The above confirms the importance of the urbanistic characteristics that limit car use. Undoubtedly a policy in favour of public transportation or the development of urbanity can contribute to this objective but it is also necessary to wonder about urban spreading out and thus increasing car use... It is the negative spiral

often denounced by the developers who would tend to settle all questions with roads construction... (Rijnders E, 2001).
On the other hand, contrary to the results presented in other studies, the weight of passive smoking appears weak.
Housing is not the fruit of a choice completely deprived of social and financial constraints. This study shows that the size and the number of rooms in a house are beneficial for air quality. Are these characteristics accessible to all purses, in a salubrious environment? The results presented show that authorities must pay special attention avoiding a social and environmental marking for certain districts, which could quickly be transformed into a regrettable stigmatization of the inhabitants.
As much as housing, the environment and its procession of harmful effects represent considerable source of pollution for oxides of nitrogen as well as BTEX. The territorial marking denounced in American writings about "environmental justice", is added to a real social marking that CSP take into account only partially.
This study underlines a certain territorial and social marking. Territorial marking is identified through two harmful effects: presence of industry or presence of heavy automobile traffic.
Social marking is especially apprehended in Grenoble where the CSP (Socio-professional Categories) are all represented contrary to the other cities. Nevertheless, it is necessary to be careful in exploitating these results because the air quality is combined with many other factors to characterize and stigmatize a territory.

CONCLUSION

This study underlines the complexity of the air pollution phenomenon. The prevention to be implemented can have effects differentiated according to pollutants. Thus, this study could emphasizes the beneficial effects of individual housing as for the oxide levels of nitrogen. These same residences are penalized when the BTEX are looked at.
This complexity and the absence of results proposing an individualized medical risk should not lead to inaction. The policy of precaution must be active as well in order to advance research and to define strategies of prevention.

ACKNOWLEDGEMENTS

We want to thank all volunteers who have accepted up to 48 h. long experiment for improving scientific knowledge. We also thank the many collectivities, who trusted us to realize this study.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

THE VOLCANO Mt ETNA: FIRST APPRAISAL ON THE HEALTH EFFECTS OF VOLCANIC-ASH

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ABSTRACT

After the recent emissions of volcanic-ash from the a side crater on Mt Etna the School of Hygiene of Catania University started an observational epidemiological study survey to study eventual effects on human health. Data was collected from Emergency Room (ER) lists of the all Hospitals of Catania and these were correlated with the most representative pathologies caused by the volcanic-ash. The period from October 20th to November 5th, in which the greatest amount of volcanic-ash was registered, was used as the study period.

The ER data that were collected from Hospitals in 2001 were compared and were divided into etiologically correlated representative pathologies. As regards the existing differences between the 2001 and 2002 lists a statistic elaboration was carried out to verify the significance differences. The statistical tests that were utilized are "Chi-squared test ($\chi 2$)" and "Z-test", both tests supported our theory and are reported in Tab. 1.

As can be seen in table 1, the differences of lists found in the two periods for the principle representative pathologies were "highly significant" in the Hospital of Catania city and mainly in the area hit by volcanic-ash. The decrease of surgical and orthopaedic interventions registered on the ER lists of the OVE and Garibaldi Hospitals could be due to the ban of motorbikes in the city areas where the hospitals are. Considering the values collected from the ER of Cannizzaro Hospital situated in the North of the city, it is particularly interesting to note the remarkable increase in orthopaedic traumas, justifiable by the present of the volcanic-ash on the roads.

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INDEX TERMS

Health Effects, Emission of Volcanic ash, Epidemiological Study, Volcanic-ash, Chi-squared test.

INTRODUCTION

The term "volcanic ash" refers to small, atmospheric pulverized cliff particles expelled during volcanic eruption.
In the case of eruptions of high explosivity, the ash is projected at high speed begins at (measured on Etna from Dubosclard-Coltelli and others, 1999) around 80-90 m/s up to tens of kilometres. The particles of smaller dimensions, that go from 1 to 15 microns, can remain in the atmosphere for some days and, transported from the tropospheric or stratospheric winds, cover remarkable distances.
The ash that fell on area of Catania, coming from eruption of the volcano begun on 19 October 2002, and is composed of minerals and fragments of volcanic glass (magnesium and aluminium silicates), it is hard, and does not melt in water, it is produced during explosive eruptions from the solid cliff and the violent magma fragmentation. After being emitted into the atmosphere, the warm ash quickly ascends to form an eruptive column over the volcano, which, depending on the atmospheric conditions, can travel great distances, as was the case of the eruption of October 2002, during which the cinereous reached the areas of Siracusa and Messina.
By our determination volcanic ash is made up of:

Table 1. Composition of volcanic ash

	Ash preleved in town 2001	***Ash preleved on volcane 2001***	***Ash preleved in town camp. 1 2002***	***Ash preleved in town camp. 2 2002***
	(mg/Kg dry weight)	**(mg/Kg dry weight)**	**(mg/Kg dry weight)**	**(mg/Kg dry weight)**
Pb	18.503	5.250	5.4	4.6
Cd	0.119	0.044	0.35	0.32
V	1.751	64.381	21.0	20.1
Al	0.259	0.323	0.21	0.91
Ni	12.509	12.965	13.2	11.6
Hg	<0.001	<0.001	<0.001	<0.001
Si	16.800	23.346	17.25	16.75
Cr	15.632	15.981	15.81	15.55

The School of Hygiene and Preventive Medicine of Catania University started a descriptive epidemiological survey to find eventual effects on human health of the emitted volcanic ash from Mt Etna. In particular, we considered the

pathologies thought to be more probably correlated to the presence of air-dispersed volcanic powder, that is the acute affections of the upper and lower respiratory tract, cardiovascular affections, the neuro-psychiatric affections, ocular affections, dermatological affections and surgical and orthopaedic pathologies of a traumatic nature.

METHODS

Data was collected from the units of the emergency rooms the Hospitals of the Catania province (Vittorio Emanuele, Ferrarotto and S. Bambino Hospitals, Cannizzaro Hospital, Garibaldi , S. Luigi-Currò, Ascoli-Tomaselli Hospitals, the Hospital of Giarre, S. Giovanni di Dio and S. Isidoro of Militello Val of Catania, S. Marta and S. Venera of Acireale, SS. Salvatore of Paternò, Biancavilla, and Bronte) for pathologies that in some way could be correlated to the cinereous emissions of the volcano. It was decided to monitor the periods between 20 October and 05 November 2002 and between 01 and 10 December 2002, these being characterized by the emissions of greater entity.
The data of the emergency rooms of the sanitary structures of the year in issue were compared to those of same periods of the year 2001. The collected data are the total accesses to the emergency rooms of the aforesaid hospitals in the studied periods and from the accesses subdivided for attributable pathologies, etiologically, to the volcanic ash. In consideration of the existing differences between accesses of the year 2002 with those of the year 2001, on these data a statistic elaboration was carried out to verify the significance of the differences. The statistical tests used were Chi-Square(c^2) and "Z test": both the tests were in agreement as can be seen in Tab. 1 and 2.
Epidemiologic observations, in fact, often find differences in the averages, the frequencies and other characteristics of population groups that are compared. It is also correct to ask if these differences are purely accidental or if they result from real differences of the compared populations: therefore such results were verified with the statistical tests (5).

We used the following tests:
Comparison between frequencies (Chi square)
Comparison between proportions (Z Test)

RESULTS

As can be seen from tables 1 and 2, the differences found in the two periods in observation, relative to correlatable pathologies, were "highly significant" in the sanitary structures that exist in the zone that was principally hit by the cinereous precipitations, with particular reference to pathologies of the upper and lower respiratory tract, cardiovascular pathologies and oculars pathologies.

Table 2a. Period 20/10-05/11/2002

	OVE		**Cannizzaro**		**Garibaldi**	
	Incr. %	Sign.	Incr. %	Sign.	Incr. %	Sign.
acute affections of upper respiratory tract	+2.73	**	+0.17	**ns**	-0.10	**Ns**
acute affections of lower respiratory tract	+1.45	**	+1.24	**	+0.10	**
cardiovascular affections	+1.18	**	+2.99	**	-0.01	**Ns**
Neuro-psychiatric affections	-0.08	**ns**	-0.01	**ns**	+0.17	**Ns**
ocular affections	+2.02	**	-0.60	*	+2.6	**
dermatological affections	+0.2	**ns**	-0.08	**ns**	-0.33	**Ns**
Surgery and orthopaedics	-1.10	**ns**	+4.36	**	+0.06	**Ns**

Table 2b. Period 20/10-05/11/2002

	AUSL 3											
	Giarre		Militello		Acireale		Paternò,		Biancavilla,		Bronte	
	Incr. %	Sig.	Incr. %	Sign.	Incr. %	Sign.	Incr. %	Sign.	Incr. %	Sign.	Incr. %	Sign.
acute affections of upper respiratory tract	+0.2	**ns**	-0.27	**ns**	-4.70	**ns**	-0.15	**ns**	-4.82	*	-0.34	**ns**
Acute affections of lower respiratory tract	+3.11	**	-0.50	**ns**	+0.09	**ns**	-0.32	**ns**	-0.63	**ns**	-0.48	**ns**
cardiovascular affections	+1.7	*	-0.30	**ns**	+7.28	*	+0.56	**ns**			-0.61	**ns**
Neuro-psychiatric affections	+1.17	**ns**			-0.16	**ns**	-0.13	**ns**	+0.07	**ns**	+0.82	**ns**
ocular affections	+0.16	**ns**			-1.83	**ns**	-0.05	**ns**			+0.05	**ns**
dermatological affections	-1.9	**	-0.46	**ns**	-0.472	**ns**	-0.44	**ns**	-0.23	**ns**	-0.15	**ns**
Surgery and orthopaedics	+5.62	*	-0.84	**ns**	-1.52	**ns**	+1.98	**	-2.55	**ns**	+0.68	**ns**

Legend:

** $p<0.01$ highly significant difference

* $p<0.05$ statistically significant difference

n.s. $p>0.05$ no significant difference

Table 3. Period 01/12-10/12/2002

	OVE			Cannizzaro			Garibaldi			OVE, Cannizzaro, Garibaldi - CT		
	Incr. %	"p"	Sign.	Incr. %	"p"	Sign.	Incr. %	"p"	Sign.	Incr. %	"p"	Sign.
Acute affections of upper respiratory tract	-0.092	0.082	**n.s.**	-0.39	0.368	**n.s.**	-0.25	0.261	**n.s.**	-0.24	0.377	**n.s.**
Acute affections of lower respiratory tract	-0.38	0.373	**n.s.**	+0.79	0.308	**n.s.**	+2.77	0.000	**	+0.63	0.033	*
Cardiovascular affections	+0.75	0.059	**n.s.**	-1.71	0.006	**	+2.96	0.000	**	+0.72	0.021	*
Ocular affections	+0.53	0.223	**n.s.**	-0.78	0.168	**n.s.**	+1.05	0.068	**n.s.**	+0.31	0.305	**n.s.**
Surgery and orthopaedics	+0.64	0.294	**n.s.**	+1.31	0.229	**n.s.**	+2.27	0.005	**	+1.09	0.014	*

Legend:
** $p<0.01$ highly significant difference
* $p<0.05$ statistically significant difference
n.s. $p>0.05$ not significant difference

DISCUSSION

In conclusion, from our study it can be seen (table 1) that the differences found in the two periods (20/10-05/11/2001 and 20/10-05/11/2002), relative to correlated pathologies with the studied event, were “highly significant” in the sanitary structures that exist in the zone mainly hit from the cineree precipitations (OVE Company, Cannizzaro, Garibaldi Company), with particular reference to acute pathologies of the upper and lower respiratory tract, to cardiovascular pathologies and ocular pathologies.

The decrease of emergencies in the ER of OVE, for surgical and orthopaedic causes, could be due to the ban of motorcycles in the urban area which the aforesaid hospital Company insisted on. In fact, as can be seen from the data from Cannizzaro Hospital, situated in the periphery, there was a remarkable increase of orthopaedic pathologies, justifiable from traumatic causes related to the presence of ash on the roads.

As far as the Hospitals of the province of Catania are concerned, there is a smaller significance in the difference of the recorded accesses, justified by the atmospheric conditions that were not so great. With the exception of Giarre Hospital, in which the accesses for acute affections of lower respiratory tract are highly significant.

In the second period (table 2) taken in examination in our study (01/12-10/12/2001 and 01/12-10/12/2002), characterized by a decrease in intensity of the cinereous emissions, only the “statistically meaningful” differences concerning

the accesses for acute of the deep respiratory feature, cardiovascular and traumatic pathologies are recorded.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

INDOOR AIR QUALITY - CHEMICAL POLLUTANTS

I Senitkova*

ABSTRACT

Numerous scientific studies show that indoors are the source of potentially harmful substances called indoor air pollutants. They come from various sources. Selected indoor chemical pollutants concerning to indoor air quality, their sources and health effects are introduced in this paper. Indoor levels are often much higher than outdoor levels and most people spend the bulk of their time indoors. As indoor air pollution is a relatively new problem, health and comfort problems are associated with it. Buildings may cause numerous symptoms commonly referred to as the Sick Building Syndrome. The starting point for studies on constituents of the indoor environment is to realize that the problem to be solved is complex. Facing the number and variety of physical, chemical and biological pollutants in indoor environment we urgently need strategies to distinguish severe from less severe health hazards. In this paper indoor air chemical pollutants in East Slovakia are presented, although it has not yet been determined how the various substances effect human beings when they interact. Main groups of chemical pollutants as radon, nitrogen oxides and formaldehyde were subjects of our special interest. Our interest has been pointed to indoor chemical concentrations from indoor air quality creation point of view.

INDEX TERMS

Indoor air quality, radon, formaldehyde, nitrogen oxides, guidelines

INTRODUCTION

Indoor environmental problems have five common causes, and more than one may be active at any time: an inadequately cleaned or maintained environment,

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insufficient ventilation, pollutants emitted from sources and activities inside the building, contamination from outside sources, and biological contamination due to a lack of moisture control. These causes can often intensify or add to the stress that occupants suffer from inadequate temperature, humidity, or level of indoor chemical pollutants. The inadequately maintained environment is the consequence of insufficient attention to different emissions and by-products of activities indoors. Poor ventilation sometimes is the result of dirty air filters that need periodic cleaning or replacement. Emission from cooking or tobacco products always need to be removed. Left alone, they accumulate, causing odors, and in some cases increasing cancer risks to humans. They need to be removed through cleaning and maintenance. Before energy crisis, most buildings were designed to provide maximum comfort to inhabitants. Heating, ventilating, and air conditioning systems were designed to provide fresh outside air for each building occupant. Later, buildings have been designed to save energy. The size of indoor space heated or cooled have been reduced, and outdoor air ventilation lowered. Moreover, many ventilation systems do not effectively distribute air to people in buildings. Inadequate air diffusion combined with reduced ventilation causes pollution levels to grow, and as pollutant concentrations rise so do health complaints. As already discussed, many indoor pollutants come from sources inside the building, while others may enter the building with outdoor air or from the soil.

INDOOR CHEMICAL POLLUTANTS

Poor quality indoor air is believed to be responsible for a substantial part of the sick building syndrome that has been reported, but the indoor environment is extremely complex and other factors also undoubtedly contribute to the problem. Thermal conditions, such as temperature and humidity, microbial agents such as dust mites and chemical pollutants can produce sick building syndrome symptoms in the indoor of buildings. The term sick building syndrome has come into vogue during the past several years and refers to a range of occupant complaints and illnesses. Classification of health effects of indoor air pollution is possible to introduce from comfort point of view. The cause of sick building syndrome remains unknown, although it is likely that there are connections between psychological factors, inadequate ventilation and the level of hygiene in the building. Factors identified as possible causative agents are briefly summarized as temperature, humidity, odors, volatile or semi-volatile organic compounds, radon, nitrogen oxides, ozone, fibers, etc. The sick building syndrome is significantly related to the total concentration of indoor chemical constituent and the sick building syndrome symptoms are more common in building construction environment without mechanical ventilation. It is evident that there is a need to increase the outdoor air supply to the indoor of buildings in order to minimize the exposure to indoor pollutants that may induce symptoms compatible with sick building

syndrome. Furthermore, building materials, building construction and indoor activities should be selected on the principle of the best possible indoor air quality according to the lowest reasonably achievable concentrations of negative agents. A draft of indoor air quality (IAQ) management guidance notes in Slovakia which are continuously worked out at Environmental Engineering Department, is concerned with twelve IAQ and thermal comfort based parameters. Temperature, relative humidity and air movement are identified as a factors affecting thermal acceptability. Carbon dioxide (CO_2), carbon monoxide (CO), nitrogen dioxide (NO_2), ozone (O_3), formaldehyde (HCHO), total volatile organic compounds ($TVOC_s$), radon (Rn), respirable particles $PM_{2,5}$, airborne bacteria are the other nine parameters listed in recommended IAQ objectives for indoor living spaces. These nine parameters more or less represent the air contaminants from building materials, human activities, indoor equipment, HVAC systems and pollutants from the outdoor environment. Table 1 lists the IAQ parameters, their suggested limits and overall range of average values (Senitkova, 2002b).

Table 1. Recommended IAQ limit values and ranges of averages

Parameter	**Unit**	**Limit**	**Range of average**
Carbon dioxide (CO_2)	$\mu g/m^3$	1 800	1 134 - 2 238
Carbon monoxide(CO)	$\mu g/m^3$	2 000	1 081 - 2 800
Nitrogen dioxide (NO_2)	$\mu g/m^3$	100	28 - 153
Ozone (O_3)	$\mu g/m^3$	50	31 - 58
Formaldehyde (HCHO)	$\mu g/m^3$	60	35 - 167
Total volatile organic compounds ($TVOC_s$)	$\mu g/m^3$	200	180 - 736
Radon (Rn)	Bq/m^3	200	118 - 199
Respirable suspended particles (RSP)	$\mu g/m^3$	20	17 - 63
Airborne bacteria	KTJ/m^3	500	198 - 560
Room temperature	^oC	20 - 25	19 - 26
Relative humidity	%	40 - 60	29 - 73
Air movement	M/s	0,2	0,03 -0,18

Carbon dioxide is commonly an indicator of air freshness and bio-effluent. The pollutants CO and NO_2, when found, may be ambient pollution and result from vehicle exhaust fumes entering the building from the street outside. Levels of CO, NO_2 and RSP were studied and found to be high especially during gas cooking and tobacco smoking (Senitkova 1996, Zimermannova 2000, Stevulova 2000a). Indoor O_3 accumulates in the spaces where the fax machines, photocopiers and laser printers are located, and is found in substantially high concentrations near the sources.

Many building materials and fabrics, cleaning fluids and adhesives emit a lot of unwanted VOC_s and formaldehyde indoors. VOC_s and other pollutants from outdoor sources may also enter the building through ventilation or through the building envelope by infiltration. A lot of measurements were done in this area (Senitkova 1998, 1999, Stevulova 2000b). Radon is particularly important for the scenario of East Slovakia because of underlying soil and building materials, which have the potential for high radon emission and are widely used for building. In buildings which are not well ventilated the emitted radon will be trapped and accumulate (Senitkova 1999, 2000a, 2000b). Moisture and condensation in buildings can act as breeding grounds for harmful bacteria. From the point of view of comfort and health, based on thermal acceptability and satisfaction with IAQ, the 12 parameters selected more or less comprehensively cover the situation.
Table 2. introduces the limit values for indoor environment according to Slovak standard concerning to indoor chemicals, particular matters, and biological factors which are valid from July 2002. Some approaches and limit values can be discussed. The traditional way of material selection for building design/construction has been primarily based on factors such as cost, aesthetic values, availability and/or durability. The environmental impact (both on the environment and occupants) has not been

Table 2. Limits interpreted as average values in determined time period

Parameter	**Unit**	**Limit**	**Period**
Carbon monoxide(CO)	$\mu g/m^3$	10 000	8 hours
Particles PM_{10}	$\mu g/m^3$	50	24 hours
Nitrogen dioxide (NO_2)	$\mu g/m^3$	100	24 hours
Ozone (O_3)	$\mu g/m^3$	120	8 hours
Sulfur dioxide (SO_2)	$\mu g/m^3$	125	24 hours
Formaldehyde (HCHO)	$\mu\mu g/m^3$	60	24 hours
Ammonia (NH_3)	$\mu\mu g/m^3$	200	24 hours
Toluene (C_7H_8)	$\mu g/m^3$	8000	24 hours
Xylene ($C_4H_4(CH_3)$)	$\mu g/m^3$	4800	24 hours
Styrene (C_8H_8)	$\mu g/m^3$	800	24 hours
Tetrachloroethylene (C_2Cl_4)	$\mu g/m^3$	250	24 hours
Carbon disulfide (CS_2)	$\mu g/m^3$	100	24 hours
Sulfane (H_2S)	$\mu g/m^3$	150	24 hours
Asbestos (*fibre length to diameter ratio 3:1*)	$Fibres/m^3$	1000	
Airborne bacteria	KTJ/m^3	500	Medium

addressed till very recently. Evidence from a variety of building investigations and studies suggest that many of the materials used in buildings, either as structural materials or as furnishings, are the main source of indoor air pollution. These sources of pollution have been recognised in the ventilation standard (ASHRAE 1999), which requires that the ventilation rate specification should be based on the contribution from building materials and equipment as well as occupants. Material emissions are often the result of several mass transport processes. Interactions of these processes commonly occur and their effects on material emissions are complex. With regard to toxicity, radon, formaldehyde and nitrogen oxides as major components constitute the non-occupational indoor air pollutants with greatest risk to human health because of both frequent exposure and probable health effects. In contrast, risks by other well-known indoor air pollutants were assumed to be lower. On the base of our measurements it is possible to assume that exposures exceeding standards will be obtained in more than 50 % buildings for radon, formaldehyde, VOC, particles or nitrogen oxides (Senitkova 1997, 2000).

Radon

All buildings are polluted to some extent with radon but in certain geographical areas the proportion of radon from the soil is much greater than elsewhere. Depending on the building design and particularly on how they are vented and heated, radon and its decay products may be trapped within buildings and accumulate in them. Radon is one of the rare examples of agents which leads to scientifically accepted health effects under environmental exposure situations. Until now there is no general consensus on what risk level might constitute a health hazard. Radon obtains one of the highest priority in ranking of selected indoor chemical pollutants in several parts of Slovakia. According to our measurements, Slovak Standard level for indoor radon (200 $Bq.m^{-3}$) was exceeded in 57 % of indoor spaces. The average measured values of radon levels at the different buildings were consistent with the type of underground construction, building material and ventilation strategies. The range of average values calculated from all rooms included in the study (118-199 $Bq.m^{-3}$) was near the standard level. On the other side the previous limit level 100 $Bq.m^{-3}$ was exceeded much more. It is necessary to say that standard limiting value need not be conceived as a limit value, but upper value of optimizing alternatives, which should lead in practice to as low levels as possible.The radon concentration in atmospheric air was between 5 - 15 $Bq.m^{-3}$ (Senitkova 1999, 2000a, 2000b, 2001a).

Formadehyde and other VOC

Numerous volatile organic compounds have been detected in indoor air. They arise from the use of adhesives, building materials, cleaning agents, cosmetics, furnishings, paints and cigarettes. A few VOCs, which are recognized hazards, occur environmentally at levels at which it is believed they constitute a risk to health. Principal among these are benzene and formaldehyde. However, none have attracted as much attention as formaldehyde, and common sense suggests that

formaldehyde really cause serious problems to health. Apart from the theoretical risk of cancer, the main problem with formaldehyde is that people may become sensitive to it and suffer from asthma when exposed to it. In Slovak indoor environment we have measured average values between 35 and 167 $\mu g.m^{-3}$. $TVOC_s$ range of average concentration was 180 - 736 $\mu g.m^{-3}$. Limit value for indoor formaldehyde 60 $\mu g.m^{-3}$ or TVOC 200 $\mu g.m^{-3}$ was generally exceeded in 52 % of indoor environments investigated. Frequency of the exposure is increased and possible health effects are expected. Most of the studies and health effects described so far are due to single compounds. In reality people are exposed to mixtures but we still do not know detailed toxicology about it. In conventionally built homes without proper insulation, air change between the inside and outside is sufficient to vent out the formaldehyde and other VOC_s escaping the materials. Concentrations of formaldehyde, toluene and benzene indoors were much higher than concentrations outdoors. In air tight homes the turnover is much slower. The tighter and better sealed a house is, the greater the concentration of VOC_s unless special precautions are taken to avoid products containing these harmful substances. It would seem to be best solution to exclude these materials from the use in building constructions and replace them by those which are more favourable for healthy living indoors (Senitkova 1998,1999, Stevulova 2000b).

Nitrogen oxides

Nitrogen monoxide and nitrogen dioxide are mainly produced by combustion at high temperatures. Both nitrogen in the fuel and nitrogen in the air participate in reactions, NO is further oxidised into NO_2 in the atmosphere. Nitrogen dioxide is the most toxic of the nitrogen oxides and is the most important from view-point of health. People are mainly exposed to indoor nitrogen oxides. Indoor air can be polluted by the use of gas for heating, and cooking appliances. The most important indoor source of nitrogen oxides is gas burning in the kitchen. The other reason of increasing indoor exposure level is environmental tobacco smoke. Nitrogen oxides as chemical pollutant with increased frequency of exposure and possible health effects were also classified as indoor pollutant of high priority. Limiting value for indoor NO_x concentrations was considered to be 100 $\mu g.m^{-3}$, and this value was exceeded in 54 % of buildings. Nitrogen oxides range of average measured concentrations was 28 - 153 $\mu g.m^{-3}$. The problem becomes serious in a short time exposure resulting from combustion and this probably involves a certain health risk. Numerous measurements were done in order to describe indoor concentration levels associated with cooking (Senitkova 1996, 2000c).

CONCLUSION

Due to the need to implement an IAQ management scheme, a research team from Civil Environmental Engineering Department of Kosice Technical University want to carry out a pilot study on the feasibility of IAQ assessment by these IAQ and

thermal comfort parameters in the buildings premises. This paper lists the IAQ parameters, their limits and overall range of average values concerning to indoor air environmental auditing. A lot of buildings covering different types of premises were examined. High concentrations of chemicals were found that made a building unable to meet sustainable indoor environment. This measurement study has also illustrated the very different nature of IAQ found in different types of buildings where the indoor air pollutant sources can influence it substantially.

Analysis of the results shows that there exist some differences of indoor chemical exposure in winter and summer period. Whereas for VOC_s concentration the values are higher in summer time, for radon and nitrogen oxides the situation is usually different. The average concentrations of indoor nitrogen oxides and radon are higher in winter period than in summer what is caused by decreasing of air change level. Indoor concentrations of formaldehyde are higher mostly during the summer especially when the temperature of building structure surface is higher. The problem of sick building syndrome is significantly related to the total concentration of indoor chemical constituent. Indoor climate problems are more common in building construction environment without mechanical ventilation. It is evident that there is need to increase the outdoor air supply in the indoor of buildings, to minimize the exposure of indoor pollutants that might induce symptoms compatible with sick building syndrome. Furthermore, building materials, building constructions and indoor activities should be selected on the principle that the level of indoor air should be of the best quality or the concentration of negative agents should be as low as reasonably achievable. Creative approaches of civil engineers and designers can in the large scale influence indoor air quality. The problems concerning indoor environment in Slovak republic seems just as complicated as anywhere else. In many respects our problems seem very similar or even identical to those elsewhere. Consequently, any exchange of experiences in at least some selected areas would really be of mutual help.

Indoor climate problems are more common in building construction environment with insufficient ventilation. It is evident that there is need to increase the outdoor air supply in the indoor of buildings, to minimize the exposure of indoor pollutants. Furthermore, building materials, building constructions and indoor activities should be selected on the principle that the level of indoor air should be of the best quality or the concentration of negative agents should be as low as reasonably achievable. There are two classical approaches to reach a required level of indoor air quality in terms of pollutants. One is by dilution and other is by source control. Nowadays it seems that dilution is still the more accepted approach. It is the way of obtaining better air quality.

ACKNOWLEDGEMENTS

The authors are grateful to the Grant Agency of Slovak Republic (project No. 1/0352/03).

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

AIRBORNE FLUORIDE CONTAMINATION OF SOIL AND VEGETATION

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ABSTRACT

The damaging effects of low concentrations of airborne fluorides are related to their uptake and accumulation, mainly in plant leaves. The uptake depends on the concentration and composition of fluoride in ambient air and the duration of exposure, on vegetation structure, plant species and growth conditions. This paper describes the accumulation of fluoride in Scots pines (Pinus sylvestris), olive trees and soil located near an aluminium plant, which was destroyed during the aggression on Croatia in 1991. Samples were collected from seven sites - including one reference site in an unpolluted area - in spring and autumn over six-years (1996-2001). Fluoride levels ranged from 0.63 to 80.66 μg F^-/g dw in soil, from 2.14 to 31.10 μg F^-/g dw in Scots pines, and from 1.50 to 14.10 μg F^-/g dw in olive trees. Statistical analysis showed that there were no significant differences in the fluoride content between spring and autumn.

INDEX TERMS

Airborne fluoride, Phytotoxic air pollutants, Soil contamination.

INTRODUCTION

Gaseous fluorides, particularly hydrogen fluoride, are among the most phytotoxic air pollutants and have been a threat to vegetation on a local or regional scale in the

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highly industrialised countries (Klumpp, Domingos, and Klumpp G, 1996). Relatively few studies have been directly concerned with the effects of fluoride-containing particles on plants, and it has been generally assumed that this form of airborne fluoride is much less phytotoxic than the gaseous. Most particulate fluorides (cryolite, calcium fluoride, sodium fluoride) are stable compounds that do not hydrolyze readily with vapour in the atmosphere. Therefore, their removal from the atmosphere is controlled by dry and wet deposition. Climatic conditions are important in determining the effects of deposited particulate emissions on plants and animals. Light rains may deposit fluorides from the atmosphere on vegetation whereas heavy rains may partially wash off fluoride dusts from vegetation to soil. In arid regions, the dusts may accumulate on vegetation and be ingested by grazing animals. In areas of heavy precipitation, plants may take up washed-off fluorides from the soil. It has been estimated that > 90% of natural fluoride in soil is insoluble or tightly bound to soil particles. The mobility of fluorides in soil is enhanced if the solubility of fluorides is increased, either by increased acidity or by formation of soluble complexes. This study addresses the accumulation of fluoride in two plant species (Pinus sylvestris and olive trees) and in the soil in the vicinity of aluminium reduction plant, which was destroyed during the aggression on Croatia. Until the war the production of aluminium was 75.000 tons per year and emission of fluorides 17 kilograms per ton.

METHODS

Research was carried out during two seasons (spring and autumn) from 1996 to 2001. The monitoring stations were established 0.43-4.50 km from the emission source (Kalinić, Vađić, Hršak et al., 1997). The content of fluoride was measured in leaf samples and soil at five sites in polluted area, at one control vegetation site and two control soil sites in the control area (Figure1). Distance (km) and direction of sampling sites from the emission source are shown in Table 1.
Leaf samples were picked one by one at a height of 1.5-2m from all sides of the tree. Because of aging/accumulative effect all basal and terminal leaves were

Table 1. Distance (km) and direction of sampling sites from the emmission source

Sampling site	Distance	Direction
A	4.50	N-NW
B	0.43	NE
C	1.87	N
D	1.90	NW
E	2.33	W-SW
K	54.28	W
K1	38.65	N-NW



Figure 1. Location of measurement sites

avoided. Attention must be paid to cut the samples at the same length because the fluoride content in the different parts of the plants varies (Vike and Håbjørg 1995, Giertych, De Temmerman, and Rachwal, 1997). The mass concentration of fluoride in leaves was determined as sum of fluoride present as dust on the plant and fluoride in the plant. In this case the samples are not washed (Komers, 1976). The sample leaves were put into paper bags, dried in a drying oven at 105 °C (app. 15 hours), milled and analysed for fluoride by potentiometric method (NIOSH, 1977). The soil samples were collected at depth 0-10 cm (Hršak, Fugaš, and Vađić, 2000) and dried at 105 °C. Ten grams of soil samples were shaken for

24 hours at the room temperature with 20 cm^3 of redistilled water. The fluoride concentrations in soil extract was determined by the potenciometric method (NIOSH, 1977, Arnesen, Abrahamsen, Sandvik et al., 1995).

RESULTS

The fluoride content in Pinus sylvestris and olive trees in different seasons is shown in Figures 2 and 3. The levels of fluoride in soil are shown in Figure 4 and average fluoride concentrations and difference between the measuring periods are shown in Table 2.

Table 2. Statistical parameters of measured mass concentrations of fluoride during the whole measuring period

Statistical	Soil (μg/g)		Olive trees (μg/g dw)		Pinus sylvestris (μg/g dw)	
parameters	Spring	Autumn	Spring	Autumn	Spring	Autumn
N	40	40	11	11	35	35
Cmin	0.63	0.31	2.1	0.8	2.1	1.8
Cmax	61.8	80.7	12.6	14.1	31.1	22.6
C	10.6	11.7	5.71	5.72	11.9	9.5
STD	12.6	15.77	2.96	4.07	7.84	5.20
SE	1.994	2.494	0.893	1.227	1.326	0.879
t	0.3418		0.0036		1.4310	
P	>>0.05		>>0.05		>0.05	

N - number of samples
C_{min} - minimum value
C_{max} - maximum value
C - arithmetic means
STD - standard deviation
SE - standard error

Statistical analysis showed that there were no significant differences in the fluoride content between springs and autumn neither for vegetation, nor for soil.

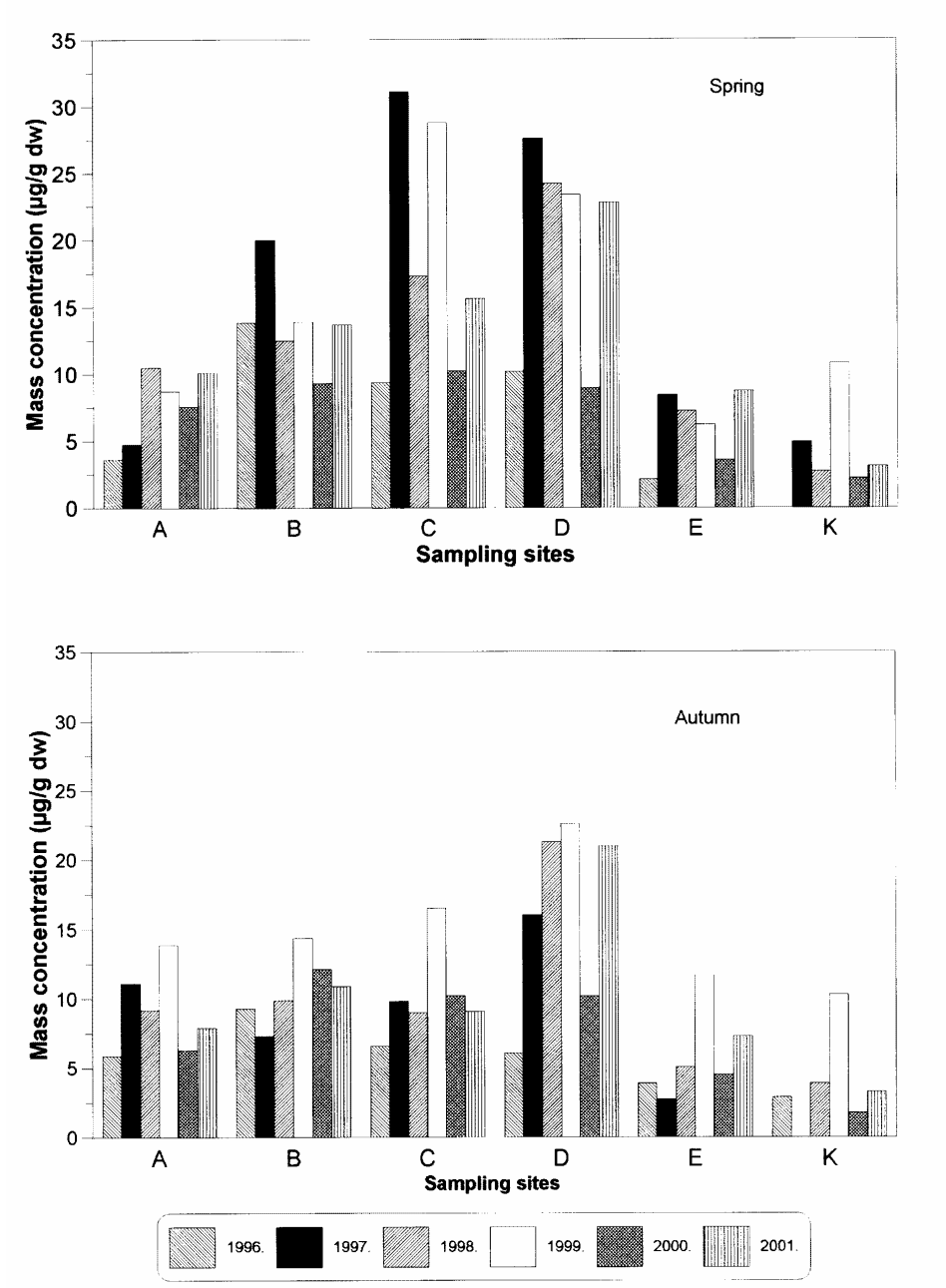

Figure 2. Fluoride in Pinus sylvestris

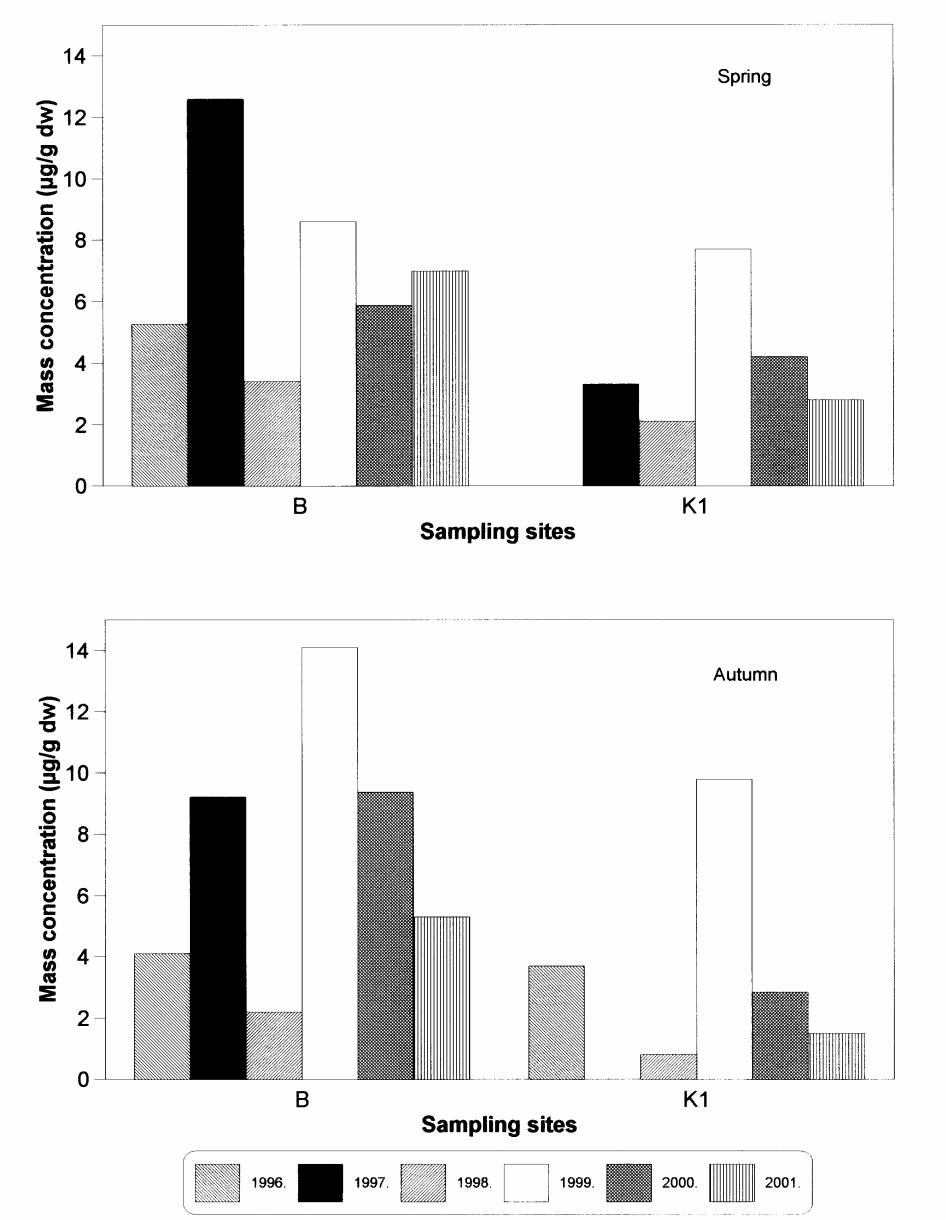

Figure 3. Fluoride in Olive trees

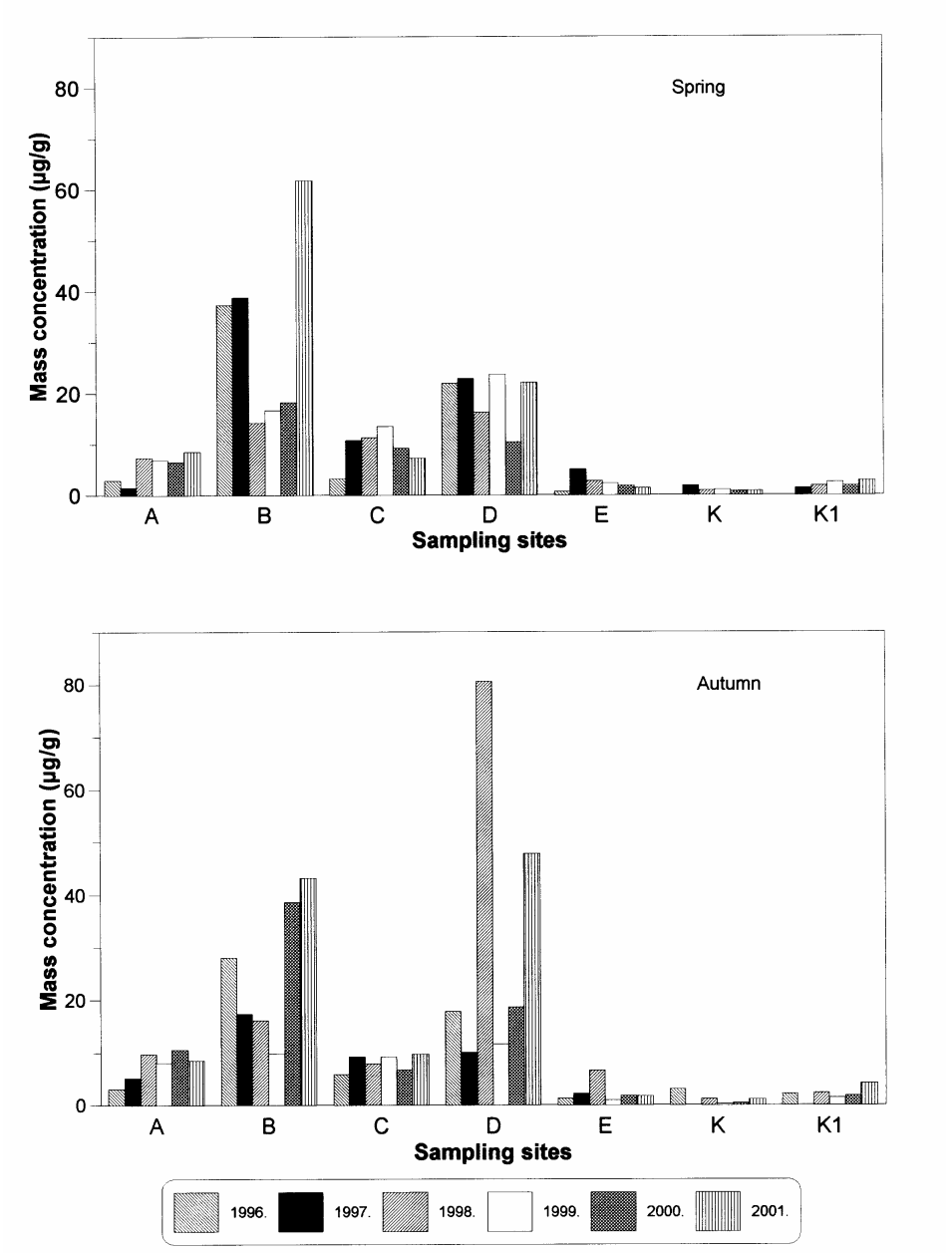

Figure 4. Fluoride in soil

DISCUSSION

The normal fluoride content of leaves has been subject of considerable disagreement, but it generally ranges from 2 to 20 μg/g on a dry weight basis (NAS, 1971). It will vary with the species (and even the variety) of plant, the age of the leaf, characteristics of the soil, use of fertilizer, irrigation etc. (Zimmermann et al., 2000). This "background" fluoride is derived mostly from the soil, which normally contains from 20 to 500 μg/g. A comparison of the values obtained in this study with recommendations in the literature (WHO, 1971,Van der Eerden, 1991) showed that fluoride concentrations were exceeded in seven samples of Pynus sylvestris in the spring and three samples in the autumn. Mass concentrations of fluoride in olive trees and in the soils were relatively low.

CONCLUSION

The both plant species used in the present study proved to be adequate bioindicators of airborne fluoride, as the dominating species in areas with high and long exposure to fluoride pollution. The monitoring of fluoride in the same species and in the soil at the same sampling sites has continued and the results will be compared.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

AIRBORNE FUNGI IN NATURALLY VENTILATED AND AIR-CONDITIONED INDOOR SPACES AND OUTDOOR AIR IN ZAGREB (JUNE, 2002)

M Šegvić*, Z Cvetnić and S Pepeljnjak

ABSTRACT

Airspora of several fungi are known to induce numerous human diseases such as chronic bronchitis, asthma, fungal allergies, hypersensitivity pneumonitis and aspergillosis. Research was carried out on the presence and variation in occurrence of airborne fungi in naturally ventilated houses (N=50) and apartments (N=50), air-conditioned buildings (N=50), and outdoor air (N=50) in Zagreb (June, 2002). Samples were collected using Air-sampler Mas 100 Eco (air flow rate 100 L/min) and Sabouraud agar plates. Samples were incubated at 25°C±2, 5-7 days. The data obtained as colony forming units in cubic meter (CFU/m^3), were statistically analysed by a one-way analysis of variance (repeated measures ANOVA) followed by a multiple comparison procedure (Bonferroni test). The Pearson correlation coefficients between the CFU/m^3 in the indoor and outdoor samples were also analysed. Probability values less than 0,05 ($P<0,05$) were considered significant. The significantly higher airspora concentrations were found in naturally ventilated houses (275,60 CFU/m^3) and apartments (186,20 CFU/m^3), and outdoor air (277,10 CFU/m^3), than in air-conditioned buildings (49,06 CFU/m^3) ($P<0,001$). Airspora belonging to 16 fungal genera were identified, and allergologicaly significant fungi, *Cladosporium, Penicillium, Alternaria*, and *Aspergillus* were dominating in all sampling sites. *Cladosporium, Penicillium* and *Alternaria* was found in significantly lower concentrations in air-conditioned buildings then in other sampling fields ($P<0,05$). Air-conditioned systems, which are well-designed and well-maintained, can prevent and reduce the airspora indoor concentrations.

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INDEX TERMS

Airborne fungi, Fungal allergies, Aspergillosis, Air-conditioning, Outdoor air

INTRODUCTION

Fungi are ubiquitous microorganisms that can be found as saprophytes or parasites on different substrata and from there they pervade outdoor and indoor air. Airspora concentration of outdoor and indoor environment depends on few factors: seasonal and daily variations, climatic factors (temperature, humidity, wind, rainfall, vegetation), air pollution, agricultural, industrial and other human activities (Horner et al., 1995). Ventilation and air-conditioning of indoors is widespread nowadays, and include various components such as filters, humidifiers, cooling and warming system. These systems sometimes have certain risk factors including low efficiency filters, stagnant water condensation, and deficient maintenance conditions. Thus, airspora can concentrate and spread indoors (Parat et al., 1997). Exposure to airborne fungi is sometimes associated with several respiratory diseases such as chronic bronchitis, asthma, fungal allergies, hypersensitivity pneumonitis and aspergillosis (Horner et al., 1995). Therefore, the purpose of this study was to determine composition and concentrations of airborne mycoflora in naturally ventilated houses and apartments, air-conditioned buildings and outdoor air in Zagreb (June, 2002).

METHODS

Sampling sites

The study was conducted in Zagreb area in June (2002). A total of 200 samples were collected. Field measurements were conducted at 10 apartments (N=50), 5 houses (N=50), 5 air-conditioned buildings (N=50), and outdoors (N=50).

Sampling, isolation, and identification methods

Fungi were sampled using Air-sampler Mas 100 Eco (Merck) (hole-to-agar impactor), with 400 holes, and Sabouraud agar plates (9 cm diameter) with antibiotic streptomycin (50 mg/L). Air flow rate is 100 L/min. The sampling height was 70 cm-1,2 m, and sampling time was set for 2 min. After the field sampling, the plates were incubated at $25^{o}C \pm 2$ for 5 days, and colony forming units in cubic meter (CFU/m^3) were counted. The fungi were identified morphologically after subculture on Sabouraud, Czapek, Malt or Potato dextrose agar according to keys (Raper and Thom, 1949; Booth 1971; Samson et al., 1981; de Hoog et al., 2000).

Statistical analysis

The data obtained as CFU/m^3, were statistically analysed by a one-way analysis of variance (repeated measures ANOVA) followed by a multiple comparison procedure (Bonferroni test). The Pearson correlation coefficients between the

CFU/m^3 in the indoor and outdoor samples were also analysed. The level of P<0,05 was considered statistically significant for all tests performed.

RESULTS

The mean, standard deviation (SD) and range (min-max) concentrations of airborne viable fungi are given in Table 1 for each sampling site. The concentrations of airborne moulds were significantly higher in AP, H, and OA than those found in ACB (P<0,001). Also, concentration of airborne moulds in H and OA was significantly higher than in AP (P<0,05). Significant correlation between outdoors and indoors was not found (P>0,05). Concentrations of yeasts were significantly higher in AP and H than in ACB and OA (P<0,05). Significant correlation was found between AP, H and outdoor environment (P<0,05).

Table 1. Concentrations of viable airborne fungi in outdoor and indoor sampling sites in Zagreb (June, 2002)

Sampling sites	*N of samples*	*N of moulds (CFU/m^3)*		*N of yeasts (CFU/m^3)*	
		Range	*Mean±SD*	*Range*	*Mean±SD*
Apartments (AP)	50	0-355	186,20±80,66	0-465	105,30±100,30
Houses (H)	50	5-970	275,60±246,60	0-255	80,80±61,06
Air-conditioned buildings (ACB)	50	0-190	49,06±49,73	0-195	42,00±46,90
Outdoor air (OA)	50	50-755	277,10±154,8	0-175	43,10±41,38

Airspora belonging to 16 fungal genera and nonsporulating "sterile mycelia" were identified (table 2). The most abundant were *Cladosporium*, *Penicillium*, *Alternaria*, and *Aspergillus*, in all sampling environments. Other moulds identified were found in lower concentrations (0-2,8 CFU/m^3), with exception of *Chrysosporium* that was found in higher concentration in AP (5,3 CFU/m^3), than in other sampling fields. *Aspergillus* genera was represented with 7 species and *Aspergillus* sp. Between them *A. fumigatus* and *A. niger* were the most frequent; with highest concentration in H (2,8 CFU/m^3), and OA (2,4 CFU/m^3). Other aspergilla were present in concentrations lower than 1 CFU/m^3 in all sampling sites.

The concentration of *Cladosporium* (Figure 1) was significantly higher in OA (221,80 CFU/m^3), H (212,90 CFU/m^3), and AP (136,30 CFU/m^3), than in ACB (32,70 CFU/m^3) (P<0,01). In AP concentration of cladosporia was significantly lower than in H and OA (P<0,05). Significant correlation between *Cladosporium* concentrations in outdoors and indoors was not found (P>0,05). Lower concentrations of *Penicillium* (Figure 2) were found in OA (15,60 CFU/m^3) and ACB (8,00 CFU/m^3) than in H (32,60 CFU/m^3) (P<0,05). Between penicillia concentrations in H and AP (21,80 CFU/m^3) and among other groups, significant difference was not found (P>0,05). Significant correlation was found between

Table 2. Abundance of airborne fungi in outdoor and indoor air in Zagreb (June , 2002)

FUNGI	AP CFU/m^3	H CFU/m^3	ACB CFU/m^3	OA CFU/m^3
Absidia	0,3	1,1	-	0,4
Acremonium	-	1,3	-	2,8
Alternaria	7,8	11,5	3,1	21,7
Aspergillus	2,9	6,0	2,0	3,3
A. flavus	0,1	1,5	0,1	0,3
A. fumigatus	0,9	2,8	0,9	0,4
A. glaucus	-	-	0,1	-
A. lutescens	-	-	0,1	-
A. niger	0,7	1,1	0,1	2,4
A. ochraceus	0,3	0,1	0,2	-
A. versicolor	-	-	0,1	-
Aspergillus sp.	0,9	0,5	0,4	0,2
Chrysosporium	5,3	0,6	0,1	0,4
Cladosporium	136,3	212,9	32,7	221,8
Culvularia	-	-	0,3	0,1
Fusarium	2,8	0,8	0,3	2,8
Mucor	-	0,4	-	0,2
Paecilomyces variotii	0,3	-	2,2	-
Penicillium	21,8	32,6	8,0	15,6
Phoma	2,1	0,1	0,1	-
Rhizopus	0,2	0,2	-	0,1
Sclerotium	-	0,3	-	0,1
Sterile mycelia	0,9	0,2	-	0,4
Trichoderma	-	-	0,2	-
Ulocladium	0,4	1,8	-	2,3
other moulds	1,9	6,7	0,7	3,4

"-" not detected

Penicillium concentrations in H and OA. The concentration of *Alternaria* (Figure 3) was highest in OA (21,70 CFU/m^3) comparing to H (11,50 CFU/m^3), AP (7,80 CFU/m^3) and ACB (3,10 CFU/m^3) ($P<0,01$). Between *Alternaria* concentrations in H and AP, also AP and ACB, significant difference was not found ($P>0,05$).

Airborne *Aspergillus* was found with lowest concentration in ACB (2,00 CFU/m^3) and highest in H (6,00 CFU/m^3), but significant difference was not found comparing sampling fields. Also, there were no significant correlations between outdoors and indoors *Alternaria* and *Aspergillus*.

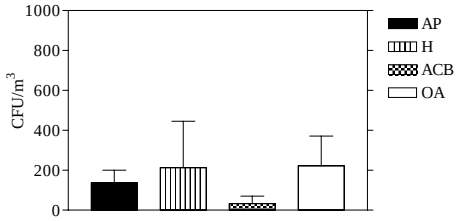

Figure 1. Concentration of *Cladosporium* in the indoor and outdoor air

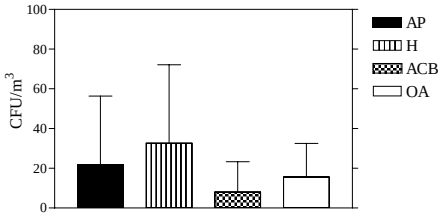

Figure 2. Concentration of *Penicillium* in the indoor and outdoor air

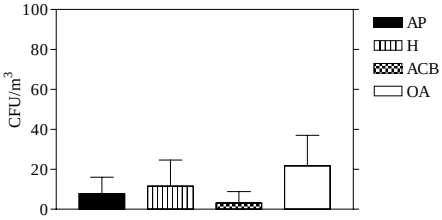

Figure 3. Concentration of *Alternaria* in the indoor and outdoor air

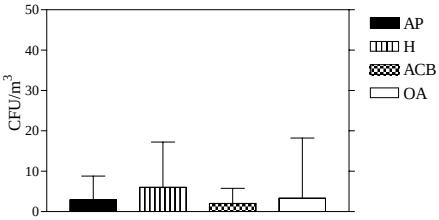

Figure 4. Concentration of *Aspergillus* in the indoor and outdoor air

DISCUSSION

Indoor air and outdoor air are the complex environmental systems influenced by physical, chemical and biological factors. Qualitative and quantitative airborne mycoflora composition can have impact on human health since many of airborne fungi are known to induce several respiratory diseases (chronic bronchitis, asthma, fungal allergies, hypersensitivity pneumonitis and aspergillosis) (Horner et al., 1995). In our study the dominant moulds recorded indoor and outdoor were allergologicaly significant species: *Cladosporium*, *Penicillium*, *Alternaria* and *Aspergillus*, which is in agreement with other studies (Asan et al., 2002; Chih et al., 2000; Cvetnić and Pepeljnjak, 2001; Parat et al., 1997; Pepeljnjak and Šegvić, 2003). These moulds can cause allergic response via spores or mycelium structures. Tilak (1991) estimated that between 2 and 30% of respiratory allergies are due to fungal spores, and cited *Alternaria* and *Cladosporium* as producing the highest number of allergies. The studies that have been taken among asthmatic children reported prevalence of reactivity to *Cladosporium* (31-37%) and *Alternaria* (14%) (Croner and Kjellman, 1992). Spores, mycelium and sclerotia can also contain mycotoxins. Mycotoxin formation and accumulation in the spores are influenced by sporulation rate, temperature and water activity, particularly in the case of

Aspergillus, which can form afltoxins in spores and sclerotia (water activity ≥86, temperature ≥ 18^{0}C) (Vujanovic et al., 2001). In our study, qualitatively, airborne mycoflora is roughly similar inside and outside, which confirms the influence of the outdoor mycoflora composition on the indoor air. Very high concentrations of airborne fungi recorded especially in the naturally ventilated houses (275,60 CFU/m^3) and outdoors (277,10 CFU/m^3) were due to a high incidence of *Cladosporium* (66,65%-80,03%), which showed highest peak in spring and summer in many aerobiological studies (Asan et al., 2002; Chih et al., 2000; Cvetnić and Pepeljnjak, 1997; Parat et al, 1997, Sarica et al., 2002; Pepeljnjak and Šegvić, 2003). These concentrations are more or less the same in houses and outside. In naturally ventilated apartments fungal concentration (186,20 CFU/m^3) was significantly lower suggesting that influence of outdoor concentration on the level of indoor fungi is less for apartment type, probably because of lower air exchange rate (Chih et al., 2000). In air-conditioned buildings we found the lowest concentration of airborne fungi (49,06 CFU/m^3), which must be due to a special filters that stopped most spores. On the other side, greater variety of *Aspergillus* species was recorded in air-conditioned buildings, even the concentration of airborne aspergilla was lower (but not significantly) than in other sampling environments. It is well known that low efficiency filters, stagnant water and dust of air-conditioning systems can increase counts of indoor moulds and their sporulation, which increase risk of exposure to mycotoxin (Vujanovic et al., 2001), especially in the case of aspergilla. This study demonstrates that compared to naturally ventilated houses and apartments, the air-conditioning systems, which are well designed and well maintained can improve air quality of indoors.

CONCLUSION

The significantly higher levels of airborne fungi were found in naturally ventilated houses and apartments and outdoor air, compared to air-conditioned indoors. Very high concentrations of airspora found in naturally ventilated indoors and outdoors, were due to high levels of *Cladosporium*, which was the most dominant mould species in all sampling sites. In air-conditioned indoors lowest levels of airborne fungi were recorded, which suggests that proper design and maintenance of these systems can prevent and reduce airspora concentrations and decrease risk of fungal respiratory allergies.

ACKNOWLEDGEMENTS

This work was supported by the Croatian Ministry of Science and Technology (No. 0006641).

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Air Quality Studies

The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

NEW EU VERSUS CROATIAN AIR QUALITY STANDARDS

N Barbalić[1, *], G Marijan[1]

ABSTRACT

The Croatian air quality standards promulgated in 1996 were based on the then most demanding standards used worldwide. During the period 1999-2002, the European Union issued new air quality standards for the most relevant pollutants in the ambient air (sulphur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter, lead, benzene, carbon monoxide, ozone), which probably reflect the up-to-date European knowledge and experience in the field of air quality protection and improvement. The question is whether it is necessary to harmonise the Croatian with the new European air quality standards and, if so, how urgent is it. Therefore, a comparison has been prepared with regard to the structure of air quality standards, strategies for achieving the environmental goals incorporated in them, and stringency of air quality limit values. The comparison shows that the structure of the Croatian and EU air quality standards is actually identical. They only differ in strategy contained in the standards used to achieve the defined and desired environmental goals. Although the ultimate environmental goals are identical, the strategy of the EU legislation, unlike the Croatian legislation, sets firm time framework for their fulfilment. The differences in stringency of the limit values vary for different pollutants and they are either 'positive' or 'negative'. The 'negative' differences are not such that they would demand urgent modification of the Croatian air quality standards. The only exception are the air quality limit values for ozone. The most important reason for harmonisation of the Croatian with the EU air quality limit values could be the efficiency of the strategy incorporated in the EU standards where the goals are strictly assigned corresponding deadlines for their fulfilment.

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INDEX TERMS

Air quality standards, Croatia, European Community, comparison, harmonisation

INTRODUCTION

In order to assist the authorities in introducing a harmonised system of air quality standards, Krstić, Fugaš and Barbalić (1992) have proposed air quality determiners (set at three levels), which permit for both classification of areas depending upon the existing degrees of air pollution and development of a control strategy, necessary to achieve the defined goals. This is strictly stipulated by the Air Protection Act (Act, 1995) and the Ordinance on Air Quality Recommended and Limit Values (Ordinance, 1996). The Ordinance (1996) stipulates the recommended values (*RV*) and limit values (*LV*) of air quality as per individual pollutants. Based on the set up *RV* and *LV* values, the Act (1995) distinguishes between three categories of air quality for a certain area:

1. The first category air quality: clean or slightly polluted air (*RV* not exceeded).
2. The second category air quality: moderately polluted air (*RV* exceeded, *LV* not exceeded).
3. The third category air quality: excessive air pollution (*LV* exceeded).

and stipulates that:

Table 1. Air quality guidelines and goals (Krstić, Fugaš and Barbalić, 1992)

Basis for	Guideline for	Existing degree of air pollution	Air quality level	Control strategy
Transient local regulations in a limited number of highly polluted areas	Emergency levels (4 pollutants)	Alarm 2	VII	Warning to the public about possible risks and recommendation to reduce activities which may cause air pollution and to susceptible population groups to stay at home
		Alarm 1	VI	
		Alert	V	
		Above upper limits	IV	Urgent control measures to reduce air pollution to or below upper limits
Standards (regulation)	Upper limits For polluted areas (13 pollutants)	Up to upper limits	III	Measures to achieve gradual improvement of air quality with the goal to reach desirable limits
Guidelines (recommen-dations)	Desirable limits Not to be exceeded in clean areas, a long-term goal for polluted areas (28 pollutants) Protected areas	Up to desirable limits for humans	II	Measures to prevent any land use, development or activity which may cause deterioration of present air quality
		Up to desirable limits for plants	I	
		Below desirable limits	O	

(i) In the area with the first category air quality, precautionary measures are to be taken to prevent the *RV* from being exceeded as a result of building and development of the area.

(ii) In the area with the second category air quality, measures for air pollution reduction are to be taken so as to achieve the *RV*.

(iii) In the area with the third category air quality, rehabilitation measures are to be taken so as to achieve the *LV* as a short-term and the *RV* as a long-term goal.

(iv) In the third category air quality area no site and building permit and no inspection certificate shall be issued either for a new pollution source or for reconstruction of the existing one, unless the new construction or reconstruction are to ensure: a) replacement of the existing inappropriate facility with a new one which reduces air pollution, b) that the increase of air pollution near the facility shall not exceed 1 % of the *LV*, provided that the rehabilitation programme for the existing pollution sources is in the process of implementation.

Further, the Act (1995) offers an option of introducing the emergency levels of air quality (alert, alarm), which actually means setting up of the forth air quality category. However, considering the air quality recorded in Croatia during the last decades, there has been no need for determination of the emergency levels. Considering its structure and the selected *RV* and *LV* values, it was confirmed that the Croatian legislation on recommended values (*RV*) and limit values (*LV*) was drawn from the practices of the most demanding European and world regulations, as was for the emission limit values in the air from stationary sources

Table 2. Sulphur dioxide: Air quality standards in Croatia and EU (T = 1 year)

	Limit value	Index	τ h	p	X_{zp} μg/m$_n^3$	Remark
Croatia	*RV*	*a*	1	$1 - \tau/T$	350	-
		b	24	$1 - \tau/T$	125	-
		c	8760	$X_{zp} = \overline{X}$	50	-
	LV	*a*	24	0.98	250	Particulate matter: $c_{24;0.98} > 350$ μg/m$_n^3$
		b	24	0.50	80	Particulate matter: $c_{24;0.50} > 150$ μg/m$_n^3$
		c	24	0.98	350	Particulate matter: $c_{24;0.98} > 350$ μg/m$_n^3$
		d	24	0.50	120	Particulate matter: $c_{24;0.50} > 150$ μg/m$_n^3$
European Union	*ELV* (human health)	*a*	1	$1\text{-}24\,\tau/T$	500	to 31/12/2000
		b	1	$1\text{-}24\,\tau/T$	$X(n)^*$	1/1/2001–31/12/2004 $= 500 - (n - 2000)\cdot 30$
		c	1	$1\text{-}24\,\tau/T$	350	after 1/1/2005
		d	24	$1\text{-}3\,\tau/T$	125	after 1/1/2005
	ELVE (ecosystems)	*a*	4380	$X_{zp} = \overline{X}$	20	(1 October to 31 March)

$^*n$ – calendar year (2000, 2001,…)

Table 3. Oxides of nitrogen: Air quality standards in Croatia and EU (T = 1 year)

	Limit value	Index	τ h	p	X_{tp} µg/m$_n^3$	Remark
Croatia	*RV* (NO_2)	*a*	24	0.98	60	-
		b	8760	$X_{tp} = \overline{X}$	40	-
	LV (NO_2)	*a*	1	0.98	200	-
		b	24	0.98	120	-
		c	8760	$X_{tp} = \overline{X}$	60	-
European Union	*ELV* (human health) (NO_2)	*a*	1	1-18 π/T	300	to 31/12/2000
		b	1	1-18 π/T	X (n)*	1/1/2001– 31/12/2009 = 300 – (n – 2000)·10
		c	1	1-18 π/T	200	after 1/1/2010
		d	8760	$X_{tp} = \overline{X}$	60	after 1/1/2005
		e	8760	$X_{tp} = \overline{X}$	X (n)*	after 31/12/2000 = 60 – (n – 2000)·2
		f	8760	$X_{tp} = \overline{X}$	40	after 1/1/2010
	ELVV (vegetation) (NO_2)	*a*	8760	$X_{tp} = \overline{X}$	30	-

*n – calendar year (2000, 2001,…)

(Barbalić, Marijan and Marić, 2000). During the period 1999-2002, the Council of the European Union issued three directives related to the limit values for the most important pollutants in ambient air: Directive (1999): sulphur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter and lead; Directive (2000): benzene, carbon monoxide; Directive (2002): ozone.
The topics to be considered are: (i) comparison of structures of the Croatian and EU air quality standards; (ii) comparison of stringency of limit values stipulated by the Croatian and EU legislation, and (iii) whether the differences are such that they demand urgent harmonisation of the Croatian standards on air quality to the corresponding EU standards.

COMPARATIVE OVERVIEW OF APPLICABLE CROATIAN AIR QUALITY STANDARDS AND NEW EU AIR QUALITY STANDARDS

Notwithstanding the details that define any air quality standard, Tables 2-8 give a comparative overview of the Croatian (Ordinance, 1996) and new EU air quality standards (Directives, 1999; 2000; 2002) for sulphur dioxide, oxides of nitrogen, particulate matter, lead, benzen, carbon monoxide, ozone. Each of the air quality limit values (*AQLV)* from Tables 2-8 is presented by its basic components: τ – averaging

time (reference period), p – quantile level, $X_{\tau p}$ – value to be compared with the correspondent concentration value $c_{\tau p}$ of the distribution function, determined by the air quality measurements for averaging time τ, T – monitoring period (generally 1 year); i.e.

$$AQLV = < T, \tau, p, X_{\tau p} >; \qquad \tau \subset T,$$

$$\text{for } \tau = T: \qquad X_{\tau p} = X_{T,1} = \overline{X} \quad \text{(average value)} \tag{1}$$

$$\text{for } p = 1 - \frac{\tau}{T}: \qquad X_{\tau p} = X_{\tau, 1-\frac{\tau}{T}} = X_{\max}$$

For an overview to be comprehensive, the Table 9 gives the alert thresholds set in EU for sulphur dioxide, nitrogen dioxide and ozone (Directives, 1999; 2002).

Table 4. Particulate matter (PM_{10}): Air quality standards in Croatia and EU (T = 1 year)

	Limit value	index	τ h	p	$X_{\tau p}$ µg/m$_n^3$	Remark
Croatia	*RV*	*a*	1	1-τ/T	300	*LV* not stipulated for (PM_{10})
		b	24	1-τ/T	70	
		c	8760	$X_{\tau p} = \overline{X}$	50	
European Union	*ELV*1 (human health) Stage 1	*a*	24	1-35 τ/T	75	to 31/12/2000
		b	24	1-35 τ/T	$X(n)^*$	1/1/2001–31/12/2004 = 75 – (n – 2000)·5
		c	24	1-35 τ/T	50	after 1/1/2005
		d	8760	$X_{\tau p} = \overline{X}$	48	after 31/12/2000
		e	8760	$X_{\tau p} = \overline{X}$	$X(n)^*$	1/1/2001–31/12/2004 = 48 – (n – 2000)·2
		f	8760	$X_{\tau p} = \overline{X}$	40	after 1/1/2005
	*ELV*2 (human health) Stage 2**	*a*	24	1-7 τ/T	50	after 1/1/2010
		b	8760	$X_{\tau p} = \overline{X}$	30	after 31/12/2005
		c	8760	$X_{\tau p} = \overline{X}$	$X(n)^*$	1/1/2006–31/12/2009 = 30 – (n – 2005)·2
		d	8760	$X_{\tau p} = \overline{X}$	20	after 1/1/2010

* n – calendar year (2000, 2001,…)

** Indicative limit values to be revised in the light of further information and experience in the application of Stage 1 limit values

Table 5. Lead: Air quality standards in Croatia and EU (T = 1 year)

	Limit value	Index	τ h	p	X_{tp} µg/m$_n^3$	Remark
Croatia	*RV*	*a*	8760	$X_{tp} = \overline{X}$	1	-
	LV	*a*	8760	$X_{tp} = \overline{X}$	2	-
European Union	*ELV* (human health)	*a*	8760	$X_{tp} = \overline{X}$	1	to 31/12/2000
		b	8760	$X_{tp} = \overline{X}$	$X(n)^*$	1/1/200–31/12/2004 $= 1 - (n - 2000)\cdot 0.1$ $^{**} = 1 - (n - 2000)\cdot 0.05$
		c	8760	$X_{tp} = \overline{X}$	0.5	after 1/1/2005.//**after 1/1/2010

$^*n$ – calendar year (2000, 2001,…)
**in the immediate vicinity of specific sources (must be specially notified)

Table 6. Benzene: Air quality standards in Croatia and EU (T = 1 year)

	Limit value	Index	τ h	p	X_{tp} µg/m$_n^3$	Remark
Croatia	*RV*	*a*	8	0.98	5	-
		b	8760	$X_{tp} = \overline{X}$	2	-
	LV	*a*	8	0.98	10	-
		b	8760	$X_{tp} = \overline{X}$	5	-
European Union	*ELV* (human health)	*a*	8760	$X_{tp} = \overline{X}$	10	to 31/12/2005
		b	8760	$X_{tp} = \overline{X}$	$X(n)^*$	1/1/2006–31/12/2009 $= 10 - (n - 2005)\cdot 1$
		c	8760	$X_{tp} = \overline{X}$	5	after 1/1/2010

$^*n$ – calendar year (2005, 2006,…)

Table 7. Carbon monoxide: Air quality standards in Croatia and EU (T = 1 year)

	Limit value	Index	τ h	p	X_{tp} mg/m$_n^3$	Remark
Croatia	*RV*	*a*	24	0.98	5	-
		b	8760	$X_{tp} = \overline{X}$	1	-
	LV	*a*	1	0.98	15	-
		b	24	0.98	8	-
		c	8760	$X_{tp} = \overline{X}$	2	-
European Union	*ELV* (health protection)	*a*	8^{**}	$1-\tau/24T$	16	to 31/12/2002
		b	8^{**}	$1-\tau/24T$	$X(n)^*$	1/1/2003–31/12/2004 $= 16 - (n - 2002)\cdot 2$
		c	8^{**}	$1-\tau/24T$	10	after 1/1/2005

$^*n$ – calendar year (2002, 2003,…)
**The maximum daily 8-hour mean concentration: will be selected by examining 8-hour running averages, calculated from hourly data and updated each hour. Each 8-hour average so calculated will be assigned to the day on which it ends. i.e. the first calculation period for any one day will be the period from 17:00 on the previous day to 01:00 on that day; the last calculation period for any one day will be the period from 16:00 to 24:00 on that day.

Table 8. Ozone: Air quality standards in Croatia and EU (T = 1 year)

	Limit value	Index	τ h	p	X_{tp} µg/m$_n^3$	Remark
Croatia	*RV*	*a*	24	0.98	110	-
	LV	*a*	1	0.98	180	-
		b	24	0.98	150	-
European Union	*ELVT* (human health) Target	*a*	8*	1-25τ/24*T*	120	Target value for 2010
	ELVO (human health) Objective	*a*	8*	1-τ/24*T*	120	Long-term objective (2020)
	AOT 40** (vegetation)	*a*	1	6000 (µg·h/m$_n^3$)		Calculated from 1h values from May to July

*The maximum daily 8-hour mean concentration shall be selected by examining 8-hour running averages, calculated from hourly data and updated each hour. Each 8-hour average so calculated shall be assigned to the day on which it ends. i.e. the first calculation period for any one day will be the period from 17:00 on the previous day to 01:00 on that day; the last calculation period for any one day will be the period from 16:00 to 24:00 on the day.

**AOT 40 (expressed in (µg/m^3)·hours) means the sum of the difference between hourly concentrations greater than 80 µg/m^3 (= 40 parts per billion) and 80 µg/m^3 over a given period using only the 1 hour values measured between 8:00 and 20:00.

Table 9. Alert thresholds in EU

Pollutant	Threshold	τ	X_τ	Remark
-	-	h	µg/m$_n^3$	-
SO_2	Alert	1	500	measured over three consecutive hours at locations representative of air quality over at least 100 km^2 or an entire zone or agglomeration, whichever is the smaller
NO_2	Alert	1	400	measured over three consecutive hours at locations representative of air quality over at least 100 km^2 or an entire zone or agglomeration, whichever is the smaller
O_3	Information	1	180	
	Alert	1	240	the exceeding of the threshold is to be measured or predicted for three consecutive hours

COMPARISON OF THE MAIN CHARACTERISTICS OF THE CROATIAN AND EU AIR QUALITY STANDARDS

The existing Croatian and new EU air quality standards should be compared for their main characteristics: structure (different levels of air quality standards and alert thresholds), strategy of achieving the defined goals, and stringency.

Structure

There is no essential difference between the Croatian and EU air quality standards. They both actually adopt an idea anticipated in Krstić, Fugaš and Barbalić (1992) – Table 1:

- the Croatian air quality standards are set up on two levels: lower– recommended values (*RV*) and higher– limit values (*LV*) with three air quality categories. Setting up of the alert thresholds is envisaged, if necessary.
- The EU air quality standards formally have only one level of limit values. However, in addition to the limit values, they specify margin of tolerance of 50 –100 %, which is practically the second level of air quality standards with 50 – 100 % higher values (tolerable limit values). Therefore, the EU legislation also divides air quality into three categories: below prescribed limit values, between prescribed limit values and 'tolerable' limit values, and above 'tolerable' limit values. However, an important difference between the Croatian and EU legislation is linear narrowing of the EU margin of tolerance on annual basis so, depending on the pollutant under consideration, the margin of tolerance is planned to be reduced to zero by 2005 or 2010.

Strategy

The strategic goals are identical (Table 1) – the ambient air quality inside the first category air quality (below the desirable limit values). The differences are:

- The Croatian strategy for achieving of the desired goals is described in the Introduction. In brief: (i) air quality deterioration is not allowed in any area, (ii) for areas with the second category air quality a goal is to achieve *RV*-level of air quality, (iii) for the third category air quality adequate restoration measures have to be taken so as to achieve the *LV* as short-term and *RV* as a long-term goals. The deadlines are not set, i.e. namely the terms 'short-term' and 'long-term' are not precisely defined. So the authorities have a liberty of free interpretation.
- In EU, margin of tolerance is linearly reduced to zero and tolerable limit values to prescribed limit values. What is important is that the whole process is set within a fixed time framework (by 2005 or 2010). Such an approach initiates permanent but gradual activities (annual controls) leading to the desired goal.

Stringency

Air quality limit value is comprehensively specified using a quadruplet *AQLV* – equation (1). Comparison of the air quality values, i.e. corresponding quadruplets *AQLV* according to their stringency is possible only if necessary simplifications are acceptable, for instance, using the model described by Barbalić, Jelavić and Marijan (1998): (i) there is a known functional dependence on averaging time of

distribution functions over the concentration field of the monitored area, that is, of parameters of those distribution functions, (ii) the distribution functions are all (approximately) log-normal. In that case, each quadruplet can only be expressed with a single value of $ROI \in \mathbf{R}$ (Barbalić, Marijan, Marić, 2000). So:

$$ROI_i < ROI_j \rightarrow AQLV_i \prec AQLV_j; \quad ROI_i = ROI_j \rightarrow AQLV_i = AQLV_j; \quad ROI_i > ROI_j \rightarrow AQLV_i \succ AQLV_j \tag{2}$$

($<$ - less than, $\prec$ - more stringent than, $>$ - greater than, $\succ$ - less stringent than). By using the relations (2), and according to the model (Barbalić, Marijan, Marić, 2000), a comparison has been performed of the EU and Croatian air quality limit values. The rank by stringency of individual air quality limit values, separately of long-term and short-term values, is found for each of the relevant pollutants indicated in the Tables 2-8.
The comparison (Table 10) indicates as follows:

Table 10. EU and Croatian air quality standards by stringency

Rank of standards			1	2	3	4	5	6	7
SO_2 (marks as used in Table 2)	short-term	standard	*RVa*	*RVb*	*ELVd*	*ELVc*	*ELVa*	*LVa*	*LVc*
		ROI	0	0.577	1.266	1.500	2.336	5.085	7.299
NO_2 (marks as used in Table 3)	long-term	standard	*RVb*	*ELVf*	*LVc*	*ELVd*			
		ROI	0	0	0.225	0.225			
	short-term	standard	*ELVc*	*RVa*	*ELVa*	*LVb*	*LVa*		
		ROI	-0.071	0	0.118	0.45	0.815		
Particulate matter PM_{10} (marks as used in Table 4)	long-term	standard	*ELV2d*	*ELV2b*	*ELV1f*	*ELV1d*	*RVc*		
		ROI	-0.27	-0.18	-0.09	-0.018	0		
	short-term	standard	*RVa*	*RVb*	*ELV2a*	*ELV1c*	*ELV1a*		
		ROI	0	0.221	0.811	3.295	5.167		
Lead (marks as used in Table 5)	long-term	standard	*ELVc*	*RVa*	*ELVa*	*LVa*			
		ROI	-0.225	0	0	0.45			
Benzene (marks as used in Table 6)	long-term	standard	*RVb*	*LVb*	*ELVc*	*ELVa*			
		ROI	0	0.675	0.675	1.8			
CO (marks as used in Table 7)	short-term	standard	*ELVc*	*ELVa*	*RVa*	*LVb*	*LVa*		
		ROI	-0.368	-0.318	0	0.27	0.689		
O_3 (marks as used in Table 8)	short-term	standard	*ELVOa*	*ELVTa*	*RVa*	*LVb*	*LVa*		
		ROI	-0.405	-0.331	0	0.164	0.171		

SO_2: *RV* air quality level is more stringent than *ELV* prescribed and tolerable level of air quality. However, *LV* level is considerably more tolerable and it is the only one that should probably be corrected.
NO_2: *RV* air quality level is somewhat less stringent than *ELV* prescribed level,

while *LV* level is somewhat more stringent than *ELV* tolerable air quality level. The corrections are not necessary.
Particulate matter: *RV* air quality level (short-term) is considerably more stringent than the corresponding *ELV* prescribed and tolerable level. The situation with the long-term limit level is opposite. The corrections are not necessary since very high stringency of the short-term limit values reduces the probability of reaching high long-term limit values. However, Croatia has not regulated the *LV* for PM_{10}, only for total particulate matter, which could be a reason for corrections.
Benzene: *RV* air quality level is more stringent than the *ELV* air quality levels. The *RV* correction would be necessary in order to loosen the limit values.
CO: *ELV* air quality levels (both prescribed and tolerable) are more stringent than *RV* and *LV* air quality level. The differences are not significant, but the corrections are necessary.
O_3: *ELV* air quality level is considerably more stringent than *RV* and *LV* air quality levels. The corrections are necessary, particularly since the EU pays much attention to O_3 impact on air quality (Directive 2002 is completely dedicated to ozone in ambient air).

CONCLUSION

With regard to the new air quality limit values for the European Union adopted during the period 1999 – 2002, Croatia has to reconsider the need for correction and harmonisation of the existing air quality values: (i) structure of the EU and Croatian air quality standards is very similar – in both cases the limit values put the air quality in three categories, (ii) the strategic goals and planned mechanisms for their fulfilling are identical; the EU strategy has a clear advantage of fixed time framework for its implementation (by 2005 or 2010) (iii) stringency of limit values varies for different pollutants and the difference is either 'positive' or 'negative'. The 'negative' differences are not such as to demand urgent modifications of the Croatian air quality standards. The only exception are air quality limit values for ozone. The most important reason for harmonisation of the Croatian and EU air quality limit values could be efficiency of the EU standards strategy that incorporates the firmly set time framework for implementation.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

NUMERICAL SIMULATION OF AIR QUALITY IN CHAMONIX VALLEY, USE OF DIFFERENT CHEMISTRY INDICATORS

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ABSTRACT

Road traffic is a serious problem in the Chamonix valley: traffic, noise and above all air pollution worry the inhabitants of the valley. The accident in the Mont-Blanc tunnel made it possible, in the framework of the POVA project (Alpine Valley Pollution), to undertake measurement campaigns with and without heavy-vehicle traffic through the valley, from France to Italy (before and after the tunnel re-opening). Numerical simulations of POVA are designed to help in explaining the process leading to episodes of atmospheric pollution, both in summer and in winter.
Atmospheric prediction model ARPS 4.5.2 (Advanced Regional Prediction System), developed at the CAPS (Center for Analysis and Prediction of Storms) of the University of Oklahoma, enables to resolve the dynamics of this terrain with complex orography. A large field (140 * 140 km) driven by ALADIN meteorological vertical (French Meteorological Office) forces a small central field (25 * 25 km). This model is coupled to the TAPOM 1.5.2 code for atmospheric chemistry (Transport and Air POllution Model) developed at the Ecole Polytechnique Fédérale de Lausanne.
Using 300-metre grid cells to calculate the dynamics and the reactive chemistry makes possible to represent accurately the dynamics in the valley (slope winds) and to process the chemistry at a fine scale.
Validation of campaign days allows to study chemistry indicators in the valley. The ratios H_2O_2/HNO_3, O_3/NOz demonstrate the particular VOC controlled regime, different from the $^{*}NO_x$ controlled regime observed in the nearby city of Grenoble.

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INDEX TERMS

Numerical simulation, Alpine valley, Reactive photochemistry, Meteorological forcing, NO_x controlled regime.

INTRODUCTION

Alpine valleys are sensitive to air pollution due to emission sources (traffic, industries, individual heating), morphology (narrow valley surrounded by high ridge), local meteorology (temperature inversions and slope winds). Such situations are rarely investigated with specific research programs taking into account detailed atmospheric chemistry coupling gas and aerosol phases. Following the accident under the Mont Blanc tunnel on March 24th, 1999, international traffic between France and Italy was stopped through the Chamonix Valley (France). The heavy-duty traffic (about 2130 trucks per day) has been diverted to the Maurienne Valley, with up to 4250 trucks per day. The program POVA (Pollution des Vallées Alpines) started in May 2000, with the objective to analyse air quality and develop atmospheric modelling in each of the two valleys, in order to study impact of traffic and local development scenarios.

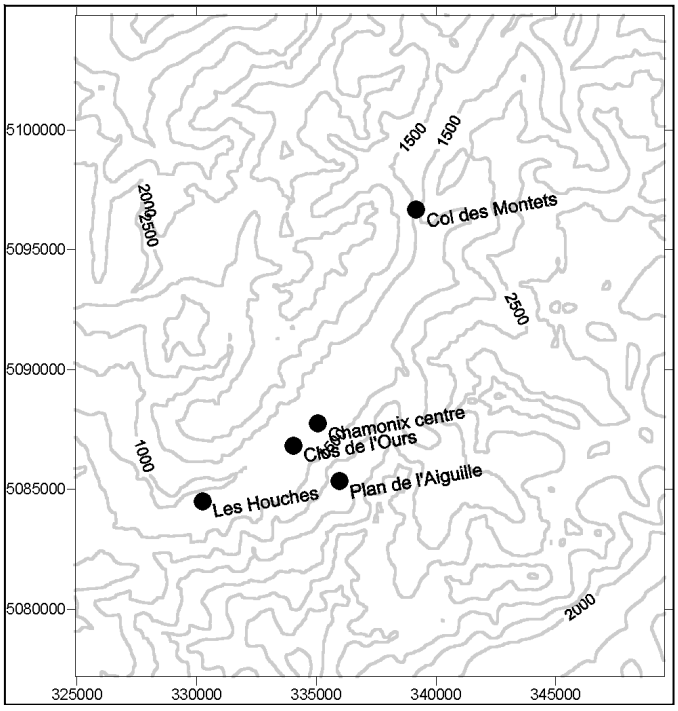

Figure 1. Topography of Chamonix valley: principals sites of mesurements and coordinates system UTM 32 in meters.

MODEL FOR SIMULATIONS

Numerical simulation combines the mesoscale atmosphere model ARPS 4.5.2 and the troposphere chemistry model TAPOM 1.5.2.
Atmospheric prediction model ARPS 4.5.2 (Advanced Regional Prediction System), developed at CAPS (Center for Analysis and Prediction of Storms) (Xue, 2000), enables to resolve atmosphere dynamics above complex terrain. A large (250 * 300 kms) field is driven by the ALADIN verticals of the French Meteorological Office and forces the field of interest (25 * 25 kms).
This model is coupled off-line to the TAPOM 1.5.2 code of atmospheric chemistry (Transport and Air POllution Model) developed at the LPAS of the EPFLausanne (Clappier, 1998; Gong and Cho, 1993). TAPOM uses the Regional Atmospheric Chemistry Modeling (RACM) scheme (Stockwell et al.,1997). 300-meters grid cells to calculate dynamics and reactive chemistry make possible to represent accurately dynamics in the valley (slope winds) (Anquetin et al., 1999) and to process chemistry at fine scale.
For the boundary conditions, CHIMERE, a regional ozone prediction model, from the European Centre for Medium-Range Weather Forecasts, gives concentrations of chemical species on five levels (Schmidt, 2001).
TAPOM is based on the reduced chemistry scheme RACM with biogenics and photoreactivity, thanks to full account of 77 species and 237 reaction steps (Stockwell, 1997).

EMISSION INVENTORY

The emission inventory is based on the CORINAIR methodology and SNAPS's codes, with a 100x100m grid and includes information (land use, population, traffic, industries,..) gathered from administrations and field investigations. The emission classes are given in the table 1.

Table 1. Emission classes in the chemical model.

Commercial boiler	Residential boiler	Gas station
Domestic solvent	Cars	Cars in city
Utilitarian vehicles on motorway	Utilitarian vehicles on road	Heavy vehicles
Aerial traffic	Forest	Grassland

The emission inventory takes into account roads and access ramps to the tunnel adjusting emissions to the slope of the road. The number of heavy trucks (92% more than 32 tons) makes corresponding emission specific of the valley.
The yearly inventory is turned into hourly emissions for a set of RACM data in specially selected cases (summer/winter, week day/week end/holidays, …) to be used in scenarios (Middleton, 1990). Then, different scenarios are tested in the

valley of Chamonix with various sources: with and without road traffic, with and without heavy vehicles, for different meteorological cases. Sunny days, without synoptic wind, explain the contribution of local sources of pollution with mixing by slope winds. Days with a constant synoptic wind in the bottom of the valley gives an insight into the pollution background and boundary conditions species.

VALIDATION

Several sensitivity tests are being performed, based on real variation of gas emission and background. The first results are very encouraging, when compared to fields measurements and will permit to simulate different scientific scenarios or to assess environmental policies.

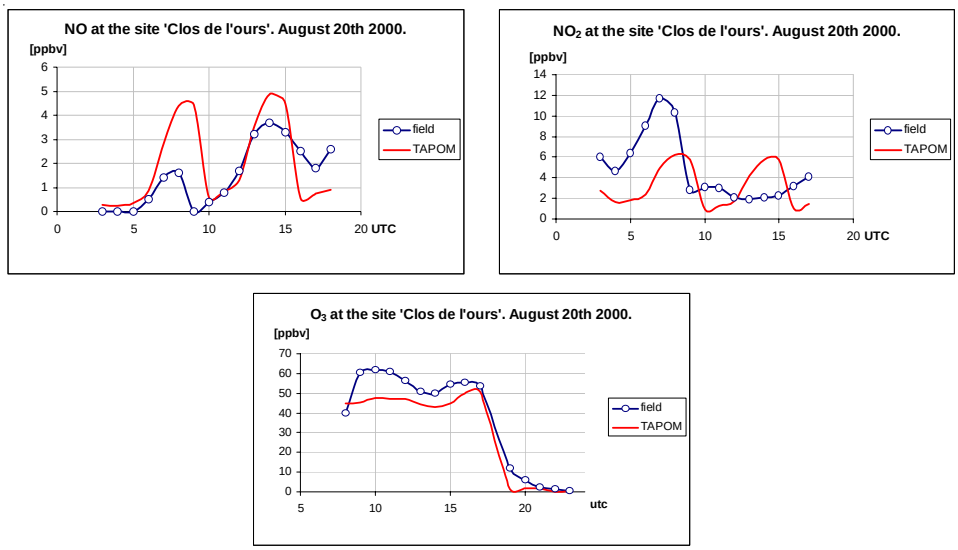

Figure 2. NO, NO_2 and O_3 concentration at the site 'Clos de l'ours' compared to fields mesurements.

PHOTOCHEMICAL INDICATORS

The simulations are done on August 20th, representative of a summer sunny day with an average pollution level. With the simulations results of August 20th, photochemical indicators (Sillam, 1995) are considered in order to determine the ozone production regime in the valley.

The difference of ozone concentration (verticals axis on the two diagrams) is given by the difference between the simulation of August 20th with full emissions and the same simulation with 50% less in emitted VOC and NO_x.

On the first diagram, figure 3. (H_2O_2/HNO_3) there is two differents aeras separate by rate of $H_2O_2/HNO_3 = 1$: the first aera on the left ($H_2O_2/HNO_3 < 1$) is sensitive

to the reduction of VOC or NO_x. The right aera on the right ($H_2O_2/HNO_3 > 1$) is not sensitive to VOC or NO_x change.The reduction of 50% of VOC leads to a diminution of ozone, but a diminution of 50% of NO_x leads to an increase of ozone concentration.
On the second diagram, figure 4., the NOz concentration ($NOz = HNO_3 + PAN$) is an indicator of the age of the air mass: the age decreases with NOz concentration. As for the first diagram, there are two aeras separated by the value $O_3/NOz = 27$. The left part is the only one to be sensitive to the VOC or NOx reduction. The two indicators lead to the same conclusion: **only a diminution of VOC leads to a reduction of ozone concentration.**
These conclusion differs from what was observed in the nearby city of Grenoble (100 km from the valley) where a NO_x controlled regime was generally observed (Couach, 2002). We can explain this situation by the particular meteorology in the valley: dynamical and chemical phenomena observed in the bottom of the valley are not coupled with the meteorology at larger scale. We often have such a situation in the valley, in winter and in summer, with very low inversion layers.

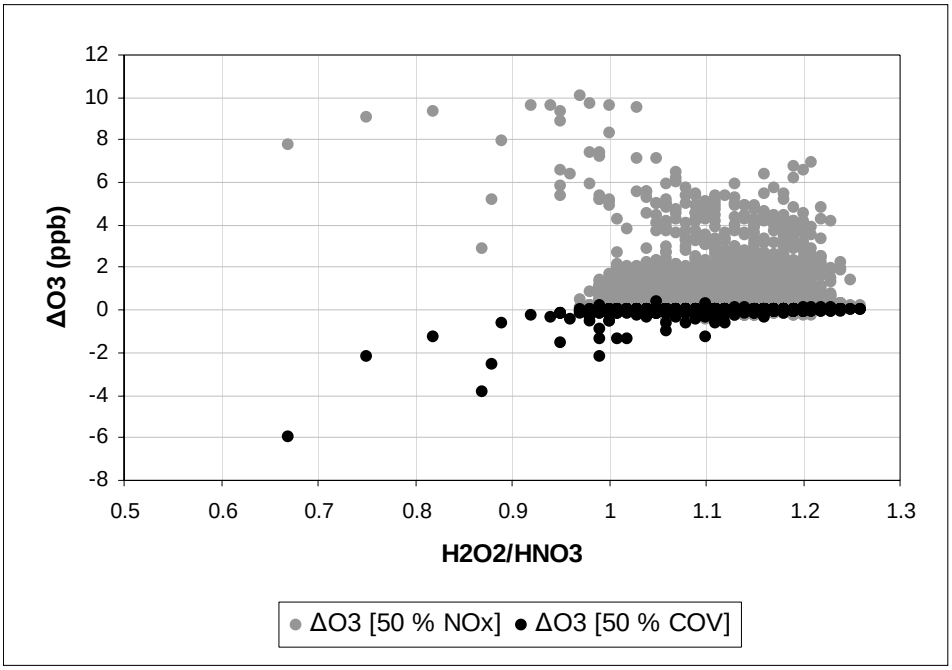

Figure 3. H_2O_2/HNO_3 and difference of ozone concentration with reduction of VOC or NO_x.

The study of NO to NO_2 ratio near the tunnel entrance is a good indicator of traffic intensity. This rate is equal to A 1 near the sources and can reach 2 or 3. Typically in a rural aera this rate is about 0.2. On the figure 5. we can see the

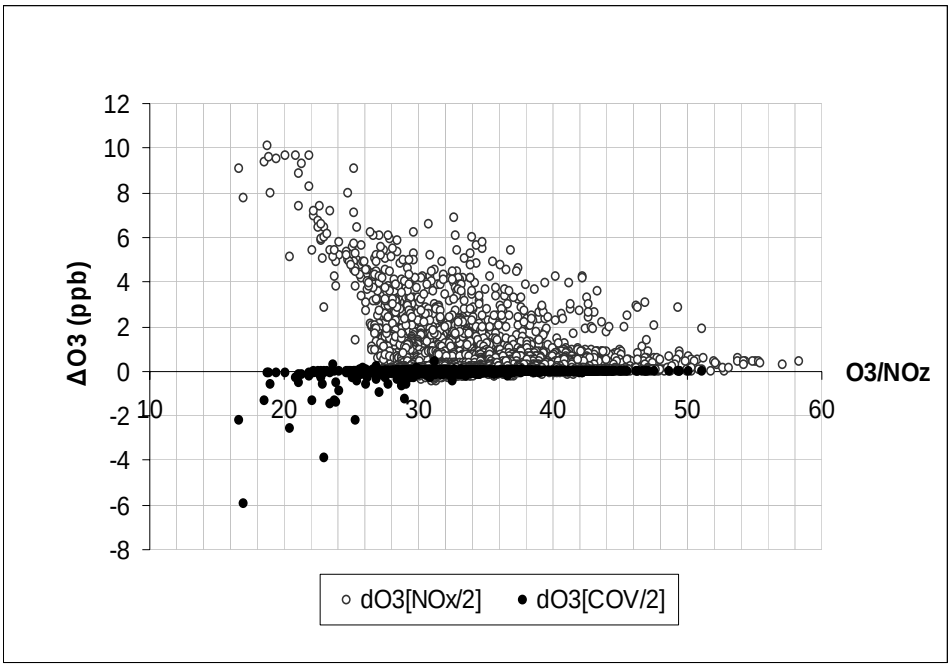

Figure 4. O_3/NOz and difference of ozone concentration with reduction of VOC or NO_x.

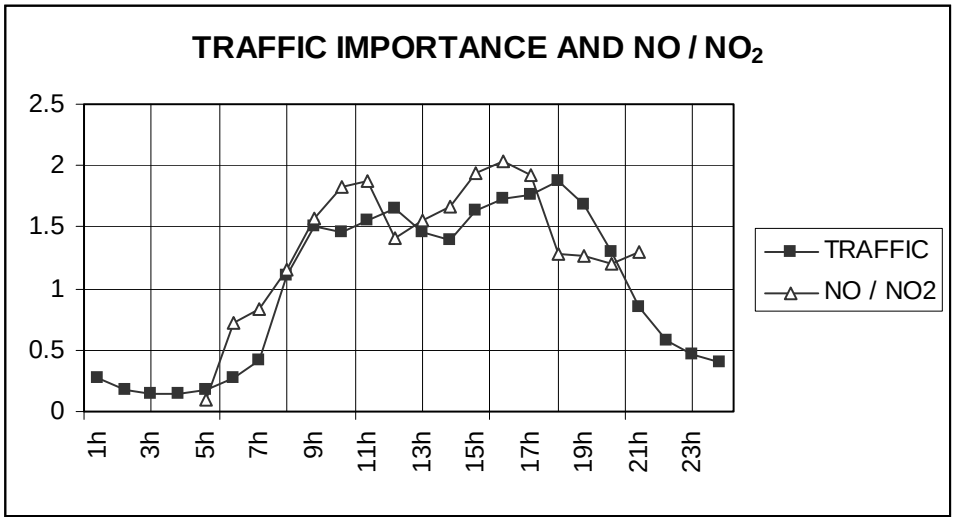

Figure 5. Traffic importance and rate NO on NO_2.

fluctuation of the ratio along the day near the tunnel, the variation of the ratio is between 0.2 and 2.It evolves similarly with the road traffic (cars and trucks).

CONCLUSION

The objective of the program is now to estimate the respective impacts of the various emissions sources present in the valleys, the regional impact and evaluate the variability in air concentrations according to changes in environmental conditions. Then the same study will begin for the other valley of the POVA program (Maurienne valley) and the impact of road traffic will be evaluated.

ACKNOWLEDGEMENTS

The program POVA is supported by Région Rhône Alpes, ADEME, METL, MEDD. Meteorological data are provided by Météo France, traffic data by STFTR, ATMB, DDE Savoie et Haute Savoie. Computations were done on Mirage.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

THE FUTURE OF INDUSTRIAL EMISSION REGULATION IN THE UK AND EUROPE

Dr Martin G Bigg*

ABSTRACT

Regulatory systems for controlling the impact of industry on the environment have evolved rapidly in the United Kingdom and Europe in recent years: EU countries have been introducing various forms of integrated pollution control in the past ten years and are now implementing the EU Integrated Pollution Prevention & Control Directive in 2000. After outlining the novel features of these systems, and reviewing the progress of implementation of the Directive, this paper seeks to identify and evaluate the key approaches likely to emerge in the next few years.

In the short term, the most significant issues are likely to be:

– how to ensure a 'risk-based' and 'outcome-focused' approach to regulation, which allows the extent of external monitoring and regulation of a company's activities to be varied in the light of the company's past performance in environmental management and compliance;

– more generally, how established environmental management systems can be more effectively linked to external regulation so as to raise environmental performance in the most cost-effective way;

– how far emissions trading, market instruments and voluntary agreements can be effectively linked with more traditional command and control mechanisms;

– at the most general level, how to ensure a visible and relevant relationship between individual decisions and the broad goals of sustainability which are now increasingly imported into environmental regulatory legislation;

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Finally, the paper briefly reviews the relative importance and respective roles of process controls and of product controls in advancing sustainable development, and how the two approaches can be more effectively related.

INDEX TERMS

Integrated pollution control, Environmental management, Emissions trading, Risk based regulation, Outcome focused regulation.

INTRODUCTION

The number, and pace, of new environmental regulations has steadily increased over the past few years and puts more and more pressure on both the regulator and the regulated. Over 80% of current environmental regulation in the UK is as a result of EU Directives. In the past 5 years we have dealt with 4 to 8 new sets of regulations per year. There is strong national and international pressure to secure integration in these initiatives which is reflected in the development of waste and water framework directives. Probably the most significant integrated directive for industry is the Integrated Pollution Prevention and Control (IPPC) Directive.

INTEGRATED POLLUTION PREVENTION AND CONTROL DIRECTIVE

The IPPC Directive (Commission of the European Community, 24 September1996) involves an integrated approach to controlling a wide variety of industrial activities, from chemical plants and power stations through to food factories and intensive pig and chicken farms. Air and water pollution, protection of the land and management of waste are all considered in a single regulatory regime. In addition energy efficiency, the prevention of accidents, noise and compliance with other EU Directives, regulations and environmental quality standards must also be addressed. The operator of an activity covered by IPPC must submit a permit application describing the installation and its environmental impacts. The regulator then consults the public before deciding whether to issue a permit. Permit conditions are to be based on the "Best Available Techniques", or BAT, for the sector.

In England and Wales, the Environment Agency is responsible for applying IPPC to about 5,000 existing installations. A separate but similar organisation, the Scottish Environmental Protection Agency (SEPA) is implementing IPPC in Scotland. The Environment Agency believes that IPPC is an effective tool to protect the environment in an integrated manner. However, we think it is important that the lessons we and other regulators have learned can inform both the ongoing implementation of IPPC and any further development of the IPPC Directive.

The permitting of existing installations has to be complete by October 2007, which creates a considerable workload challenge. The legislation (pollution Prevention

and Control Regulations, 2000) for England and Wales sets out a transitional timetable under which industry comes into IPPC on a sector-by-sector basis. This approach contrasts with many other EU countries, which are planning to implement PPC by, but closer, to the 2007 deadline. The UK government has produced detailed guidance (Department for Environment, Food and Rural Affairs, June 2002) for regulators and the regulated on the working of the IPPC directive. The Agency has published a large amount of guidance to help industry, much of it based on the "BAT Reference" documents produced by the European Commission with significant input from Environment Agency staff seconded to the European IPPC Bureau in Seville (Environment Agency web site).

In applying IPPC, it is also necessary to meet the requirements of other EU directives. Examples include the revised Large Combustion Plants Directive, the Waste Incineration Directive and the Landfill Directive. This has led to some complex regulatory requirements, and has also revealed some areas where the standards or definitions of different pieces of legislation are inconsistent or in conflict. The Agency continues to support the development of an even more coherent approach to legislation, which would support greater efficiency and effectiveness in implementation.

The Commission is currently consulting on the current state of play on implementing the IPPC Directive and the regulation of large industrial point sources and their impact on the environment. Specifically the Commission has identified major suspected or confirmed shortcomings in the legislation of most member states, identified difficulties in the implementation of the Directive and raised seven key questions in its communication.

RISK BASED AND OUTCOME FOCUSED REGULATION

Historically industrial regulation has been activity focused with technology derived standard limits applied to all industries in each sector. This approach is of particular value for simpler processes where their impact is primarily local: simplified permits for low impact installations and standardised permits for industry sectors where the technology and standards are relatively consistent across the industry. For industries with more significant environmental impact we have introduced electronic applications which include guidance on the techniques and standards we expect. This has enabled us to identify the key pollutants for each industry and the technologies we expect to be addressed by the operator in his application and the regulator in compliance assessment.

For each significant regulated industry we are producing sector reports and sector plans. The reports set the context for the industry identifying technical, economic and some social aspects of the industry and inform the sector plans. The sector plans set out the desired environmental outcomes, balance key sector drivers (including economic issues) and identify strategic tools relevant to the sector. They also set out the permitting strategy including, for example, permit type and

sector permit conditions, and detail the key performance indicators for that sector. For each sector we are preparing a sector compliance assessment plan which identifies national compliance issues and enables us to prioritise the regulatory workload on a sector by sector basis.
For industries with the potential to make a significant environmental impact more effective environmental protection can be achieved through regulation based on the risk to the environment and effect on the environment. For industries coming under PPC the Environment Agency has developed its Operator and Pollution Risk Appraisal (OPRA) tool which is designed to reflect our regulatory effort. It assesses the company against the following attributes:

- Complexity
- Emissions
- Location
- Operator Management: management systems and compliance history

ENVIRONMENTAL MANAGEMENT SYSTEMS

Business must take responsibility for the environmental impacts of its activities. Delivering consistent and continuing management of environmental impacts requires a business to take a structured approach. Environmental Management Systems (EMSs) provide a way for businesses to do this. Many organisations choose to operate in-house, or informal, EMSs to manage their environmental impacts. Others use the recognised worldwide standard ISO 14001, or go on to achieve a higher standard through the EU Eco-Management and Audit Scheme (EMAS). EMAS requires, for example, legal compliance, independent verification and public access to company environmental reports. However, a site having an EMS is not a guarantee of good environmental performance. There must be a continuing management commitment.
The Environment Agency considers legal compliance and good environmental performance to be fundamental. The Agency formally recognises EMSs in its risk-based approach to regulation via the OPRA scheme.
Studies suggest that sites with EMSs don't necessarily deliver better compliance with permit conditions, have fewer incidents or better general environmental performance than those that do not have them. However the scope of a site EMS will often address issues that go beyond regulatory requirements. It may be that by introducing an EMS, a site's environmental performance will improve at a faster rate than if it does not implement one. We have set ourselves targets to help increase the proportion of waste and process industry sites regulated by the Agency that have externally verified EMSs.
In collaboration with the Dutch and German environmental regulators and supported by the EU the Agency has established the REMAS project to assess the benefit of environmental management to operators, regulators and the environment.

EMISSIONS TRADING AND VOLUNTARY AGREEMENTS

While voluntary agreements have played only a limited role in industrial environmental protection the use of emissions trading is already playing a role in reducing emissions of green house gases. The EU Greenhouse Gas Emissions Allowances Trading Directive will put in place a mechanism for trading emissions from 1 January 2005. This requires permitting of installations by 31 March 2004. The UK already has some experience of trading greenhouse gases and sees trading as a valuable tool to achieve its Kyoto commitments.

Trading also has the potential to make a significant difference to the regulation of other key pollutants from industry. In the UK the industries capable of achieving major reductions in emissions of sulphur dioxide and nitrogen oxides are the electricity supply industry, refineries, the iron and steel industry and other large combustion processes. Together these contribute some 77% and 25% of total U.K. emissions of sulphur dioxide and nitrogen oxides, respectively. Therefore, efforts to reduce the national emissions are best targeted at these industrial processes. The Agency is working with the devolved administrations and other regulators to devise a U.K. strategy, which will set reduction targets for 2010.

REGULATING CHEMICALS

The control of the industries manufacturing chemicals is currently often more effective than restricting the chemicals they produce as the present national and EU frameworks are predicated on evidence of harm being provided by the authorities rather than evidence of safety from industry. There is often no consensus on what level of evidence is actually necessary. The current approach is a labour and time intensive one of looking at and acting on chemicals substance-by-substance. The importance of many chemicals to wide sectors of economic life means that any attempt to restrict them will be examined intensively and is likely to be challenged. The nature of the chemicals industry and its market means that single market and international trade rules must be considered whenever action is proposed, and may stand in the way of such.

The European Commission is currently developing proposals for a new EU chemical strategy. This resulted from the *'Strategy for a Future Chemicals Policy'* (Commission of the European Community, 2001), which proposed a new system for chemical management EU termed REACH (registration, evaluation, authorisation of chemicals).

In the UK we are seeking to control the chemicals of highest concern without overwhelming the regulatory system or imposing an excessive burden on industry. As a starting point we are developing criteria on what the substances of very high concern are and use these to decide which chemicals to investigate further. We have already identified 36 substances of potential environmental significance. We want to place the onus on industry to demonstrate that the substances they

sell do not meet those criteria. This can be reinforced by the "no data, no market" principle. On the basis of this information we can then create a list of those substances of very high concern. We can then advise users to move away from using substances on the list as quickly as possible; create a phase-out mechanism for all uses except approved essential uses. By this means the control of specific chemicals will complement industry regulation rather than complicate it.

FUTURE REGULATORY TOOLS

In the last few decades the concept of sustainable development has forced business to try to take an even wider view, and to relate their everyday decisions to issues which have a far longer timescale and a far broader – even global – application. There therefore needs to be a visible and coherent link between immediate practical regulatory decisions and long-term global goals, which are broad and aspirational (National Society for Clean Air and Environmental Protection, October 2001). This linking is made more difficult by other contemporary approaches to environmental regulation – the emergence of a wide but still incoherent range of policy instruments; more complex patterns of multi-level governance; and the breakdown of the traditional operator/ regulator relationship with the emergence of new stakeholders.

Regulation alone cannot deliver sustainable development. That requires a wide range of other policy instruments and voluntary action. But regulation underpins those other systems and sets out the framework for voluntary action. Given that the role of regulation will remain crucial, sustainable development must be placed firmly at its heart.

Traditional site-specific regulatory systems, in particular, are unlikely to prove adequate to the needs of sustainability. They need increasingly to be matched by a more coherent framework of national strategies, targets, and sectoral agreements through which site-specific decisions can be linked to broader sustainability criteria. We are exploring the scope for giving companies which operate effective management systems and accept demanding targets in the reduction of environmental impacts, framework authorisations which allow them far greater discretion than at present to vary their processes, products and systems. This will allow the wider perspectives and long timeframe of sustainable development to be better reflected in regulation, and reflect the rapid changes in technology and market conditions to which companies now must continuously respond.

We are already working to make environment protection more objective-led and more focused on actual environmental outcomes; to link them more coherently to planning, health and other related systems; and to reflect better the circumstances and impacts of smaller and medium-sized enterprises, rather than large scale industry which has been the traditional focus. Our regulatory approach at any site will always be informed by the observed standards of environmental protection and management, including permit breaches, incidents and complaints from the pubic.

CONCLUSIONS

In order to meet the increasing expectations of national and international environmental legislation and expectations a range of regulatory and non-regulatory tools are required to achieve a risk based and outcome focused approach to environmental protection and sustainable development. These tools will be successful in preventing and controlling pollution from industry if:

- industry operates in a way that minimises adverse effects on people and the environment
- freeloaders are prevented from undermining the commitment of the majority
- clear requirements are established and maintained
- public confidence is established and maintained
- real environmental improvements are delivered

ACKNOWLEDGEMENTS

The author acknowledges the help and support of colleagues in the Environment Agency.

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THE ATMOSPHERIC FINE PARTICULATE IN LOMBARDY (ITALY)

M Giugliano, M Grosso, G Lonati*

ABSTRACT

PM_{10} concentration data series collected at 40 sites by the regional air quality monitoring network of Lombardy in years 2000-2001 are analysed by means of descriptive statistics. The monitors are mainly located at sites characterised by different exposure to emission sources: residential urban areas, both in the highly populated main cities and in minor cities, areas mainly exposed to traffic emissions, industrial areas and in suburban areas. The attainment of the current and prospected air quality standards for PM_{10} are evaluated. Weekly behaviours of concentrations levels are separately presented for the cold and warm season and the observed reduction of Sundays concentration levels with respect to working days is closely examined. Concentration levels are quite uniform over the entire region, with the lowest values for the residential sites and the highest for the traffic-exposed and the industrial sites. Current air quality standards are attained at about half of the sites, while the standards prospected for 2005 are largely exceeded by data sets of year 2001. Weekly behaviours generally show a progressive increase of the daily concentration, reaching a maximum on Wednesdays, followed by a downward trend towards the minimum always observed on Sundays, when concentration levels are reduced of about 25%. The reduction in concentration levels is consistent with the observed reductions of the circulating traffic volume between Sundays and workdays.

INDEX TERMS

PM_{10}, descriptive statistics, standard attainment, weekly behaviour, traffic reduction effect.

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INTRODUCTION

Atmospheric pollution of airborne fine particles is an environmental issue of major concern, principally due to the evidence of their adverse human health effects observed in epidemiological studies (Dockery D.W. et al., 1998; Kunzli N. et al., 2000; Samet M.J. et al., 2000; Stieb et al., 2002). In Lombardy, Italy's most industrialised and populated region, both long-term and short-term standards for PM_{10} are largely not attained during the winter period, when frequent restrictions of the circulation for some categories of vehicles are enforced, in order to control the acute episodes of pollution. But the strategies oriented to standard attainment require the understanding of the principal pathways leading to high concentration of the fine particulate in atmosphere, the role of the primary emission, as mobile sources and domestic heating, and the extent of the nucleation and condensation processes leading to formation of secondary fine particulate from the primary pollutants (Pun B.K., Seigneur C. ,1999).

The aim of this work is to provide a first contribute to the knowledge of the fine particulate in Lombardy by developing primarily a statistic descriptive analysis of the time series concentration data, collected in the years 2000-2001. The statistical approach allows to define the pollution level of the area, the behaviour of the concentration in typical periods and the check of the standard attainment. The behaviour of the concentrations observed during the week and in particular the systematic differences between the values of the Sundays and weekdays concentrations, allows to evaluate the role of the traffic as primary source affecting the presence of fine particulate in the area.

METHODS

Monitors and site characteristics

The regional air quality monitoring network encompasses 150 monitors for primary and secondary atmospheric pollutants. During year 2000 and 2001, 40 PM_{10} monitors were operating, the most part (32) equipped with Tapered Element Oscillating Microbalance (TEOM) and the other 8 equipped with Beta-Gauge samplers. Concentration data are collected every two hours; only in a few monitoring stations data are available every 3 hours. Data time series have been collected at monitoring sites characterised by different exposure to primary emission sources. The monitors are mainly (19 out of 40) located in residential urban areas, both in the highly populated major cities (5) and in minor cities (14), and in areas exposed to traffic emissions (13), with some kerbside location too. A few (5) monitors are located in industrial sites and in suburban areas (2), that is in a backward position with respect to primary emission sources.

RESULTS

Descriptive statistic

In Figure 1 the distributions of PM_{10} annual average concentrations observed at monitoring sites of similar characteristics are synthesised: minimum and maximum values, the mean value and the range of 2 standard deviations around this latter are represented for year 2000 and 2001 separately. Since for some monitors data capture is quite poor, only data series characterised by adequate consistency, in terms of validated registered values are considered for the statistical analysis. The lowest minimum value (26.8 $\mu g\ m^{-3}$) is observed in the residential area of a minor city, while the highest maximum value (62.3 $\mu g\ m^{-3}$) is observed on the kerbside location of a huge trafficated street, with another very close maximum value (61.8 $\mu g\ m^{-3}$) observed at an industrial site. The mean values are all included within a quite narrow range (36-47.5 $\mu g\ m^{-3}$), with the lowest values for the residential sites and the highest for the traffic-exposed and the industrial ones. Inter-annual variations of the mean values are not significantly different, with the only exception of the 2 suburban sites (42.3 and 24.2 $\mu g\ m^{-3}$ respectively in 2000 and 2001).

PM_{10} air quality standards attainment

The implementation of the European Union's Directive 1999/30 has established both long and short-term ambient air quality standards for PM_{10} to be attained at the latest by 2005. The former standard refers to the annual average concentration (40 $\mu g\ m^{-3}$), the latter to the daily average concentration (no more than 35 days per year exceeding 50 $\mu g\ m^{-3}$). For each year in the meanwhile, margins of tolerance to the limit values have been laid down and shall apply: according to the 20% margin set for year 2001, the long-term standard value for the annual average is 48 $\mu g\ m^{-3}$, while the short-term standard requires no more than 35 days exceeding a daily average concentration of 75 $\mu g\ m^{-3}$.

The standard for the annual average was not attained at 27 out of the 33 sites, where data series present adequate consistency for standard verification (i.e. at least 75% of validated registered values): non-attainments are observed at a residential site, an industrial site and 4 traffic exposed sites. The standard for the daily concentration was attained at 16 out of 33 sites: the non-attainments are observed at residential sites in the minor cities (8) and main cities (2), at the traffic exposed sites (6) and at 1 industrial site. The distributions of the annual number of days with daily average concentration exceeding 50 $\mu g\ m^{-3}$ are presented in Figure 2, where the 35 allowed exceedances are also indicated. The average number of exceedances is always largely greater than 35: at the residential sites very small differences are observed between main and minor cities locations for the two years, ranging from 62 to 70 exceedances, while larger differences result for traffic exposed and industrial sites.

In the perspective of the standards coming into force in 2005, the data series of year 2000 and 2001 have been also analysed for standards attainment, without considering

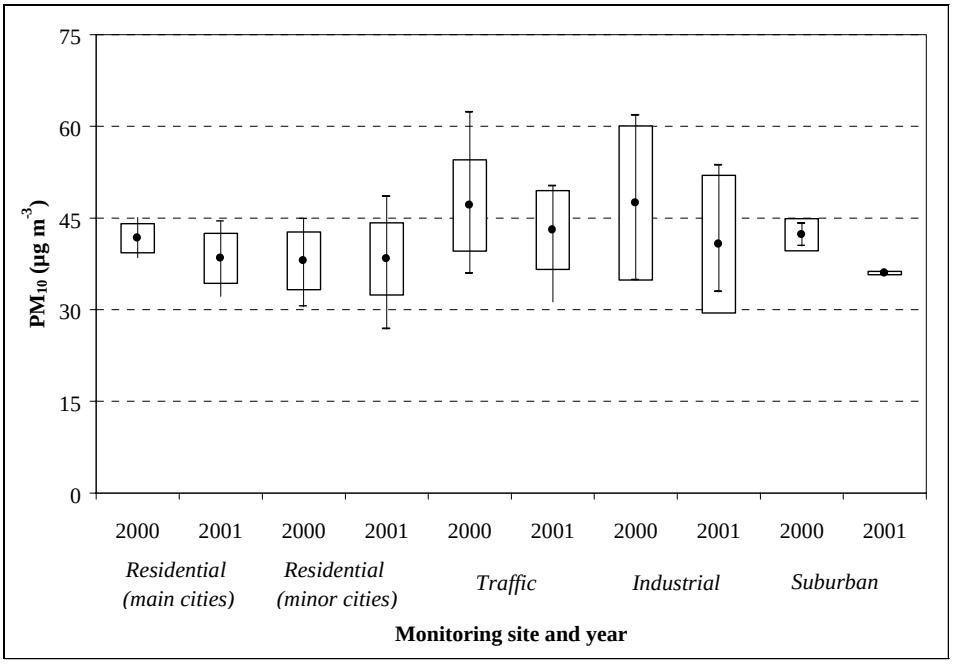

Figure 1. PM_{10} annual average concentrations distribution: minimum, mean, maximum value and 2 standard deviation range around the mean value.

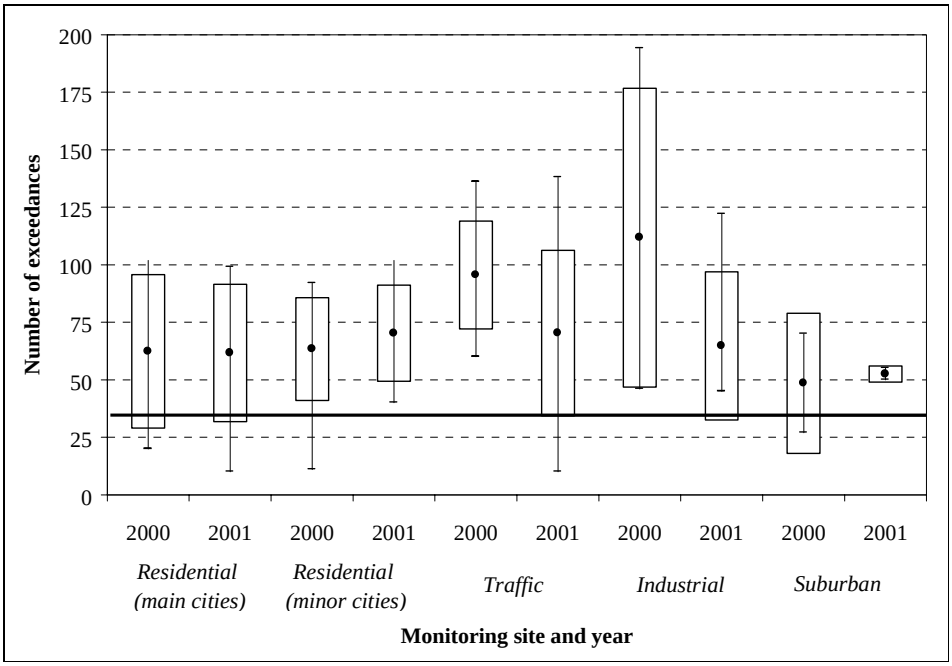

Figure 2. PM_{10} annual number of exceedances (50 μg m^{-3} for the daily average concentration) distribution: minimum, mean, maximum value and 2 standard deviation range around the mean value.

the margin of tolerance: the standard for the annual average is not attained at 70% and 45% of the 33 sites, in 2000 and 2001 respectively, whilst the corresponding non-attainment percentage for the daily average standard are 88% and 100%.

Weekly behaviours of PM_{10} concentrations

Weekly behaviours (Morawska et. al., 2002), separately evaluated for the cold and warm season, have been analysed for each monitoring site by pooling together the data sets of year 2000 and 2001 and the representative week has been subsequently calculated for each of the 5 groups of locations. The resulting behaviours are very similar for the residential and traffic exposed monitoring sites: as shown in the boxplots of Figure 3 and 4 referred to these latter group, a progressive increase of the daily concentration, reaching a maximum on Wednesdays, followed by a downward trend towards the minimum on Sundays is observed. With respect to the cold season, the warm season weekly behaviour is either characterised by lower concentration levels and by narrow ranges of daily concentration values. On average, at the traffic exposed sites Sundays concentration levels are about 25% lower than on Wednesdays (27.5% in winter and 23.1% in summer) and about 22% lower than on the mean of the working days (24.3% in winter and 21.4% in summer), as a consequence of the reduced circulating traffic volume. The corresponding figures for the residential sites are 22% (21.5% in winter and 23.3% in summer) and 19% (18% in winter and 19.4% in summer).

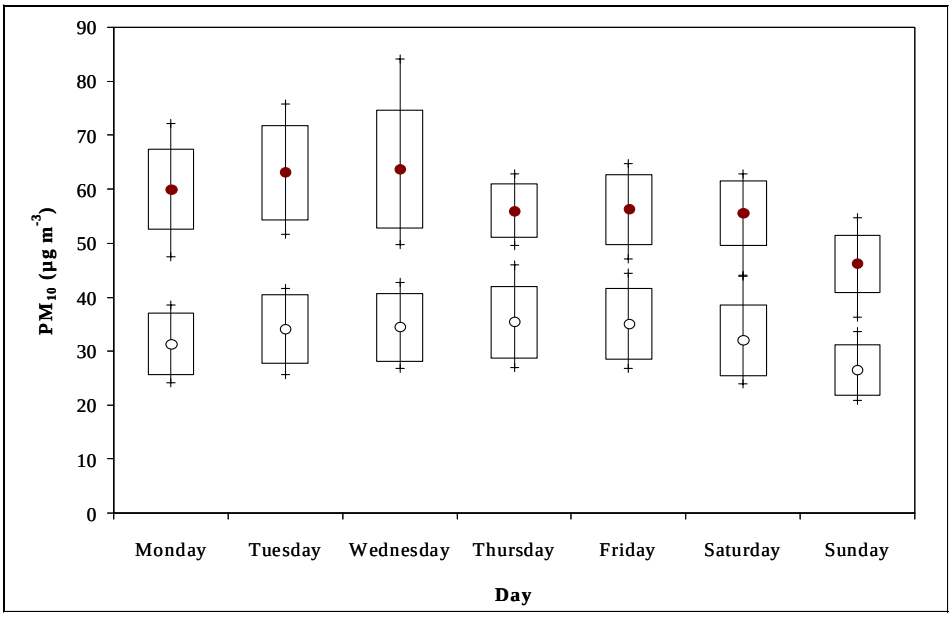

Figure 3. PM_{10} cold (black dots) and warm (white dots) season weekly behaviour; daily average concentrations distribution: minimum, mean, maximum value and 2 standard deviation range around the mean value – Traffic exposed sites.

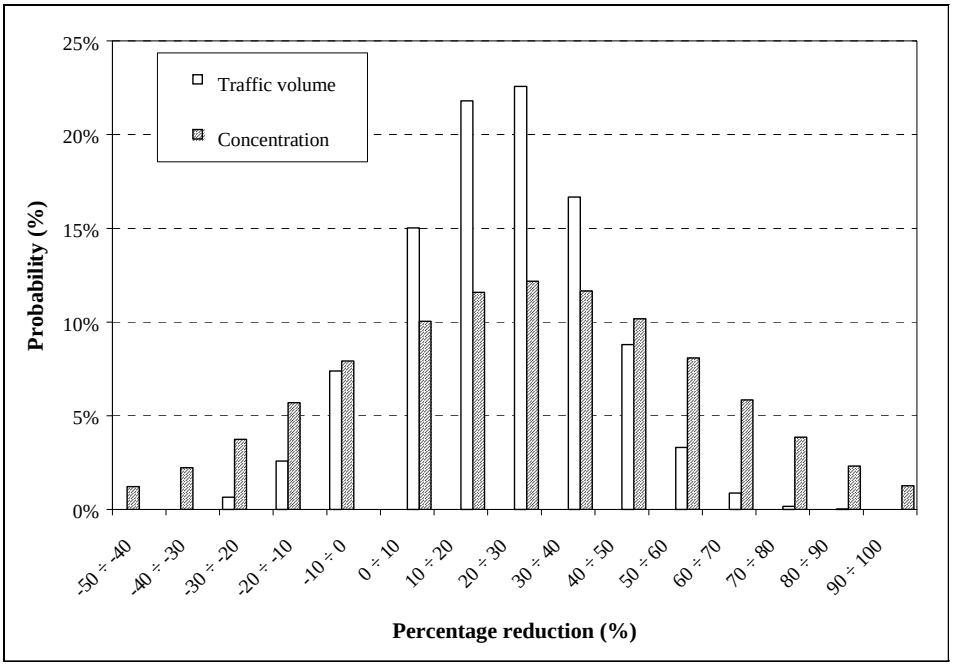

Figure 4. Probability distribution of percentage reduction of Sundays' traffic volume and PM_{10} daily average concentrations with respect to the mean working days levels – Residential site warm season.

Based on these acquisitions, a detailed analysis of the reductions in concentration levels observed on Sundays has been performed for each monitoring site considering all the weeks available and calculating the percentage reductions between the Sundays concentration levels and the average levels of the working days. The wide data sets obtained, 52 values for both cold and warm season in the 2000-2001 period, were subsequently analysed for their distribution; similar evaluations have been performed for the traffic where systematic measurements of the vehicular fluxes were available. The resulting probability distributions of percentage reduction of Sundays' traffic volume and PM_{10} daily average concentrations with respect to the mean working days levels are presented in Figure 4 for a residential site during the summer period. The percentage reductions of the traffic volume and of daily average concentrations show very similar and correlated behaviours ($R^2 = 0.8$), pointing out the role of the traffic as the primary source affecting the presence of fine particulate in the area.

DISCUSSION AND CONCLUSION

Annual PM_{10} concentration levels are quite uniform over the entire Lombardy region and daily data series are highly correlated, especially in the metropolitan

area of Milan, the main city of the region, standing for a substantial homogeneity of the distribution of emissions sources, essentially domestic heating and vehicular traffic, as well as of the secondary production processes of fine particulate. The annual average concentrations are about 40 μg m^{-3}, but ambient air heating required by TEOM measurements could lead to an underestimation of cold period concentrations because of the volatilisation of semi-volatile particle components and secondary organic compounds (Babich et al., 2000). According to preliminary evaluations, this artefact of measure could result in a 20-30% underestimation of the annual average concentration. Taking into account this fact, the standard for the annual average, attained at 27 out of the 33 sites in 2001, should be very difficult to be respected by 2005, when the prospected standard will come into force; even more problematic will be the situation for the standard for the daily average, currently hardly attained in half of the monitoring sites. On a weekly basis, the highest PM_{10} daily average concentrations are observed on Wednesdays and the lowest on Sundays, both at traffic exposed and residential sites. On average, the reduction of the traffic volume on Sundays, when light duty commercial vehicles and commuters' passenger cars are not circulating, results in concentration levels about 20% lower than on weekdays.

ACKNOWLEDGEMENTS

The authors wish to thank Regione Lombardia for financial aid to the research.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

DRY DEPOSITION FLUXES OF PARTICULATE PAHS AT THREE SITES AT KOREA IN 1999

JY Lee[1], SM Yi[2] and YP Kim[1,*]

ABSTRACT

The dry deposition fluxes of particulate PAHs were measured at three sites in August and November, 1999 in Korea and compared with the estimated values based on the ambient size distributions of PAHs. The measured dry deposition fluxes of total PAHs were between 6.9 and 9.9 μg m^{-2} day^{-1} in August and between 5.9 and 8.5 μg m^{-2} day^{-1} in November. Individual PAH fluxes were dominated by high molecular weight (MW) PAHs at all sampling sites in August. But dry deposition flux of low MW PAHs were higher than high MW PAHs at all sampling sites in November. By using the Sehmel-Hodgson model, the dry deposition velocities of PAHs as a function of particle size were estimated. Based on the measured atmospheric size distributions of particulate PAHs, dry deposition fluxes of PAHs were calculated and compared with the measured dry deposition fluxes. The measured and estimated PAHs fluxes were in good agreement. The calculated apparent deposition velocity of total particulate PAHs was 0.35±0.48cm s^{-1}.

INDEX TERMS

Dry deposition, PAHs, Korea, Deposition velocity, Deposition model

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) consist of two or more benzene rings interlinked in various arrangements. PAHs are mainly formed during incomplete combustion processes of organic matter. Several PAHs compounds are carcinogens

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or mutagenic compounds. Thus, measurement of ambient concentration of PAHs and their fluxes is important to understand the ambient characteristics of PAHs, to estimate their health effects, and to develop effective control strategies against them. Atmospheric deposition is an important mechanism controlling the fate of ambient trace species and their transfer from the atmosphere to the natural surfaces (Yi et al., 1997). Dry deposition fluxes are difficult to measure directly and instead are often estimated as the product of the dry deposition velocity, V_d and the corresponding pollutant concentration, C:

$$F = C \times V_d \tag{1}$$

Eq. (1) has been widely used due to its simplicity and easy applicability. However, particle size effect is not considered in Eq. (1) which should be important. Multi-step model has been used to estimate dry deposition flux more accurately:

(2)

where C_i is the particle concentration at the size interval i, n is the number of size cut, and V_{di} is the dry deposition velocity at the size interval i. The dry deposition velocity can be calculated either from Eq. (1) or from various size segregated models. In this work, dry deposition fluxes and the particles size distributions of PAHs were measured at three urban and rural areas in Korea in August and November of 1999 and the dry deposition fluxes were estimated, and compared with the measured fluxes (1) to understand the behavior of the dry deposition fluxes of individual PAH compounds and (2) to check applicability of a dry deposition model.

EXPERIMENT

Samples were taken at three sites (two urban areas; Seoul and Inchon, and one rural area; Yangsuri) between August 10 and 14 and between November 9 and 14, 1999 during daytime only without rain. The sampling and analytical method of PAHs used in this study are described in detail by Lee et al. (2003). Dry deposition samples were collected on the greased surrogated plates. A cascade impactor was used to collect particles with D_p d $\leq 9\ \mu$m and particles with $D_p > 9\ \mu$m were collected using a Coarse Particle Rotary Impactor (CPRI). The procedure for the analysis of PAHs consists of three steps: (1) extraction of the target compounds from the sample matrix, (2) clean-up of the extract, i.e., isolation of the target analytes from interfering compounds present in the extract, and (3) qualitative and quantitative instrumental analysis with a gas chromatography with a mass selective detector (HP GC 6890/MS 5974). Quality assurance and quality control (QA/QC) procedure of the data were performed for the chemical and instrumental analysis of the samples.

RESUTS AND DISCUSSION

The measured dry deposition fluxes of mass and total PAHs are shown in Table 1. The dry deposition fluxes of PAHs in rural area (Yangsuri) were comparable to those in urban areas (Seoul and Inchon). The PAHs fluxes for urban area in Korea (Seoul and Inchon) were lower than or similar to the values measured in Chicago, USA. But the particulate PAHs fluxes for rural area in Korea (Yangsuri) were about 6-50 times higher than those at in USA (Lee et al., 2003). It suggests serious PAHs pollution levels in rural areas of Korea due to local emission sources in addition to the transport from urban major source areas. The same observation has been also observed by Bae et al. (2002).

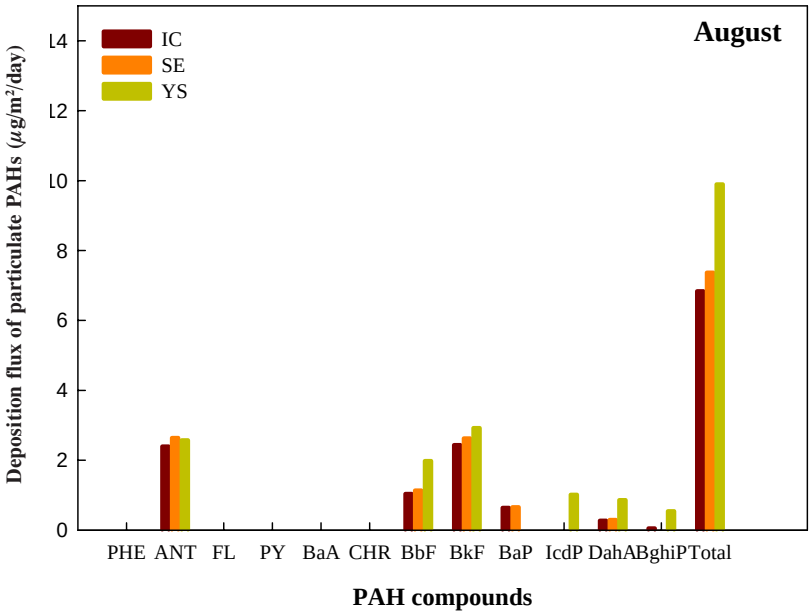
Figure 1 shows dry deposition fluxes of individual PAH measured at the sampling sites. Individual PAH fluxes were dominated by high molecular weight (MW) PAHs (BbF, BkF, BaP, and DahA) except ANT at all sampling sites in August. In November, dry deposition fluxes of low MW PAHs such as PHE, ANT, FL, PY, BaA, and CHR mainly emitted from diesel motor vehicles were distributed at all sampling sites. BaP is detected at all sites with the fluxes between 0.2 and 2.4 μg m^{-2} day^{-1}.

Table 1. Measured flux of total particles (μg m^{-2} day^{-1}) and PAHs (μg m^{-2} day^{-1}).

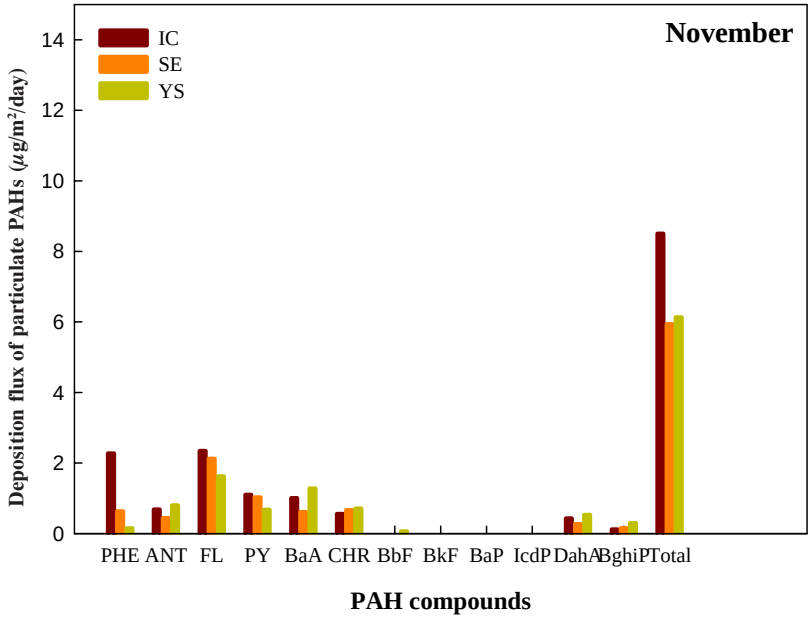
Seasons	Flux	Sites		
		Seoul	Inchon	Yangsuri
August, 1999	Mass	198.0	34.3	120.0
	∑PAHs	7.4	6.9	9.9
November, 1999	Mass	160.0	246.0	289.0
	∑PAHs	5.9	8.5	6.1

The Sehmel-Hodgson model (Sehmel and Hodgson, 1978) is used to estimate dry deposition velocities as a function of particles size. Details on this model are given by Yun et al. (2002). The measured total PAHs fluxes with a smooth greased plate agree well with the model estimate except Inchon in August as shown in Figure 2. Note that both mass and PAHs fluxes at Inchon in August were low because the sampling was carried out just after a rain shower. It demonstrates that the multi-step model can be used to estimate dry deposition fluxes of PAHs and particle size dependency of dry deposition velocities.

The estimated average dry deposition velocity of PAHs in this study based on Eq. (1) was 0.35±0.48 cm s^{-1}. Reported values for the particulate dry deposition velocities of PAHs from other studies are also summarized in Table 2. It should be noted that some of the values are not directly comparable to the result of this study because of the differences in experimental procedures, estimation techniques employed and physical properties of the compounds. The values reported by Sheu et al. (1996) were similar to the dry deposition velocities calculated in this study with the similar sampling procedures.

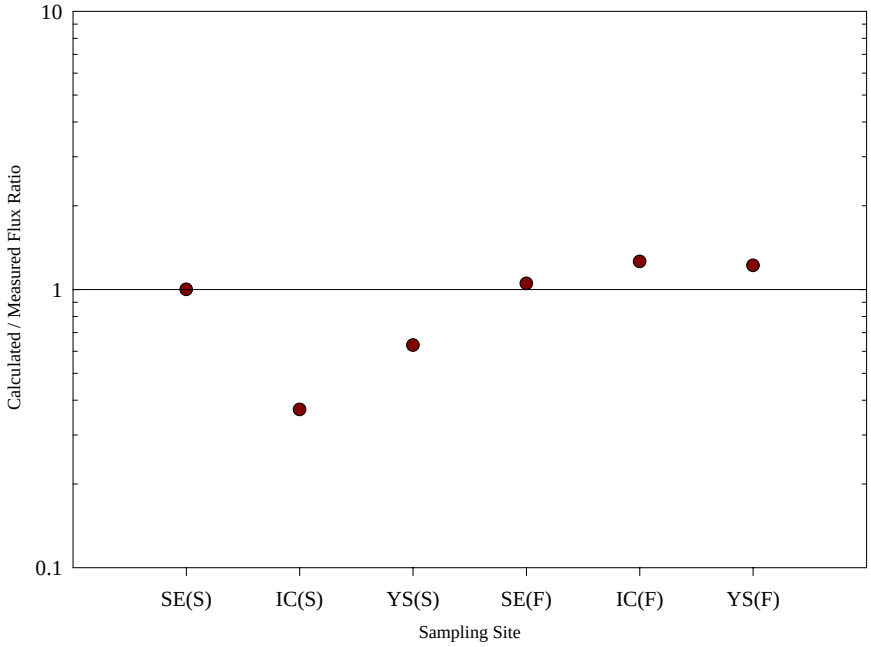


(a) August.



(b) November.

Figure 1. Histograms of the dry deposition fluxes of particulate individual PAH compounds measured with a dry deposition plate.



SE: Seoul, IC: Inchon, YS: Yangsuri.
(S): August, 1999 (F): November, 1999

Figure 2. The ratio of the calculated and the measured total particulate PAHs fluxes.

Table 2. Dry deposition velocity, *Vp*, for particulate PAHs.

Vp (cm s^{-1})	Comment	Reference
0.35±0.48	Dry deposition plate	This study
0.99	Calculated by a mass balance model	Mcveety and Hites (1988)
0.53	Gas + Particle	Mcveety and Hites (1988)
0.67~1.8	Dry deposition plate	Sheu et al. (1996)

ACKNOWLEDGMENT

This paper was supported by the Climate Environment System Research Center a SRC program funded by the Korea Science and Engineering Foundation and the Ministry of Environment, Korea.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

IMPROVING AIR QUALITY THROUGH LOCAL AIR QUALITY MANAGEMENT. A CRITICAL REVIEW OF BRITISH EXPERIENCE AND PRACTICE

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ABSTRACT

The Air Quality Management (AQM) framework in Great Britain is an effects-based, risk management process designed to provide a dynamic solution to public health issues associated with elevated concentrations of seven air pollutants. The statutory basis of the AQM process is provided by The Environment Act 1995, which required an Air Quality Strategy to be published by Government that introduced a series of air quality objectives in Regulations. The Act provides a framework in which national and local actions are required to identify and remediate areas of poor air quality. The Act places a series of duties and responsibilities upon Local Authorities to review and assess local air quality against air quality objectives set on the basis of best available epidemiological information. Local Authorities are required to identify areas in which air quality objectives will be exceeded by a target date and to declare them as Air Quality Management Areas (AQMA). In such locations a Local Authority must develop an Action Plan detailing both the measures to be taken and the time scale for implementation in order that air quality is improved within the AQMA. Local Authorities began the process of review and assessment in 1998 and the first round of the process concluded in 2001 following which some 130 Local Authorities have AQMAs. Following the first round of the review and assessment process, elements of the framework were subjected to an evaluation and the essential elements of this process have been confirmed as fit for purpose. Local authorities are now embarking on a second round of reviews and assessments, which although the

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guiding principles remain the same, the implementation has been streamlined. This paper will briefly review the experiences of local authorities in undertaking the first round of review and assessment and reflect on some early indications relating to the implementation of Round 2. Finally the transferability of the process to other Countries will be commented upon.

INDEX TERMS

Air quality management, review and assessment, local authorities, policy.

INTRODUCTION

The UK experience of air pollution has changed significantly since the smogs of the 1950s and 1960s (Longhurst *et al.*, 2002). At that time, air pollution resulted from the widespread use of coal, in industrial processes and for domestic heating. The Clean Air Acts of 1956 and 1968 addressed coal based air pollution, but new emissions sources and pollutants were increasing in significance with regards to effects on health. The most significant source change in Europe in the last 50 years being the increase of traffic, both in terms of vehicle numbers and vehicle kilometres travelled. The resulting increase in complexity of emissions sources has led to a need for a new regime to control emissions from a variety of sources. In 1990, the Government (DoE, 1990) introduced a new direction for air quality control building upon the existing technology-based controls by adding an *effects-based*, risk management approach through the formulation of a series of air quality standards (Longhurst *et al*, 1996). The new framework was termed *Local Air Quality Management* and was incorporated into the Environment Act 1995 (Part IV, Air Quality) (HM Government, 1995), the primary legislation for the process of air quality management. The Act applies only to Great Britain[1]. The Act required the Secretary of State to publish a National Air Quality Strategy (NAQS) (DoE, 1997), outlining methods and targets to be pursued by Government based on health effects standards for eight pollutants. The NAQS was reviewed in 1998/99 to reflect developments in European legislation, technological and scientific advances, improved air pollution modelling techniques and an increasingly improving understanding of the economic and social issues involved. Government have described the purpose of the Air Quality Strategy as "to make sure everyone can enjoy a level of ambient air quality in public places which poses no significant risk to health or quality of life" (DETR *et al*, 2000).

The Air Quality Strategy has set out a range of measures and policies to reduce emissions of regulated pollutants. Concentrations of lead, carbon monoxide, 1,3

[1] Northern Ireland introduced a bill in 2002 and intend to bring regulations into force in 2003. The bill in Northern Ireland is based on the experience in GB and in many aspects reflects the issues discussed in this paper.

butadiene are unlikely, to exceed objectives in the relevant year because of the measures and policies introduced nationally and enforced by government and its national agencies. In some industrial locations, sulphur dioxide, benzene (2010 objective) and lead exceedences may occur. However, in the case of nitrogen dioxide, PM_{10} and in some cases sulphur dioxide, local action is needed to complement and enhance the effect of national polices and actions. Such action is defined by the Act and Strategy as Local Air Quality Management (DETR *et al*, 2000). Section 82 of the Act required Local Authorities to undertake a review of local air quality and to assess the likelihood of achieving a number of health based air quality objectives. The objectives are derived from the standards but take into consideration economic and other practical implications. Where air quality objectives are not likely to be achieved, local authorities are required to designate Air Quality Management Areas (AQMAs) and put in place action plans to improve the local situation. An Air Quality Objective specified in the *Regulations*[2] may be exceeded only when public exposure occurs. This is the heart of the risk management approach to Local Air Quality Management, for the process of Review and Assessment is designed to identify those areas where poor air quality coincides with public exposure.

Local authorities have now finished the first *round* of reviews and assessments[3] and those local authorities who identified a problem and designated an air quality management area(s) are currently undertaking the action planning stage of the process. This remainder of this paper is a brief review of the first round of air quality reviews and assessments and reflects on some of the issues and lessons learnt prior to the second round of reviews and assessments. In 2003, local authorities have embarked on the second round of review and assessment, which is part of a rolling programme of review and assessments under a new annual reporting regime. See Defra *et al*. (2003) for details.

Review and assessment: Round 1

The first aspect of the LAQM regime is a three-stage review and assessment of air quality in the local authority's area, whereby each stage of the process increases in depth and complexity, consistent with the risk of failing to achieve the air quality objectives. The first stage of the process is essentially a desktop study of emissions sources within, and impacting on, the local authority area. Stage 2 introduces screening models and interpretation of available monitoring data. Stage 3 is a complex modelling and monitoring exercise assessing air quality concentrations against the specified objectives. At each stage pollutants can be omitted from the process where it can be shown that the air quality objectives are

[2] The Regulations incorporate the Air Quality Regulations 2000, the Air Quality (England) Amendment Regulations 2002 and their equivalents in Scotland and Wales.

[3] Commenced with the issuing of guidance in 1998 with the assessment phase being largely completed by the end of 2001

likely to be achieved[4]. On completion of a third stage review and assessment, and in areas where air quality objectives are predicted to exceed by their target date, an Air Quality Management Area (AQMA) must be designated. Where AQMAs have been designated, local authorities are required to prepare a written action plan identifying how the air quality objectives are to be achieved and improved upon in the designated area.

Review and assessment: Round 2

Defra commissioned an evaluation of Round 1 (Air Quality Consultants Ltd and AQM Resource Centre, UWE, 2002) and acting on the recommendations streamlined the approach for Round 2. Local authorities are now working within a two step process designed *to identify those matters that have changed since the last review and assessment, which might lead to a risk of an air quality objective being exceeded* (Defra *et al*., 2003). The first step of the process is an Updating and Screening Assessment, which is undertaken by all local authorities. This is based on a checklist to identify those matters that have changed since the first round was completed, and which may now require further assessment. Changes may include new monitoring data, new objectives, new sources, significant changes to existing sources or other local changes that may affect air quality. Where an updating and screening assessment has identified a **risk** that an air quality objective will be exceeded at a location with relevant exposure, the authority will be required to undertake a Detailed Assessment. The aim of the Detailed Assessment, which is comparable to Stage 3 in the first round of review and assessment, is to identify with reasonable certainty an further exceedence of an air quality objective, or conversely whether an existing AQMA needs to be amended or revoked.

Support mechanisms for local authorities

Following publication of the NAQS, local authorities expressed concern about the lack of necessary tools or indeed expertise to undertake their AQM responsibilities effectively. Central government responded by making available national resources (Elsom 1999) including guidance documents, Internet based information including monitored data, emissions inventories, and telephone and email help desks (Beattie *et al*, 2001b).

METHODS

Data presented here are from work undertaken by the authors for Defra and the devolved administrations (AQC Ltd and AQMRC, 2002) and also research results from a 5 year programme examining the implementation of the Environment

[4] For examples of reports produced at each stage of R&A see: www.uwe.ac.uk/aqm/review/examples/index.html

Act Part IV by urban local authorities in England[5]. The survey work is designed to identify, track and evaluate capacity in local authorities to manage local air quality. The methodology allows both technical (e.g. modelling, monitoring) and managerial (e.g. communication strategies, consultation, policy integration and joint working) capabilities to be considered. The surveys have included environmental professionals, who have been responsible for pollution legislation within local authorities and are, in most cases, co-ordinating their air quality management efforts, as well as other local authority professionals. For a fuller description of the methodology used, see Beattie *et al*. (2001b).

RESULTS

AQMAs designated

Annual mean nitrogen dioxide (NO_2) is the objective for which most exceedences are predicted[6]. There is also widespread exceedence of the short-term PM_{10} objective. Over 95% of AQMAs are designated as a result of traffic emissions. Four of the seven regulated pollutants are predicted to remain below their objective concentrations or to have no exceedences in areas of public exposure, and only predicted exceedences of the sulphur dioxide (SO_2) objectives will require a small proportion (5%), of authorities to declare AQMAs other than for nitrogen dioxide and particulates. Those AQMAs to be declared as a result of SO_2 are due to industrial point source emissions, or combinations of emissions from a number of such point sources, or other sources such as shipping.

Local Authority Practice

The results of the questionnaire surveys show a gradual increase in the technical capabilities of local authorities for undertaking air quality management. By 2001, all urban local authorities were undertaking some form of monitoring with the pollutants monitored reflecting those causing greatest problems in achieving the air quality objectives. Local authorities modelling work has increased from just 5% doing some sort of modelling in 1994 (Elsom & Crabbe, 1995), to 99% undertaking modelling in 2001. Questionnaire surveys have shown that some 50% of local authorities have an internal group working on air quality and that the majority are engaged in regional working on air quality management. Regional working is undertaken on policy and technical issues.

Studies of outside agencies in the review and assessment process show that health authorities' now give health advice relating to air pollution whilst the Environment Agency, who regulate large industrial sources in England and Wales, has in some

[5] For more information on research currently being undertaken at the University of the West of England, Bristol, see www.uwe.ac.uk/aqm/research

[6] An up to date record of declared AQMAs can be found at www.airquality.co.uk/archive/laqm/laqm.php

areas taken a proactive approach to managing air pollution sources in their jurisdiction. Throughout the four years of the survey their input into local air quality management has remained static. Over 90% of Environment Agency respondents had supplied information to local authorities even in 1998. The Highways Agency, who oversee the management of motorways and trunk roads in England and Wales, has had less involvement. The Highways Agency as a whole had little previous knowledge or expertise in air quality. Many exceedences of the air quality objectives are caused by Highways Agency sources and, with little involvement in the management, solutions will be difficult to secure by the deadline.

DISCUSSION

Local authorities have gained capacity and confidence in the review and assessment process having started from a heterogeneous position. In most cases local authorities have discharged their functions in an effective and efficient manner. Surprisingly however, the survey evidence points to a series of managerial as opposed to technical difficulties being faced by local authorities. Difficulties have been reported in policy integration and communication within local authorities. Questionnaire surveys have shown that local authorities do not appear to have the capability to manage air quality issues between local government departments. There have also been problems in communicating the outcomes of the review and assessment process to the public.

Local authorities have made substantial progress in managing a complex and dynamic atmospheric environment against a legislative framework that has seen substantial changes since its inception. Government Guidance issued for the process is intended to provide consistency by way of specifying the minimum expectations for the AQM process. However, survey data has illustrated a divergence in capability and achievement in LAQM practice within urban local authorities in England. A related study investigating rural local authorities (Ing *et al*, 2001) has shown urban areas to be in advance of rural authorities, suggesting an even greater divergence in practice between local authorities in the UK. A number of reasons may have caused this divergence, notably the greater experience of urban authorities in addressing more acute air pollution problems. Rural authorities, in contrast, are more financially constrained and have a potential absence of historical air pollution monitoring and modelling data and officer capability. With AQMAs being declared in smaller, rural locations these constraints are likely to hinder the subsequent action planning process.

The amended time-scale for reviewing and assessing air quality has caused problems for integrating air quality objectives into transport planning processes, one delivery mechanism for solutions to identified problems. The UK has, over the time-scale of the first round of reviews and assessments, experienced a rapid change in relation to transport policy. Local Transport Plans (LTPs) replaced the former Transport

Policy and Programmes (TPP) system for allocating resources for local transport capital expenditure (Beattie *et al*, 2001a). The first complete round of LTPs was completed in July 2000. The LTP process bids for funding for the next 5 years and in many cases the reviews and assessments were not completed in time[7].

Approach for Round 2 and Conclusions on the British Approach

Some of the difficulties discussed above have been addressed by the change in emphasis for Round 2. The divergence in local authority capacity (Ing *et al,* 2001) has been addressed by a prescriptive approach to government guidance. Local authorities supported this change. Reporting time scales have also been adjusted with a schedule now in place up to 2010.

Local authorities are at the stage of writing and implementing action plans following designation of AQMAs. The review and assessment process up to designation has been mainly a scientific process, although collaboration has been required with other departments and outside agencies, particularly for information such as traffic and health data. However, as local authorities move into implementing solutions through air quality action planning, the collaborative aspects of the process will be central to the success of air quality management.

CONCLUSIONS AND IMPLICATIONS

Evaluation of the evidence presented here suggests that the LAQM process in GB is an effective one, worthy of adoption by other nations. The AQM process in Great Britain is characterised by health-effects based objectives and a risk management approach. It provides a model against which other industrial states could evaluate their existing procedures. Clearly no system of environmental management is directly transferable between different countries without adjustment for local circumstances, history and philosophy. The air quality management process is no different. However, there are certain elements that are judged to work well. These include national support actions for local authority review and assessment such as training, internet support, help desks, prescriptive guidance and a high quality national monitoring network. The existence of a technical consensus about the way in which guidance for review and assessment should be implemented is a significant contributory factor to the success of the British system. In addition to the formal technical guidance commissioned and issued by Government, organisations such as the National Society for Clean Air and Environment Protection provided informal guidance on aspects of the process and this was supported by training activities. Important to the success of these activities was the support of Government for the approach being taken.

[7] There are parallel processes being implemented within the Devolved Administrations and London

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

AIR POLLUTION DISTRIBUTION ON TEMPORAL AND SPATIAL SCALES FOR NORTHERN PORTUGAL URBAN AREA OF CHAVES

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ABSTRACT

In recent years, the question of environmental protection has become a priority issue. One of the main objectives is to reduce the emission of gases that are harmful or that contribute to the greenhouse effect. To analyse the spatial distribution of a pollutant in a city, networks of air quality monitoring often use diffusion tubes as simple devices of measurement. In order to map the pollution distribution on temporal and spatial scales, we carried out NO_2 and O_3 measurement campaigns with passive diffusion measurement tubes located over the urban agglomeration. We have shown that over Chaves, a medium-sized city situated in northern Portugal, O_3 is spatially distributed with concentrations increasing from urban to suburban areas. The mean trend was observed to have lower values where higher values of NO_2 were found, which is due to the consumption of ozone in the NO to NO_2 conversion. The major concentrations of atmospheric NO_2 were near the urban centre, where traffic density is higher. In fact, values above 29 μg NO_2 m^{-3} were found only in the urban centre. This pattern was found in two campaigns in 2003. A traffic management policy, whose aims are to reduce the use of critical parts of the road network, has been proposed as a possible strategy for discouraging the use of private cars in the highly congested city centre. Local authorities or governments may also request an evaluation of the impact of new infrastructures or projects on the environment in order to ascertain whether the proposed development will be environmentally sustainable.

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INDEX TERMS

Air pollution distribution, Nitrogen dioxide, Ozone, Passive samplers, Urban air.

INTRODUCTION

Tropospheric ozone (O_3) is a secondary pollutant formed by chemical processes. There are no significant anthropogenic or natural emissions of ozone to the air. NO_2 is an important contributor to ozone formation in the lower atmosphere, whilst nitric oxide reacts with ozone temporarily removing it. The high reactivity of ozone to other atmospheric gases, along with photochemical production within the boundary layer results in large temporal and spatial variations in ambient concentration (Fowler *et al.*, 1997). Ozone concentrations in urban areas are generally lower than in the surrounding countryside due to the scavenging of ozone by NO emitted from vehicle exhaust emissions and other combustion sources.

Epidemiological studies have demonstrated that both acute and chronic exposure to nitrogen dioxide have effects on lung function, but ozone is the most irritant of the common air pollutants (Fowler *et al.*, 1997). For this reason, ambient air quality control is important for assessing of population exposure to air pollution. In Portugal the measured ozone concentrations are elevated, especially at higher altitudes in the northeast of the country (DGA, 2001). This is of great importance in the context of sustainable management strategies for the upland Mediterranean urban areas like Chaves city.

The main objectives of this study are to evaluate the air quality to provide relevant data through a proper characterisation of the air pollution situation in terms of spatial, temporal and compound resolution. This research also aims to introduce a cost-effective air pollutant monitoring technique in northern Portugal urban areas, demonstrating its potential as an important tool for decision-makers in urban air quality management.

METHODS

The study area is located in the city of Chaves at the northern border of Portugal with Spain. Chaves municipality includes an area of about 600,12 km^2, with a total population of 43 667, essentially resident in the city and in the suburban villages. Chaves is surrounded by non-industrialized municipalities, where the great majority are composed of rural grounds, forestry and small villages.

The measurement survey on urban sites was conducted in two distinct periods, each providing average concentrations of nitrogen dioxide (NO_2) and ozone (O_3) over a week. The first measurement campaign took place from January 4-11, 2003, and the second from March 23-30, 2003. All measurements were carried out with passive samplers. Passive samplers were installed at 22 measurement sites distributed according to a multiscale grid ranging from 500 to 1000 meters, with distances between

sites increasing from urban centre, where higher variations are expected, to suburban areas (Figure 1). A GPS (Global Positioning System) was used to determine geographic positions of the different monitoring sites used during the air quality monitoring campaign. All samplers were mounted in special shelters (an opaque cylindrical box) to protect them against weather conditions. Two passive samplers for NO_2 and O_3 were installed at each site, three of each in more than 50% of the sites, in order to assure the reproducibility of the measurement method. The passive samplers used were made and analysed in Passam AG Laboratory (under ISO/IEC 17025 accreditation). The collected NO_2 was determined spectrophotometrically by the Saltzmann method and the O_3 by the MBTH (3-methyl-2-benzothiazolinone hydrazone hydrochloride) method (Bernard *et al*., 1999).

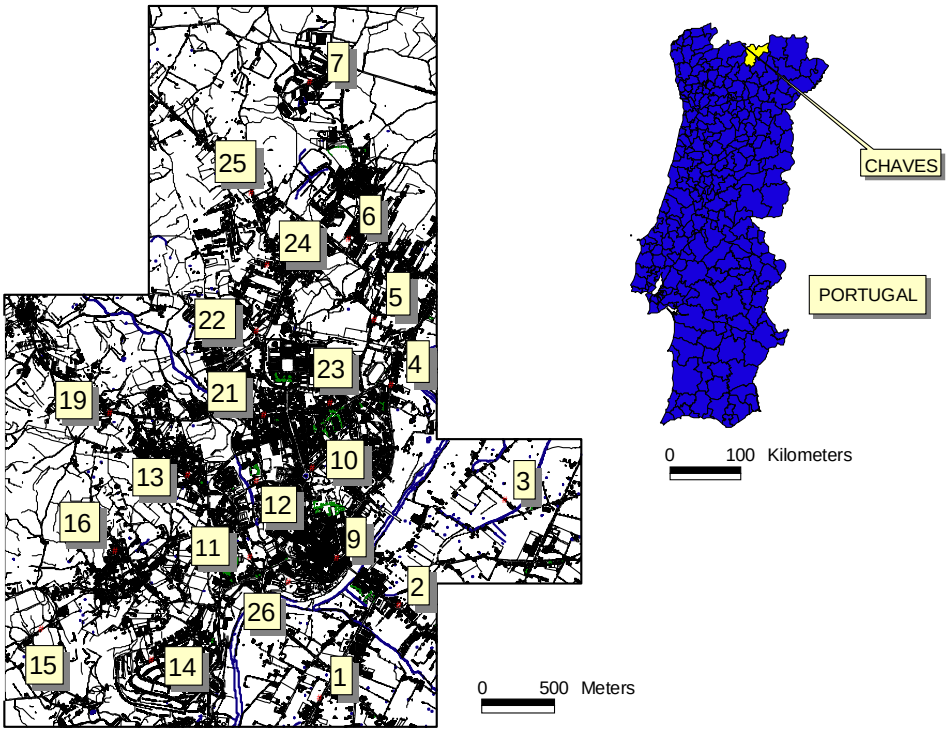

Figure 1. Measurement points distributed in the city of Chaves.

Aiming to fit the measured values with reference values, a comparison with Portuguese limit values was done, although the measured values cannot be paralleled to these values. A regression analysis was calculated to check the relationship degree between average concentration of NO_2 and O_3 in each campaign. The average values from the two campaigns were used to map NO_2 and O_3 in the study area during two different seasons. For this, the geostatistical algorithm, called ordinary kriging, was used.

RESULTS AND DISCUSSION

The two measurement campaigns in January and March provide valuable information about the air quality level over Chaves. The NO_2 and O_3 average concentrations at 22 sites in the city of Chaves are presented in Figure 2. The NO_2 values haven't exceeded the Portuguese annual limit value for human health protection in both campaigns. However, the highest values (41 and 46 mg m^{-3}) were approximately 76 and 85% in the first and second campaigns, respectively, of the legislated value. In the second

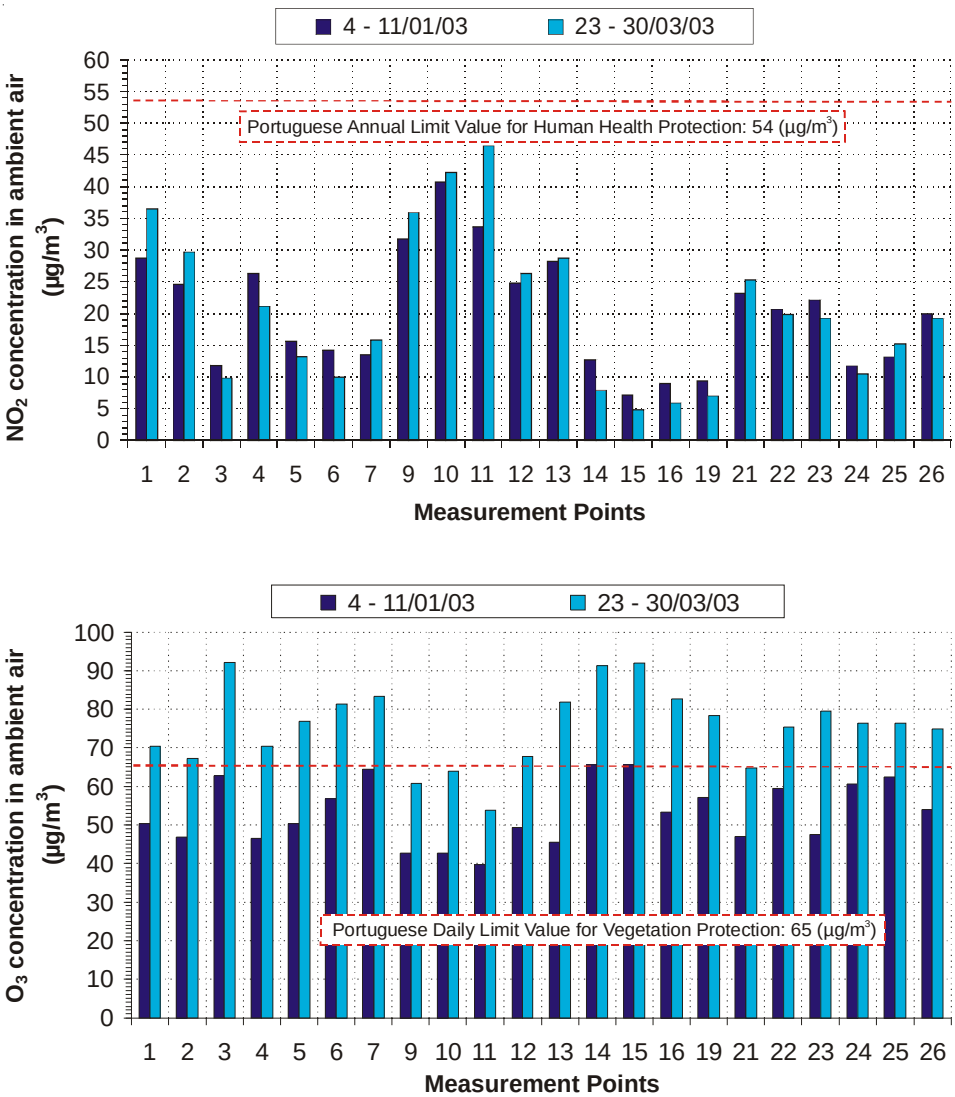

Figure 2. Nitrogen dioxide and ozone concentrations in ambient air from Chaves measured with passive samplers during two distinct periods (4-11/01/2003 and 23-30/03/2003).

campaign, 82% of the ozone values exceeded the Portuguese daily limit value for vegetation protection (65 mg m^{-3}). In truth, all the sites had an increased ozone concentration value during the second campaign. Note that the obtained results cannot be directly compared with the Portuguese limit values because both campaigns were too short in time; this comparison is only an indication.

Linear regression analysis was used to study the association between O_3 and NO_2 levels. Both periods showed a high inverse correlation between NO_2 concentration and O_3 concentration (Figure 3). However, it seems that in the first campaign, NO_2 and O_3 ambient air concentration values were slightly better correlated (R^2=0,72) than in the second campaign (R^2=0,70). This could be the result of: (1) increased radiation from January to March, inducing the production of ozone more effectively than the NO to NO_2 conversion; (2) higher concentrations of

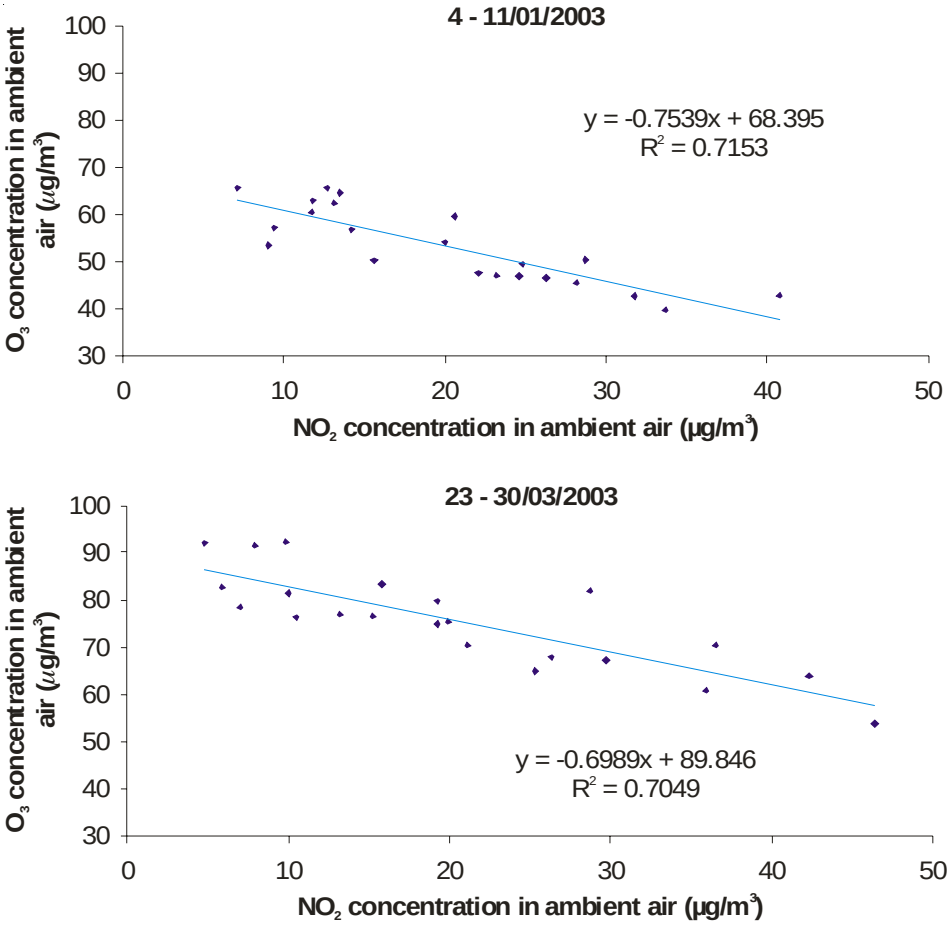

Figure 3. Linear regression analysis on the NO_2 with O_3 ambient air concentration values measured with passive samplers in the city of Chaves during two different periods (January and March 2003).

ozone tend to increase NO_2 levels above the local trend (Fowler *et al.*, 1997), which has effects on the slope of the linear regression; (3) strong dependence on ozone, increased in March, on regional air trends more than local trends.
The distribution of NO_2 and O_3 over the city in January and March is given in Figure 4. An emission inventory has shown that over Chaves the emission of

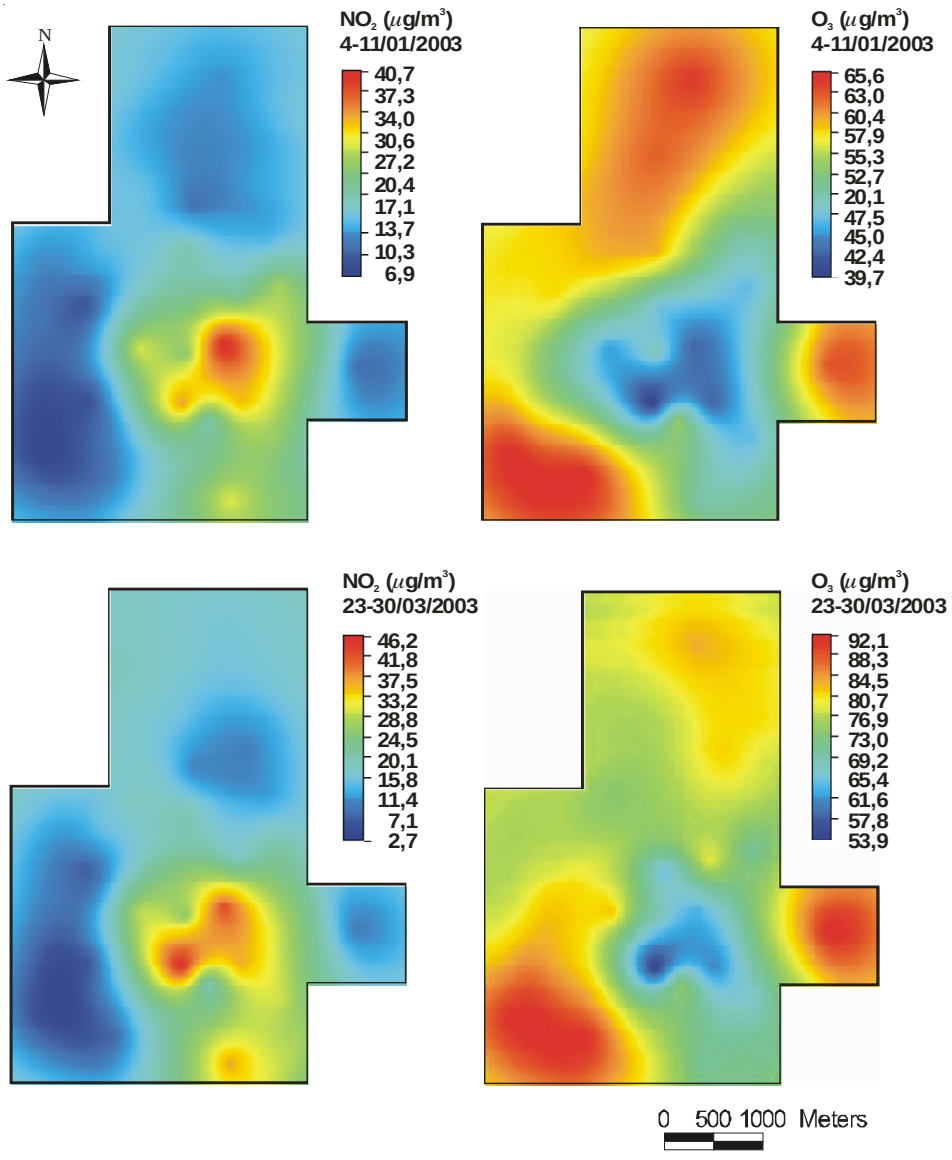

Figure 4. Distribution of nitrogen dioxide and ozone concentrations in Chaves, Portugal, during January 4-11, and March 23-30, 2003. Results from the geostatistic analysis.

nitrogen oxides (NO_x) is due more to the motor vehicle emissions than to the industrial emissions (Marques, 2003 not published data). Thus, high concentrations of NO_2 are observed near the urban centre, where traffic density is higher. In fact, values above 29 $\mu g/m^3$ are found only in the urban centre. This pattern is found in both campaigns. Background values (under 14 $\mu g/m^3$) were found almost homogeneously throughout the suburban area of Chaves. The contribution from urban mobile sources increased the background levels in the urban centre by a factor of three to four.

Ozone is spatially distributed with concentrations increasing from urban to suburban areas. The mean trend was observed to have lower values where higher values of NO_2 were found, which is due to the consumption of ozone in the NO to NO_2 conversion. Differences in the configuration of the maps obtained from each campaign were probably a result of different meteorological conditions observed in each sampling period. Mobile source emissions from the urban centre lead to a reduction in ozone values of about 40 to 41% for the first and second campaign, respectively.

The findings of this study are in agreement with what is generally known about the environmental conditions for O_3 pollution, namely, the importance of motor vehicle traffic. In this context, a traffic management policy, whose aims are to reduce the use of critical parts of the road network, is needed to discourage the use of private cars in the highly congested city centre. Local authorities or governments may also request an evaluation of the environmental effects of new infrastructures or projects in order to ascertain whether the proposed development will be environmentally sustainable.

CONCLUSION AND IMPLICATIONS

The use of passive samplers, in combination with a careful selection of measurement sites, has shown to be an important method for air quality management, which can be applied during a relatively short time period at reasonable costs. Now, the municipality of Chaves possesses a cartographic representation of NO_2 and O_3 distribution over the city, even if this representation is influenced by the choice of sampling sites. Low O_3 concentrations were noted in areas with dense traffic. The concentrations therefore increased with distance from the city centre and were highest in suburban areas. The simple regression of NO_2 concentration with O_3 shows that the two gases are negatively correlated. In the study area, NO_2 is in its majority a by-product of mobile sources. Major concentrations of NO_2 are observed near the urban centre, where traffic density is higher. This finding, in conjunction with the factors influencing NO_2 and O_3 levels, can be used to assess the level of the city dwellers personal exposure to atmospheric pollution. Therefore, it is very important to realize the seasonal influences in more comparisons of data from passive sampling in this city, particularly in the summer.

ACKNOWLEDGEMENTS

We thank Engineer Paulo Gomes from SONDARLAB and the environmental engineering students from Universidade de Trás-os-Montes e Alto Douro, Tânia Pereira, Elsa Gomes, Paula Esteves and Joana Almeida for their assistance in this research.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

IMPROVED POINT SOURCE INVENTORY - DEMONSTRATION OF THE NEW REPORTING SOFTWARE FOR CONSOLIDATED REPORTING OF CRITERIA AND TOXIC EMISSIONS

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ABSTRACT

Starting with the 2000-2001 reporting period the South Coast Air Quality Management District (SCAQMD) consolidated both the Annual Emissions Inventory Report Program and the Toxic Emissions Inventory Report Program to establish a comprehensive point source emission inventory for criteria and toxic emissions. The consolidated Annual Emissions Reports (AER) filed by over 3,000 facilities provide the basis for the SCAQMD point source emissions inventory. The challenging task of consolidation was greatly facilitated by Ecotek's development and implementation of a new AER reporting software.

The new AER reporting software was instrumental in providing a simplified reporting option allowing the linkage and integration between the criteria and toxic air pollutants. Furthermore, the new AER reporting software is user friendly, reduces chances for errors, improves the data quality and accuracy, and assists the users with the transition to the new consolidated program. Accuracy of the emissions inventory has significant implications since it is used for planning, rule development, and emission fee calculations, as well as determining the applicability of federal, state, or local programs. The software increased the AER program's overall efficiency both at user and District levels.

This demonstration will illustrate the use of the new SCAQMD AER reporting software for consolidated reporting of criteria and toxic emissions.

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INDEX TERMS

Software, Program Funding, Criteria and Toxic Emissions, Emissions Inventory, Point Source Emissions

INTRODUCTION

Beginning in 1995-96, the SCAQMD privatized portions of the Annual Emissions Reporting Program, which were historically implemented by the SCAQMD staff, to enhance the Program's overall efficiency, reduce costs, improve services to facilities, and enable the SCAQMD staff to conduct a more detailed engineering audit of the annual emissions reports. For the last seven years, Ecotek has been SCAQMD's consultant for the AER program. Ecotek's responsibilities include assistance with design of the reporting forms and supplemental instructions, software development, information dissemination and public assistance including internet support, information tracking and record keeping, compilation of data files relative to emissions and fees, and performing limited quality assurance (QA) and quality control (QC) of the emissions and fee data.

Historically the SCAQMD had two separate inventory programs: Annual Emission Report and Assembly Bill 2588 - state wide Air Toxic "Hot Spot" Program (AB2588). Detailed information about those programs is available at AQMD's web site at www.aqmd.gov. Those programs resulted in two separate databases. In order to optimize and to increase the utilization of the information collected in those distinct databases, the SCAQMD decided to: 1) streamline the reporting process, 2) improve the toxic emission data quality, 3) minimize necessary financial and human resources for both the facilities and the SCAQMD, 4) meet Air Resource Board (ARB) and Environmental Protection Agency (EPA) needs, considering that those agencies are moving toward consolidation of toxic and criteria pollutant reporting, and 5) most importantly, provide a linkage and consistency between emission data for reported criteria and toxic pollutants.

SCAQMD CONSOLIDATED ANNUAL EMISSION REPORT

Facilities Required to Report

At the beginning of each reporting cycle, the SCAQMD develops a mailing list of facilities potentially subject to the consolidated AER program, which include:

- Facilities subject to SCAQMD Rule 301(e) http://www.aqmd.gov/rules/html/r301.html) which emit:
    1) 4 tons per year or more of any of the criteria pollutants of Volatile Organic Compound (VOC), Nitrogen Oxides (NO_x), Sulfur Oxides (SO_x), Particulate Matter (PM), and/or
    2) More than 100 tons per year of the criteria pollutant Carbon Monoxide (CO), and/or

3) Any of the Toxic Air Contaminants (TACs) or Ozone Depleting Compounds (ODCs) listed in Rule 301(e) Table IV (24 toxic families including more than 68 individual compounds) exceeding specified thresholds.

- Facilities in the AB2588 Program, which are required to report all above mentioned criteria pollutants and all AB2588 toxics (73 toxic families including more than 176 individual compounds) once every four-years.

Under SCAQMD Rule 301(e), facilities subject to the AER Program are required to report their emissions and pay corresponding fees. Currently, the mailing list includes over 3,000 facilities. Although those facilities represent only about 12% of the permitted stationary source facilities in the SCAQMD, emissions attributed to these facilities represent the approximately 90% of the point source emissions.

AER Program overview

The AER Program relies on a number of forms that are designed specifically for collecting emissions and fees based on the specific type of equipment, process, or industry. Currently, there is a total of 44 forms in the AER Program consisting of detailed criteria pollutant forms, detailed toxic forms, summary forms and general information forms. These forms were designed by SCAQMD staff and incorporated into the software by Ecotek. Given the number and complexity of the forms the software plays a critical role in streamlining the reporting process. Some of the forms are designed for the more common emission source categories such as internal and external combustion equipment, coatings and solvents, fugitives and above-ground tanks while others are intended for specific industries such as refineries, power plants, body shops, and dry cleaners. Emissions calculations methodology is built-in to the forms and are generally calculated based on the fuel, material, throughput, emission factor, and control efficiency, if applicable. Step by step instructions provide guidance to the user on necessary data, common sources of data and emissions calculations. Every year, the forms and instructions are reviewed in order to reflect the latest available emission factors, calculation guidelines, and SCAQMD rules and policies, as well as to improve the forms based on the lessons learned.
Typically, the reporting process for facilities consists of the following steps:

- Read the instructions;
- Identify the applicable forms;
- Following the step-by-step instructions of the specific form: collect fuel, material usage and throughput data, and identify the applicable emission factors;
- Complete applicable forms based on facility-specific data.

An emission source category refers to a single piece or a group of identical equipment or process (unique fuel, material, activity code, and criteria and toxic

emission factors) as reported on each reference row of each detailed form. Facilities are first required to report the criteria pollutant emissions from specific source (emission source category) on the applicable criteria emission forms, in order to create an Emissions Source reference. The Emission Source reference consists of the form name and row number where each specific source is first reported. Using the same Emission Source reference, facilities are then required to report their toxic emissions on the applicable toxic forms, thus linking the criteria and toxic data.

Upon receipt of the reports, the data is entered into a database and data files containing detailed emissions and fees data for all facilities filing annual emission reports are generated. The QA/QC of the reported data are conducted to identify and correct any discrepancies and errors. Data files are then submitted to the SCAQMD for engineering audits.

Detailed Information about the Annual Emissions reporting format is maintained on an Internet site created by Ecotek for the SCAQMD (http://www.ecotek.com/aqmd/). All printed program information and software programs are available for download (http://www.ecotek.com/aqmd/Download.htm).

THE EMISSIONS REPORTING SOFTWARE

One of the main values of the software is that it guides the user and eliminates the most common mistakes illustrated in Table 1. The software was particularly helpful in conveying the new reporting requirements of the consolidated AER Program considering:

- The additional complexity resulting from the consolidation (e.g., new forms),
- The need to accommodate over 176 toxic compounds required to be reported by some facilities,
- The linkage that has to be established between each emission source and multiple toxic compounds,
- The possibility of single combustion source resulting in emissions of up to 40 different toxic compounds,
- The number of individual entries on Form TAC at times reaching or exceeding 800.

It also allows time and resource savings, which can then be used by the SCAQMD for QA/QC or for future program improvements. Since its first introduction in 1996, the software has been continuously enhanced. In addition to the modifications that reflected SCAQMD's changes to the reporting program, the software has constantly been improved to be more user-friendly through additional features, performance improvement, more on-screen reminders, more warnings for possible problem situations and more navigational features.

Table 1. List of the Most Useful Software Features That Result in an Improved Data.

Common Mistake or Problem	Software Feature	Benefits of Software Use
• User not computer inclined. • Apprehensive about software.	• AER format provided on CD. • Improved Installation.	• User friendly with step-by-step instructions. • Installation fast, easy and simple.
• Over 40 forms to choose from, often confusing for the paper user.	• Form Selection in Interview Module.	• Forms automatically selected based on user's answers. • Guides the user from Start to Conclusion.
• Lengthy report preparation. • Don't know where to start.	• Import function.	• Allows previous year data to be simply imported /updated. • Provides for consistency and completeness of the reports.
• Incorrect values listed.	• Pull-down menus. • Build-in default emission factors.	• Provides only correct choices. • Directs user to enter data in the assigned format. • Default emission factors are automatically used by checking box.
• Wrong units, incorrect format, material reported in pounds and emission factor listed in lbs/gal, data exceeds common thresholds.	• Pop-up labels. • On screen reminders. • Build-in warnings. • Validation checks.	• Hints on needed information. • Eliminates common errors and incorrect format. • Directs the user. • Warns the user if data entered exceeds thresholds.
• Unit conversion errors.	• Unit Conversion Calculator.	• Automatically converts the commonly used units. • Eliminates unit conversion errors.
• Arithmetic errors. • Incorrect fees assigned.	• Automatic calculation of emissions and fees.	• Eliminates arithmetic errors in calculations. • Eliminates incorrect fees.
• Incorrect transfer.	• Automatic transfer.	• Eliminates incorrect transfer between forms. • Automatically creates all summary forms.
• Missing data. • Incomplete submittal. • Errors. • Invalid data.	• Audit. • Submit Module.	• Audit automatically performed. User has to correct errors prior to submitting the data. • Warns user of the data that exceeds the thresholds. • Creates submittal file and prints submittal forms.
• Uncertainty or guesswork.	• Help System.	• Provides context sensitive full online Help for all software features.
• Incomplete supporting documentation or submittal.	• Submittal Checklist.	• Based on data entered, generates checklist to assist user in verifying the completeness of the submittal including supporting documentation.

Improvements to the AER program benefit both the reporting facilities and the SCAQMD. The AER software meets this ideal by providing numerous benefits. The Software improves the quality of AER submittals and therefore data accuracy of the Point Source inventory for numerous reasons:

- Data submittals are complete. Submitted data conforms to validation requirements that are programmed into the software.
- Submitted data conforms to calculation methodologies and report preparation procedures. This is in sharp contrast to the unlimited degrees of freedom available to facilities in completing paper forms.

- Data transfer mistakes are eliminated since data is automatically transferred between forms and summary forms.
- Software simplifies the report preparation and the submittal process. Emissions and fees are calculated for the facility after throughput and emission factors are entered. Uncertainty and guesswork are reduced since helpful pop-up hints and on-line help are provided.
- Software contributes to the consistency and the completeness of the reports from year to year. Software can be enhanced each year to refine features, add new features, and incorporate user feedback.
- Software reduces the time required to prepare an AER and therefore saves facilities money. This obviously benefits the facilities, but also benefits the SCAQMD. Reducing the time required to prepare the AER should also reduce the number of late filers. It is more efficient to perform batch processing according to a smooth flow process, rather than perform exception processing.
- The AER data file provides a valuable starting point for the next year AER submittal since this data can be imported and updated for the next year. This is a key benefit to facilities because after they invested the effort in the first year of their software submittal, future years are much simpler since data only needs to be updated. This can help contribute to consistency and completeness of reports from year to year.
- AER software facilitated the development of automated data processing and QA/QC screening. A data entry system was developed to collect submitted data, facilitate quality control review of submittals, and track the processing of submittals.
- AER software submittals also reduce the time and effort involved with data processing, data validation, and quality control review. A software submittal is simply uploaded from the data submittal disk. This is one of the most significant benefits of software submittals since the data entry process is eliminated. Uploading a software submittal can be done within a minute whereas the time required to process an individual paper submittal can range from less than an hour to several days or sometimes weeks.
- Simplifying the reporting process has improved the quality of the reported data thus reducing the level of effort required by SCAQMD to produce quality emissions inventories. Quality control review work is limited to evaluating certain review flags that are triggered based on SCAQMD criteria.
- The time saved as a result of improved data quality has allowed for expansion of QA/QC criteria and efforts. The QA/QC criteria have increased from 19 during the 1995-96 reporting period to 51 in the 2001-2002 reporting period.
- As a result of greater use of the reporting software, the number of problematic flags was drastically reduced.

Table 2. Selected flags reduction.

Flag #	Flag Description	Flags triggered in 1995-1996	Flags triggered in 2001-2002
81	Emission Factor >1 kg/kg	350	4
91	Fee Discrepancy	708	170
93	>2 Tons Discrepancy	259	50

What is the software's performance and industry acceptance?

The software has helped the SCAQMD to improve data quality and program efficiency, and has made the reporting process significantly easier and more efficient for the facilities in the program. Numerous software features, on-going improvements based on facility inputs, and user-friendliness have resulted in grater software use, despite added complexity due to the consolidation. The success of this AER reporting software can be measured by the large and constantly growing number of facilities choosing software as a reporting option. In this past year, 82% of the reporting facilities used the AER reporting software.

It is worth noting that software usage has been consistently higher (89% last year) among the facilities emitting 10 tons or more of criteria pollutants.

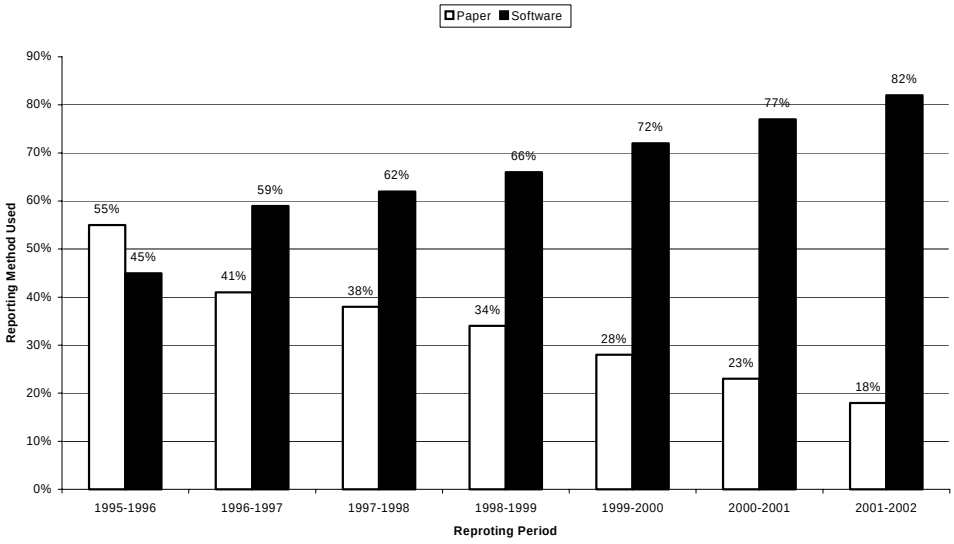

Figure 1. Percentage of Overall Reporting Method Used

CONCLUSION

Merging and Streamlining of both programs, historical AER and AB2588 through this consolidation effort has resulted in an improved, optimized and integrated emission inventory.

The overall efficiency of the consolidated Annual Emission Reporting Program was greatly improved through reporting software and automated data processing and auditing procedures. The new AER reporting software reduces errors, improves the data quality and accuracy, and assists the users with the transition to the new consolidated program. The new user-friendly AER reporting software was instrumental in providing a simplified reporting option for linking and integrating the criteria and toxic emissions data.

ACKNOWLEDGEMENTS

The authors would like to express their gratitude to Michael Meskal and Erna Milos who provided valuable suggestions in the preparation of this paper.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

EVALUATION OF THE AIR QUALITY STATE IN THE REPUBLIC OF CROATIA WITH NATIONAL ACTION PLAN

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ABSTRACT

Within the framework of the National Environmental Strategy and National Environmental Action Plan (Official gazette of the Republic of Croatia, No. 46/ 02) the Republic of Croatia has determined its long-term emission reduction objectives for the main air pollutants. The objectives are determined in accordance with exisiting and future obligations under the Convention on Long-range Transboundary Air Pollution (LRTAP) and its protocols.
Emission pollutants calculation has started in Croatia under obligations arisen from the ratified UNECE LRTAP Convention and it has been implemented in accordance with the European EMEP/CORINAIR methodology. The necessity to prepare the emission calculation arises from the Law on Air Quality Protecion as well (Official gazette, No 48/95). The emission calculation includes five "major" pollutants (SO_2, NO_2, CO, NMVOC, NH_3), nine heavy metals (Cd, Pb, Hg, As, Cr, Cu, Ni, Se i Zn) and four groups of persistent organic pollutants (PAH, HCH, HCB i PCDD/F).
Based on the last Environmental State Report, the paper gives a review of the major emission pollutants, emission trends for the period 1990 to 2000 as well as air quality assessment and trends in urban settlements. The major elements of air protection policy are given as it is defined within the National Environmental Strategy and National Environmental Action Plan for the period until 2010.

INDEX TERMS

Emission pollutants, air quality

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INTRODUCTION

In Croatia, the first calculation of pollutant emissions was performed for the year 1990, by including Croatia into the European project of data base of air pollutants-CORINAIR. Today, the calculation is being performed in compliance with the obligations under the 1979 Convention on Long-range Transboundary Air Pollution (CLRTAP) of the United Nations Economic Commission for Europe (UNECE), and according to the SNAP97 nomenclature, EMEP/CORINAIR methodology. The necessity to prepare the emission calculation arises from the Law on Air Quality Protection as well (Official gazette, No 48/95).

The emission calculation includes five «major» pollutants (sulphur dioxide SO_2, nitrogen dioxide NO_2, carbon monoxide CO, non-methane volatile organic compounds NMVOC and ammonia NH_3), nine heavy metals (cadmium, lead, mercury, arsenic, chromium, copper, nickel, selenium and zinc) and four groups of persistent organic pollutants (polycyclic aromatic hydrocarbons PAHs, pesticides and dioxins/furans PCDD/F).

The Law on Air Quality Protection distinguishes the following air quality categories:

- air quality category I – clean or slightly polluted air (recommended air quality values RV not exceeded);
- air quality category II – moderately polluted air (recommended values are exceeded, but not air quality limit values LV);
- air quality category III – excessively polluted air (air quality limit values LV exceeded).

The recommended (RV) and limit concentration values (LV) for particular harmful substances expressed in terms of statistical values are prescribed by the By-Law on Recommended and Limit Values on Ambient Air Quality (Official gazette, No 101/96, 2/97).

In Croatia ambient air quality monitoring started in 1963 at stations for monitoring smoke and sulphur dioxide concentrations in Zagreb. The number of towns and/or settlements in which air quality is monitored has been increasing from year to year, but so has also the number of pollution cases monitored in particular towns.

POLLUTANT EMISSIONS INTO THE AIR IN CROATIA

Emission calculation for major pollutants

Pollutant emissions into the air have been reduced during the last ten years and air quality has improved. The 2000 pollutant emissions from anthropogenic sources into the air were considerably lower than those of 1990: SO_2 by 68%, NO_2 by 12.4%, CO by 38.6%, NMVOC by 24% and NH3 by 39.1%.

Emission of SO_2 and NO_2. In 2000 a substantial reduction in SO_2 emissions was recorded in relation to the previous year, primarily in the power industry sector, which is a consequence of the drop in generation of electrical energy by thermal power plants of the Croatian Electric Power Industry, and the combustion of coal

with lower sulphur content (< 1%) in the Plomin Thermal Power Plant, including the installation of the desulphurization plant in Plomin 2 Thermal Power Plant. Ten years ago Plomin Thermal Power Plant emitted 44,000 tonnes of SO_2 yearly, but in 2000, with power generation three times as big, the emission was 3,654 tonnes. The major part of the SO_2 emission in 2000 is a consequence of fuel combustion in thermal power plants and plants for energy transformation (51%), combustion in industry contributes to the emission with 21% and road traffic and non-road traffic contribute to the total emission with about 15%.

In 2000 total *NO_2 emissions* were 77.5 kt, i.e., about 12% lower as compared to the total emission in 1990**.** The highest share of NO_2 emissions in 2000 comes from traffic (44%), followed by other mobile sources and machinery (22%). Stationary power sources emitted 14% of the total emission. The NO_2 emission is mainly the consequence of liquid fuel combustion.

Emission trends of SO_2 and NO_2 for the period 1990-2000 in Croatia is given in Figure 1.

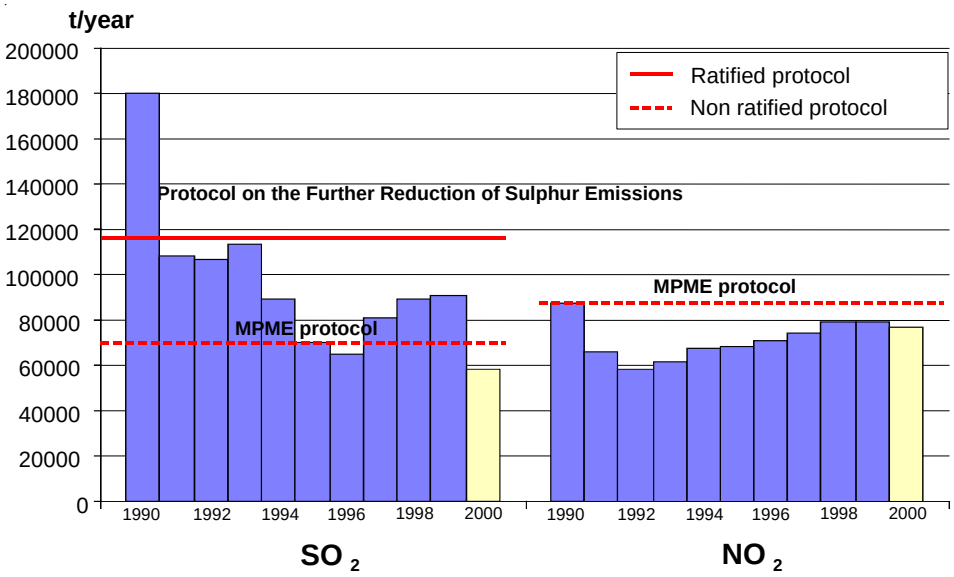

Figure 1. Emission trends of SO_2 and NO_2 in the period 1990-2000 for Croatia

*Emissions of CO, NMVOC and NH_3***.** In 2000 emissions of CO, NMVOC and NH_3 were maintained approximately at the same level of emissions as in the previous few years, but in relation to 1990 total emissions are substantial lowers.

The *CO emissions* are a consequence of incomplete fuel combustion, mostly in vehicle engines and small combustion plants. In the year 2000 the total CO emission was about 423 kt. The major part of the CO emission in 2000 comes from road traffic and non-road traffic (53%), while combustion in commercial, institutional and residential sectors (30%), combustion in industry (8%) and other sources contribute to the total emission with 9%.

In 2000 the total *emission of NMVOC* was 146 kt, whereof 45% came from natural sources (leaf and coniferous forests). The anthropogenic sources of emissions are mostly road traffic (24% of the total emission), the sector of solvent use (13%) and production processes (5%). Emission from the non-industry sector is relatively low (6%) coming from combustion of firewood and coal in small combustion installations. A significant part of emission is a consequence of fuel evaporation during oil production in refineries, then in the procedure of fuel pour off at the petrol stations and in the transport and distribution of liquid oil fuels as well (4%).
In 2000, *ammonia emissions* were 30.1 kt. Excluding emissions coming from nature (natural soil and vegetation), the emission was by 25% lower and amounts to 22.6 kt. The anthropogenic sources of emissions are mostly agriculture (62%), specifically from cattle excrement and use of mineral fertilisers**,** then from industry producing ammonia, nitrogen acid an fertilizers (11%). After 1992, emissions of NH_3 have mostly maintained the same level.
The emission trends of CO, NMVOC and NH_3 in the period 1990-2000 is given in Figure 2.

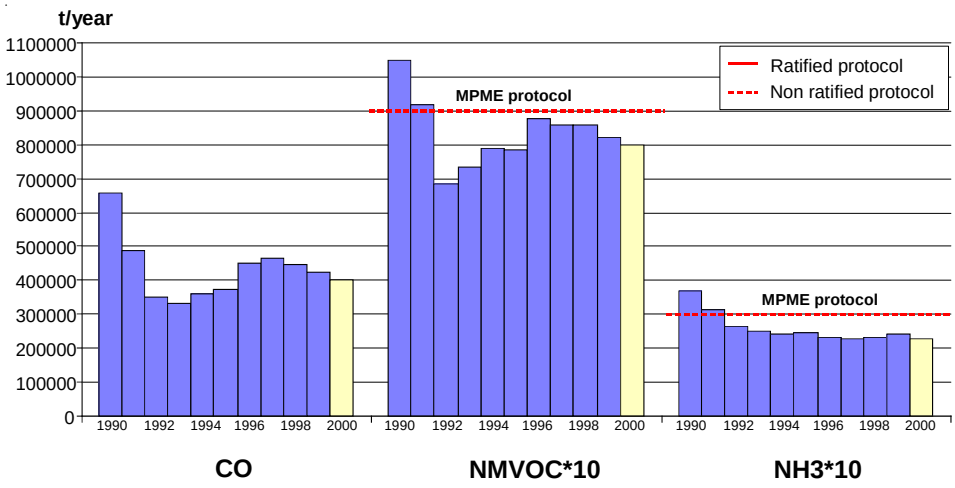

Figure 2. Emission trends of CO, NMVOC i NH_3 for the period 1990-2000 in Croatia

Heavy metals emission

Emissions of all nine heavy metals in 2000 show significant drop in relation to the emission in 1990: Pb 68%, Cr 67%, Hg 64%, As 53%, Ni 42%, Cd 37%, Cu 33%, Se 30% and Zn 27%.

Lead (Pb) emissions are predominantly caused by road transport (93% in the year 2000). The drop in lead emission is a result of an increased share of unleaded petrol (65.7% of the total consumption in 2000). Emissions are also produced by other mobile sources (about 4%), stationary power sources (1.1%) and production processes without fuel combustion (1.7%).

Mercury (Hg) emissions are mainly a consequence of combustion of firewood in small household furnaces (41%), combustion of natural gas or coal in stationary power sources (29%) and in industry (26%). Mercury is also emitted in cement industry, by electric arc furnaces in steel production, in the production of non-ferrous metals and glass, by thermal treatment of waste and when using abrasives in metal processing industry (2.7%). By installing production units for mercury extraction from natural gas in the CPS Molve plant the emission of mercury in Croatia drastically decreased in relation to the year 1990.
Stationary power sources have the highest share in *cadmium emissions* (81% in the year 2000), primarily due to combustion of fuel oil, while mobile sources, i.e. road traffic, account for 12% of emissions. Cadmium emissions are also produced in processes without fuel combustion (7%) and in the production of iron, steel and ferrous alloys, cement, glass, nonferrous metals, fertilizers and to a certain extent during sandblasting in the metal processing industry.

Persistent organic pollutants (POPs) emission

In 2000 emission of POPs show a significant drop in relation to 1990: PAH 40%, lindane 26% and PCDD/F 39%.

*Pesticide emissions***.** According to the List of Plant Protection Agents Approved for Sale and Application in the Republic of Croatia (Official gazzete, No 93/96), only hexachlorocyclohexane, i.e. lindane (HCH) of all the substances mentioned has been approved for production and application in agriculture. In 2000 consumption of lindane, as active substance in insecticide production, was 9.8 t. Assuming that approximately 5% remained unused, in 2000 emission of hexachlorcyclohexane was 7 t and it represents an increase of about 40% in relation to 1999 as a result of increased consumption of lindane as active substance in pesticide production.

Emissions of polycyclic aromatic hydrocarbons (PAH). Following the recommendation of the CLRTAP Protocol, emissions of four polycyclic aromatic hydrocarbons are monitored for the purpose of emission calculation: benzo(a)pyrene, benzo(b)fluorantene, benzo(k)fluorantene, indeno(1,2,3-cd)pyrene. The major sources of emissions are fuel combustion processes in households, thermal power plants and industrial furnaces. In 2000 the PAH emission was 9.1 t and in relation to 1999 it increased by approximately 15% as a result of the increased consumption of firewood that represents the major source of PAH.

Dioxin and furan (PCDD/F) emissions. The highest emissions of PCDD/F are produced by combustion of firewood and combustible scrap wood in households and industry (85%). Other important sources are processes of steel production in electric arc furnaces, road transport and fuel combustion processes in power generating plants (thermal power plants, district heating plants and energy transformation plants). The emission coming from PUTO, a plant for thermal treatment of industrial waste, is below 0.1% of dioxin and furan emissions in

Croatia. In 2000 the total emission of PCDD/F was 109.05 gTEQ and in comparison with emission in 1990 it shows an increase by about 11% as a result of increased consumption of firewood in households.

AMBIENT AIR QUALITY IN URBAN SETTLEMENTS IN CROATIA

At present the ambient air quality is monitored in 41 towns and/or settlements at a total of 123 stations. In most cases they monitor SO_2, smoke and total deposited matter (TDM), followed by NO_2 ,NH_3 and H_2S. The monitoring of other indicators such as suspended particulate matter (PM), ozone, phenols, chlorides, benzene and polycyclic aromatic hydrocarbons is noticeably less present, depending on concrete air pollution problems in the certain area, or rather the level of special measurements. If the total population of towns and settlements that implement any kind of measurement is calculated, it can be stated that the existing air quality monitoring network covers about 38 per cent of the total population of Croatia or rather 90 per cent of population in towns and settlements. The coverage of urban population by monitoring may be considered satisfactory, but a number of other factors point to the need to revise and/or optimize the present air quality monitoring system.

Pollution trends for SO_2, NO_2, ozone, PM, Pb, NH_3 and H_2S

The *results of SO_2 measurements* carried out in towns of the Republic of Croatia during ten years, i.e. from 1991 to 2000, show that concentrations measured in the majority of towns belonged to the level of air quality category I and that RV and RV_{98} were not exceeded. During the period of time monitored, limit values with respect to SO_2 were not exceeded.

The worst situation in terms of SO_2 in the past period was found in Rijeka, where at one measuring station RV were exceeded over a period of six years, at another station over a period of eight years, and at a third station over nine years, resulting in air quality category II.

The improvement of air quality from the aspect of SO_2 is due to the decreased coal consumption, the construction of the gas supply network, the development of centralised systems for heat supply and the reduction in sulphur content of liquid fuels used by combustion plants and traffic.

The *results of NO_2 measurements* in towns of the Republic of Croatia during ten years, i.e. from 1991 to 2000, show trends of air quality improvement, however there are still towns or settlements with air quality category II.

The concentrations measured in Zagreb at all the five measuring stations during all the ten years exceeded RV, in Rijeka the NO_2 concentrations measured at one measuring station exceeded RV during all the ten years, in the centre of Pula RV were exceeded during nine of the ten years in which measurements were performed; in Kraljevica air quality category II was found in the period 1993 to 1997, and in Kutina NO_2 measurement results reveal a growth trend with RV exceeded at three measuring stations in 2000.

The pollution with nitrogen dioxide is mostly traffic-related, and in Kraljevica and Kutina it is due to emissions from industrial sources. During the ten years observed, limit concentration values of NO_2 were not exceeded at any of the monitoring stations.
A continuous monitoring of *ozone concentrations* started in Zagreb in 1996. During the entire period of monitoring until the year 2000, the concentrations measured were at the level of air quality category I. Targeted measurements carried out in the vicinity of Zagreb in 2000 showed ozone concentrations in the wider area of the city (Lučko, Ivanja Reka, Velika Gorica) to be considerably higher than those measured in the closer area of the City of Zagreb.

*PM measurement***.** The pollution with suspended particulate matter is mainly a consequence of dust particles raising from the streets and then a consequence of traffic and combustion plants. The results obtained indicate that levels of the total suspended particulate matter in Zagreb belonged to the second category of air quality at all monitoring stations until 1999, when a drop in concentration was recorded, and in the north and west part of the city these concentrations decreased to the level of air quality category I. In Rijeka in 1998 and 1999, air quality in terms of PM corresponded to category II, while in 2000 the air quality corresponded to category I.

Lead measurements in PM. Lead (Pb) concentrations are measured in Zagreb at four stations. During the entire period of measurement lead concentrations in Zagreb were not high, but rather belonged to the level of air quality category I. Since 1997, when unleaded petrol was put into use on a large scale lead concentrations in the atmosphere have considerably decreased.

The *results of NH_3 measurements* carried out in Rijeka, Kostrena, Kraljevica and Bakar during ten years show that recommended values were not exceeded and that the ambient air belonged to the first category air quality. On the other hand, in the period between 1991 and 1994 concentrations were very high in Kutina, but in 1995 concentration levels dropped considerably. These levels, with usual fluctuations, remained until the year 2000, and the air quality in Kutina is of category II.

The *results of H_2S measurements* show very high concentrations in Sisak during all the three years of measurement (1998-2000), which exceeded limit concentration values and for that reason the ambient air was at the level of the third category air quality. Limit concentration values were also exceeded in Kraljevica in the period 1992-1994, Rijeka-Mlaka in the period 1992-1999 and at the monitoring station in Krasica in 1994 and 1996.

Urban settlements with ambient air quality category II and III

The overview of urban settlements with the second and third category of air quality in the period from 1998 to 2000 is given in Table 1.

Table 1. Classification of urban settlements of the Republic of Croatia with respect to the level of ambient air pollution in 1998 (▲), 1999 (■) and 2000 (●).

Town	Category II	Category III	Critical indicators
Zagreb	▲▲		Smoke
	▲▲▲▲ ■■ ●●●		Suspended particulate matter (PM)
	▲ ■ ●		PM_{10}
	▲	▲▲▲▲	Total deposited matter (TDM)
	●		Cd in TDM
	▲▲▲▲▲▲▲▲ ■■■■ ●●●●		Tl in TDM
	▲▲▲▲▲ ■■■■■ ●●●●●		NO_2
	●		Benzopyrene in PM_{10}
Karlovac	●●		SO_2
	■		Smoke
		●	TDM
Sisak		■ ■	TDM
	▲ ▲▲▲ ■■■■ ●		Cd u UTT
		▲ ■ ●●	H_2S
Osijek	▲▲▲▲▲▲▲ ■ ■■■ ●		TDM
Rijeka	▲ ■ ●●●		SO_2
	▲ ■ ●		Smoke
	▲ ■		PM
	▲▲ ■ ●		NO_2
		■	H_2S
Kostrena	▲		Cd in TDM
Kraljevica	▲		TDM
Bakar	▲		Pb in TDM
Pula	▲▲	▲▲	TDM
	▲ ●		NO_2
Labin		▲ ■ ●	TDM
Kaštelanski zaljev	▲		TDM
Kutina	▲		Smoke
	▲ ■ ●		TDM
	▲▲▲ ■ ●●●●		NH_3
	●●●		NO_2
	▲	▲	H_2S

It is to be noted that in the urban settlements with the third category of air quality local self-government units are obliged to draw up restoration programmes including measures for the reduction of ambient air pollution at least to air quality category II, and in the long term to air quality category I.

Finally, it can be concluded that over the last ten years the ambient air quality in all urban settlements of Croatia has improved, especially with regard to SO_2 concentrations. The only exemption are NO_2 concentrations which are mostly a consequence of traffic-related emissions for which no improvement can be seen.

LONG-TERM OBJECTIVES FOR AIR QUALITY PROTECTION WITHIN THE NEAP

In the framework of National Environmental Strategy and National Environmental Action Plan (NEAP) Croatia has determined long-term objectives for emission reduction of major pollutants. Objectives are established in compliance with existing and future obligations arising from the CLRTAP and its related protocols. So far Croatia has international obligations under the CLRTAP Protocol on Further Reduction of Sulphur Emissions ratified in 1998 (Official gazette- International treaties, No 17/98). The objectives of emission reduction under CLRTAP and NEAP are presented in Table 2.

Table 2. Objectives of emission reduction under CLRTAP and NEAP are as follows:

Year	Sulphur Protocol	Protocol to the CLRTAP to Abate Acidification, Eutrophication and Ground-level Ozone (MPME)			
	SO_2 (kt)	SO_2 (kt)	NO_2 (kt)	NMVOC (kt)	NH_3 (kt)
1990*	180	180	87	105	37
2010	117	70	87	90	30
Reduction	- 35 %	- 61 %	0 %	- 14 %	- 19 %

* reference year for the protocols

Actions to be undertaken are as follows:

- to bring the existing legislation in line with that of the EU and international obligations assumed,
- to reduce emissions of hazardous substances in accordance with the existing legislation (especially reduction of traffic-related emissions),
- to revise and complete the system of emission pollutants and air quality monitoring.

Framework objectives by pollutants are:

- *SO_2:* Reduction of the total emission to the level as prescribed by international treaties; by the year 2010 the emission to be reduced by 61 percent in relation to 1990 and by 22 per cent in relation to 1998. The total emission from existing stationary sources to be reduced to the level of prescribed limit values.

– *NO_x:* Stabilization of the total emission to the level as prescribed by international treaties; by the year 2010 the emission to be kept at the 1990 level. The total emission from existing stationary sources to be reduced to the level of prescribed limit values.
– *NMVOC:* Reduction of total NMVOC emissions to the level as prescribed by international treaties; by the year 2010 the emission to be reduced by 14 percent in relation to 1990. Development of solvent management plans. Reduction of total emissions from existing stationary sources to the level of prescribed limit values.
– *NH_3:* Reduction of the total emission to the level as prescribed by international treaties; by the year 2010 the emissions (of anthropogenetic origin) to be reduced by 19 per cent in relation to 1990. Elaboration of an advisory code for the best agricultural practices. Reduction of total emissions from existing stationary sources to the level of prescribed limit values.
– *Heavy metals:* Reduction of total emissions of lead, cadmium and mercury, including other heavy metals, by the year 2010 in relation to 1990 emissions and in accordance with obligations arising from international treaties. Phasing out leaded petrol by 2005. Reduction of total emissions from existing stationary sources to the level of prescribed limit values. Formulation of the management plan for products containing heavy metals.
– *Particulate matter:* The total emission of particulate matter from stationary sources to be reduced to the level of prescribed limit values.
– *Persistent organic pollutants:* Reduction of the emission of persistent organic pollutants (primarily polycyclic aromatic hydrocarbons, hexachlorobenzene and dioxin/furan) by the year 2010 in relation to the 1990 emission in compliance with obligations under international treaties. Reduction of total emissions from existing stationary sources to the level of prescribed limit values. Gradual phasing out of the use of PCBs in the existing plants by the year 2010.

CONCLUSIONS

In Croatia pollutant emissions into the air from major pollution sources (stationary and mobile sources) have been reduced since 1990, this being a consequence of the general economic recession, transformation of economy and war. In the period between 1990 and 1995 gross energy consumption decreased by 22 per cent, while it has been increasing again over the current period. Similar developments are observable also in the emissions of main pollutants: there was a significant decrease in the period between 1990 and 1995, and there has been slow increase since. In the period between 1990 and 2000 the share of traffic in air pollution has increased by an average of 20 per cent, while the share of the combustion process in air pollution has decreased by an average of 11 per cent. Such development points to the fact that also in the future major pressure is to be expected from the traffic sector.

There has been an obvious trend of further air quality improvement in towns over the last five years, however there are still numerous towns having air quality category II or III. The main problems are related to nitrogen oxides, the total deposited matter and specific pollutions by H_2S and NH_3.

The main air pollution problem outside urban areas consists in higher concentrations of ground-level ozone exceeding the limits recommended for the protection of health, crops and forest. Also excessive nitrogen deposition has been occurring, which is noxious to forests.

There is a good established legislative framework for air quality protection; it is necessary to develop programmes for solving the existing acute problems and a strategy to maintain the positive trends, whereby it is important to strengthen also mechanisms of control and monitoring of the air quality, as well as to introduce economic policy instruments.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

TOTAL OZONE AND UV-B RADIATION OVER CROATIA

K Premec*

ABSTRACT

The significant role and importance of ultraviolet radiation and ozone for life on Earth initiated some researches and measurements of these parameters in The Republic Croatia at the end of the 20th century. In the lack of surface-based instruments for total ozone, zonaly averaged satellite data were analysed for latitudes 40-50°N. The data show a negative trend with the highest value in February (over 4% per decade) and the lowest value in September and October (slightly over 1% per decade). Zonaly averaged total ozone was 10 DU lower in the last decade of the 20th century than the decade before.
The Meteorological and Hydrological Service of Croatia has performed measurements of UV-B radiation with narrowband instruments in Opatija since 1997 and in Umag since 1999. The analysed data show a positive trend in UV-B radiation during the period. The highest values were found in June and July. Daily sums reached 5000 J/m^2 and hourly maxima were over 900 J/m^2. These amounts show a high level of dangerous UV radiation at midday in these months and we should be very careful during this period to avoid all harmful effects like skin cancer, eye damage and immunosuppression.

INDEX TERMS

Total ozone, UV-B radiant exposure, Health effects, instruments, satellites

INTRODUCTION

Ozone, a trace gas found in Earth's atmosphere, plays significant role in radiative energy balance of the atmosphere and in regulation of net radiation received at Earth's

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surface, especially in high biologically active ultraviolet spectrum. The discovery of "Ozone hole", region with high ozone depletion over Antarctica in 1985, intensified researches of ozone behaviour all over the world. In the Republic Croatia there are no instruments for measurement of total ozone yet, but satellite data available from web sites allow some analyses of total ozone over Croatia. Analysis of total ozone for latitudes 40-50°N that cover entire Croatia is presented here.
The ultraviolet radiation (UV) has always been an environmental factor for life on Earth, especially UV-B part (280-315 nm). Increases in UV-B radiation can cause skin damage, like sunburn and skin cancer, eye abnormalities, like snowblindness and cataract, and changes in immune system, which may alter the course of cancer or infectious disease. It can also damage aquatic and terrestrial plants and ecosystems (Commission of the European Communities, 1993). Because of these harmful effects it is very important to know changes in UV-B radiation on the Earth surface and disseminate this information to the public. Daily and annually variability of UV-B data from northern Adriatic show very high values in June and July at midday (Premec, 2002) and here is presented a trend over five-year series of data from Opatija, and three-year series of data from Umag.

METHODS

Total ozone refers to the total amount of ozone contained in a vertical column in the atmosphere above ground. Commonly used unit is called Dobson unit (DU) and it defines thickness of ozone column at standard temperature and pressure (1 DU $\approx 10^{-5}$ m). Total ozone is routinely measured with ground-based remote sensing instruments, like Brewer and Dobson spectrophotometers, or with remote sensing instruments from satellites, like Total Ozone mapping Spectrometer (TOMS) or Solar Backscattered Ultraviolet (SBUV). TOMS instruments measure the radiance of backscattered solar UV and the direct solar UV irradiance before it enters the atmosphere. Measurements are made at five wavelengths between 312 and 380 nm and appropriate algorithms developed on the results of multiple-scattering model atmospheres are used for determining of total ozone. The measurements are limited to periods of daylight and TOMS instrument provides a daily map of total ozone with horizontal resolution from 50 to 250 km. Here analysed data were gathered by TOMS instruments which have been operational on board the three different satellites (Table 1). The data are monthly means zonaly averaged for two latitude bands, 40-45°N and 45-50°N, in these papers called "southern band" and "northern band", respectively. Source of the data is the web site http://toms.gsfc.nasa.gov/.

Table 1. Satellites and periods of available data

Satellite	Available data
NIMBUS 7	1978 – 1993
METEOR 3	1991 – 1994
EARTH PROBE	1996 – 2001 (now)

UV-B part of solar ultraviolet radiation is the most interesting for measurements due to its high biological activity. Different types of sensors are used for measurement of UV-B radiation (WMO, 1996). Broadband sensors integrate over larger band of UV spectrum, narrowband sensors integrate over discrete portion of UV spectrum and spectrometers measure across a pre-defined portion of the spectrum sequentially using a fixed passband. The Meteorological and Hydrological Service of Croatia has performed measurements with narrowband instruments type CUVB 1, Kipp&Zonen, which are designed to measure continuously UV-B global irradiance. Central wavelength for CUVB 1 is at 306 nm, because it represents the centre of the biologically relevant region and full-width half-maximum is 2 nm (Kipp&Zonen, 1995). Instruments are located in the northern Adriatic in Opatija and in Umag (Table 2). Here it is used the term UV-B radiant exposure (unit Jm^{-2}) which represents hourly or daily sums of global UV-B radiation.

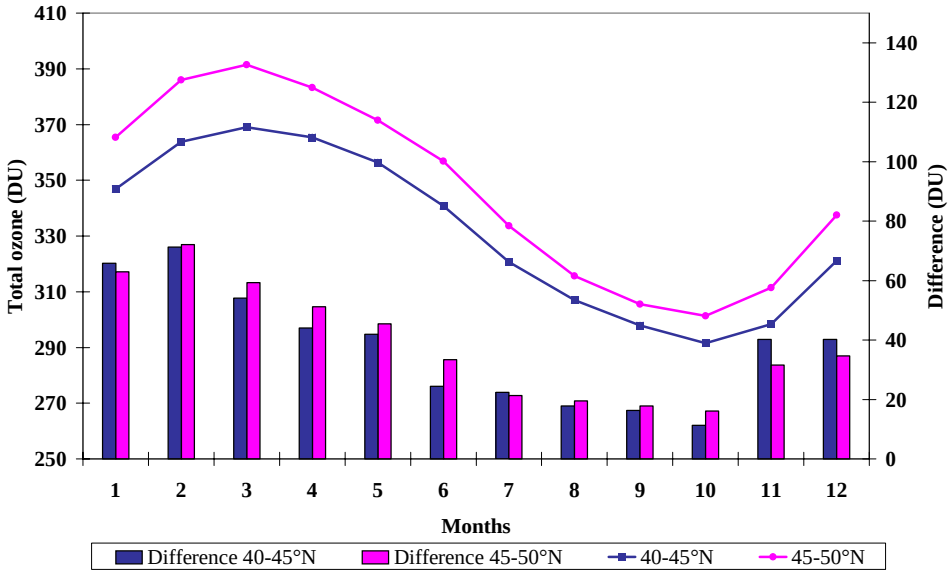
Table 2. Sites for UV-B measurement

Site	lat.	long.	alt. (amsl)	Measurement started
Opatija	45° 20’	14° 19’	5 m	13/02/1997
Umag	45° 27’	13° 32’	10 m	30/06/1999

RESULTS

Total ozone

The TOMS data clearly indicate an annual natural cycle to ozone. Averaged total ozone amounts over the analysed latitude bands are the highest in the late winter and early spring (February–April), in excess of 360 DU for latitude band 40-45 °N, and over 380 DU for 45-50°N. These ozone amounts fall over the course of the summer to their lowest amounts in
October (292 DU in southern band and 301 DU in northern band) then rise again over the course of the winter (Figure 1).
Differences between maximum and minimum monthly values behave in a similar way as the total ozone amounts. Higher differences, over 60 DU, are found in winter and lower, bellow 20 DU, in late summer and early fall. Differences between the values of the two bands behave in the same way.
Interannual dynamical variability, the El Niño Southern Oscillation, the Quasi-Biennial Oscillation (QBO), the 11-year solar cycle and occasional volcanic eruptions are main sources of ozone natural variability on a scale larger than a year (Labitzke, 1999.). The effects of two main eruptions in last two decades are seen on figure 2. The dip in 1983 is associated with the increase of aerosol in the atmosphere after eruption of El Chicón in 1982. The low values in 1992 and 1993 were result of the eruption of Mt. Pinatubo in 1991. The influences of remaining factors could be determinated from multiple linear regression models (more in Stratospheric Ozone, An Electronic Textbook, on web site).



October (292 DU in southern band and 301 DU in northern band) then rise again over the course of the winter (figure 1).

Figure 1. Monthly mean total ozone and difference between monthly maximum and monthly minimum for 1979-2000

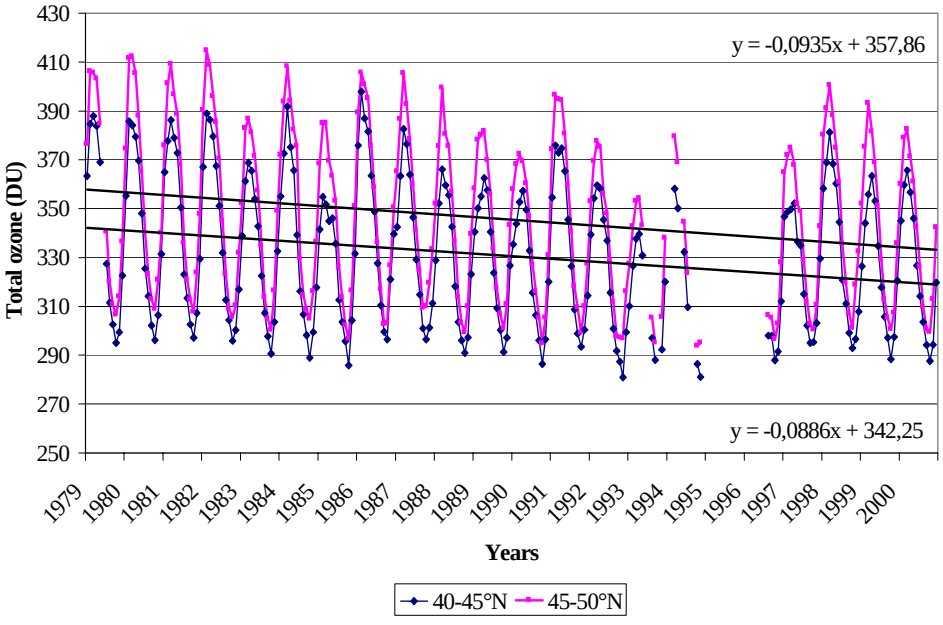


Figure 2. Monthly means of total ozone for 1979-2000

Linear trend (Figure 2) shows that total ozone has decreased during analysed period by an overall amount of 2-3% per decade. The decrease has not been uniform in time and space (Table 4). In winter and spring total ozone decreased by more than 3 %, especially in February by 4.3%, for the southern band. In summer the decrease is 1-2% and the lowest decrease is in October, 0.9%. In the northern band decrease amounts are 0.2 to 0.5 % lower in cold period of a year (November-March) but higher in spring and early fall. The highest decrease is also in February, but the lowest is in September and in December. Generally, when total ozone is higher the decrease is higher and vice versa. It is good for healthy reasons because in summer when people spend much time out in the open the decrease is small.

Table 3. Total ozone decade means (DU)

Decade	1981-1990	1991-2000
40-45°N	334	325
45-50°N	349	339

The decade averages are 10 DU lower in the last decade of the past century then the decade before. Also it is seen from Table 3 that total ozone in the southern band is 15 DU lower than in the northern band.

Table 4. Total ozone decrease (%) per decade in assumed linear trend

Month	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.
40-45°N	3,0	4,3	3,7	3,1	3,0	2,1	1,6	1,5	1,1	0,9	2,1	1,8
45 -50°N	2,5	4,1	3,3	3,3	3,3	2,7	1,6	1,5	1,2	1,4	1,9	1,2

UV-B radiant exposure

UV-B radiation at the earth's surface mostly depends on solar zenith angle, ozone amounts in the atmosphere and cloudiness. These factors create natural cycle of UV-B radiation throughout a year. Monthly maximum daily UV-B radiant exposure ranged from 450 J/m^2 in January to over 5000 J/m^2 in June and July. Monthly mean daily UV-B radiant exposures are 200 J/m^2 in January and over 1500 J/m^2 in June lower than the monthly maxima. The highest recorded value through the observed period was in June 2000. It was 5677 J/m^2 in Opatija and 5581 J/m^2 Umag. Monthly mean and maximum values from both sites are quite similar with a maximum difference below 400 J/m^2. Because of high impact on human health it is very important to know the hourly maxima of UV-B radiant exposures. Maximum hourly UV-B radiant exposure shows low values, slightly over 100 J/m^2 in January, than rises over the course of spring to summer, reaches values over 800 J/m^2 (June-August) and than falls to the values below 100 J/m^2 in December. Hourly maxima occur the most at 12 or 13 hours (MET) The highest reached values were also in

June 2000. The instrument in Opatija recorded 896 J/m^2 and in Umag it was 942 J/m^2. These amounts represent a very high level of dangerous UV-B radiation.

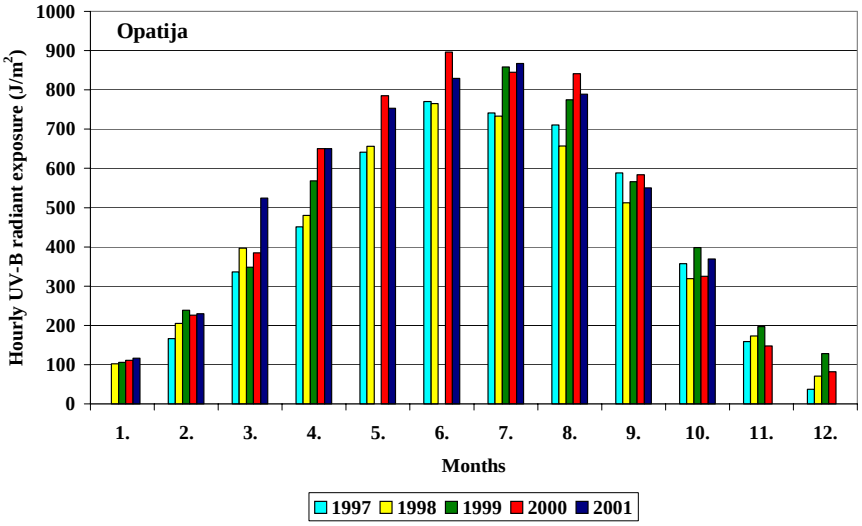


Figure 3. Maximum hourly UV-B radiant exposure in Opatija, for the period 1997-2001

First four months of a year have slightly greater values than the last four months, but in May values are even 50 J/m^2 lower than in August. In the first 4 years of the analysed period the highest values were found in June but the last year maximum shifted to July. Also it is evident that spring values in the last 2 years are much higher than at the beginning of the analysed period.

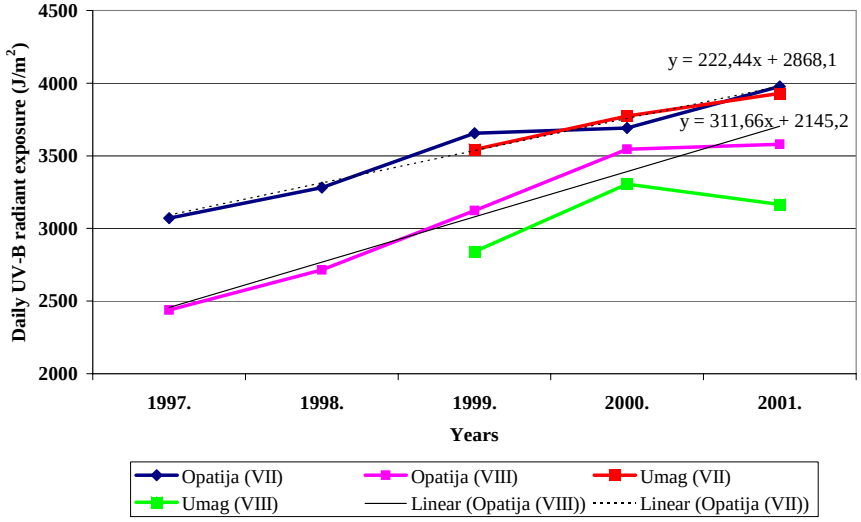


Figure 4. Linear trend over daily UV-B radiant exposure in Opatija and Umag, for June and August

Linear trend over averaged daily sums shows a positive value. It gives an average increase of UV-B radiation of about 8% per year. The highest increase is in April and October, over 16%, and the lowest is in May and July, 6.5 and 7.8%, respectively. It the three months the trend is negative. In March there is a decrease in UV-B radiant exposure for 2%, in September 2.6% and in November 0.2%. It should be noted that in November there is a missed data for the last year. Further analyses of cloudiness and other factors could help to understand the decrease of UV-B radiation in these months.

DISCUSSION

Detection of ozone changes in the atmosphere is complicated by the natural variability of ozone on several time scales, from day to year. Also it should be kept in mind that instruments in space slowly degrade over time what could mimic a trend in the data. On board calibration systems and proper algorithms help to minimise these effects. The results presented in these papers use the latest version of each data set currently available. These results of total ozone decrease are in a good agreement with those published earlier by WMO (WMO, 1998).
The increase in UV-B radiant exposure is much higher than it could be calculated from ozone decrease by RAF (Radiation Amplification Factor). The reasons could be a short time-series and a narrow passband of the instruments. It shouldn't be omitted that an increase in UV-B radiant exposure is partly result of ozone decrease but cloudiness and other factors like solar activity also have an important influence on UV-B radiation. Regular calibrations of the instruments guarantee reliability of the data.

CONCLUSION AND IMPLICATIONS

The analysis of total ozone data has quantified the amounts of ozone decrease in the region that cover whole Croatia. Total ozone shows variability also on a scale smaller than a month. Further analyses and comparison with data from the nearest ground-based remote sensing instruments could improve our knowledge of ozone changes over Croatia. Also it could be very useful to have surface-based total ozone measurement in Croatia.
Surface measurements of UV-B radiation show quite high increase throughout the measured period. Due to high biological impact more efforts should be done to establish more sites for measuring UV-B radiation in Croatia. Conversion of measured data into the UV Index and dissemination to the public would be very helpful in the prevention of harmful effects of increased UV-B radiation at the surface.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

KEY ENVIRONMENTAL RESOURCES IN STRATEGIC ENVIRONMENTAL CONTROL OF THE FIRM

S Sparacia[1,*], A Milazzo[2], G Saija[3]

ABSTRACT

The aim of this work is to define and illustrate the concept of *key environmental resources* in strategic environmental control, in order to "decipher" the approach to environmental problems adopted by the strategic and operational management of businesses. The identification of key environmental resources and the learning processes that can be triggered are crucial factors in order to make a business reactive to the perception of weak signals of change in the environmental petitions raised by the market, society and institutions.

INDEX TERMS

Strategic and operational environmental control in a business management

HOW TO IDENTIFY KEY ENVIRONMENTAL RESOURCES

The management of key environmental resources within the field of environmental management corresponds, therefore, to those production factors, tangible or intangible, that significantly influence the eco-results of a business, thereby affecting the processes underlying survival, success or failure of a business system. The main key environmental resources are processes (procedures), practices, materials or products to prevent pollution, reduce it or keep it under control and

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these include: recycling, waste treatment, changes to processes, control systems, the efficient use of resources and substitution of materials. This list is not exhaustive but represents the bare minimum (Rugman*, et al.* 1998) of key environmental factors that need to be analysed to provide the foundations for strategic environmental control using a 'systems' approach (Forrester 1968; Senge 1990) taking account of the changing reality of the firm and/or the value chain of the production area involved.

As an example, in the phase where key environmental variables are identified, procurement is a starting point to develop the processes of environmental improvement and optimisation within a business system. In this phase, choosing inputs (raw materials and secondary goods) with a lower environmental impact is fundamental in order to minimise the damage done to the environment at a process or product level and also to assess the environmental compatibility of production activity. An exhaustive description of the Input Mix forms the starting point of the production process as it enables the dynamics of the amounts of pollution produced to be evaluated, even when certain phases of the production cycle of the good or service created are assumed to be either eliminated or included. It provides information on the direct or indirect reduction of stocks of natural resources as well as the intrinsic dangers presented to the environment by using them, especially the environmental impacts relating to air emissions, discharges of waste water and refuse produced.

The information detailed also broadens the rating criteria for choosing suppliers (*supplier rating*) because the environmental variable is added to the range of factors that are normally applied to govern choices (cost, quality, delivery time). The environmental variable acts as an "eco-efficiency rating" regarding the supply of the following:

> *raw materials used in production*, potential rating data are the materials produced by the economy as well as materials extracted from nature i.e. non-manufactured items, their country of origin, the firms that supply them, the amount of hazardous material stored, in order to assess their quality and the impacts that they may have on the environment;
>
> *energy produced and consumed*, potential rating data relate to the consumption of electricity, noting whether or not renewable energy sources have been employed for its production;
>
> *water resources used,* potential rating data relate to the water coming in and going out, noting where it comes from and assessing the quality discharged after being used in production and the costs incurred by the business (and/or local community) for its treatment.

The data required for rating suppliers in part coincide with the Life Cycle Inventory phase of LCA and are prerequisites for the preparation of an eco-balance, here relating exclusively to the inputs entering a business. The level of detail used in the analysis depends on the importance of the materials used and the cumulative

flows of inputs/outputs generated as well as the logistic system adopted. The decision regarding whether to provide a greater or lesser degree of detail must be taken after studying real life cases, analysing and comparing the marginal costs/benefits obtainable as a result of the greater degree of accuracy necessitated by the implementation of a Green accounting system.

A further stage of analysis relates to ***production***. In this stage data are extracted on the outputs generated during processes of transformation, direct and indirect, and therefore unfinished products (work-in-progress), finished products, co-products, by-products, scraps produced during manufacturing, wastes, emissions, pollution of surface and underground water and in the soil and subsoil. By the term *waste* we mean the definition contained in Italian law (art. 6, comma 1, lett. a, D. Lgs. no. 22/97 issued to accommodate for three EC Directives: 91/156/EEC on waste, 91/689/EEC on hazardous waste and 94/62/EC on packaging and waste from packaging). This states that waste is: "any substance or thing that falls under the categories stated in attachment A and which the holder has, or has decided to, or is obliged to dispose of". Article 7 of the Italian law D.Lgs. no. 22/97 sets out two parallel yet distinct "horizons" for the classification of waste: the first classifies waste according to its origin, adopting the categories municipal waste and special waste, whilst the second, depends on whether or not the waste is considered harmful, thereby classifying waste as hazardous or non hazardous. Besides the denomination and classification of waste, the following details are also required in order to acquire all relevant information concerning it: characteristics (composition, concentration, etc.); amount produced in the period of reference; type of disposal method used (disposal site, temporary storage, regeneration, incineration, composting, etc.); destination of waste (whether waste is disposed of in-house or done externally, by authorized third parties, by the state service provided or by exportation); the name of the external company charged with its disposal; and the country in which it is ultimately disposed of. In the case where the business disposes of the waste on its own land or in a waste disposal site belonging to it, then it is necessary to calculate the costs of reclaiming and recovering the site so that it may be used for a different purpose. The data reported concerning the treatment of packaging regarding its use/reuse and/or recovery or disposal is an area that receives particular attention.

In order to collect the abovementioned data there is a document in Italy that is extremely helpful and important. This is the year–end return that businesses are obliged to submit called the 'Modello unico di dichiarazione ambientale' (MUD), which is basically a report form modelled along the lines of a tax return but dealing with environmental matters. The MUD is made up of two separate chapters. Chapter 1 entitled 'Waste' deals with the rules and the subject matters set out in Italian law arts. 11, 19 c. 4 bis and 37 c. 2 of D. Lgs. 5 February 1997 no. 22 and contains the following sections: "general registration data", "waste", "costs and net income for municipal refuse disposal", "commerce and trade" and "packaging" together with the application of the new code on waste to conform with the

Directive dated 9 April 2002 "Guidance for the complete and correct application of EC regulations no. 2557/2001 on the transport of waste and in relation to the new listing of waste items" (Italian Official Gazette - G.U. - no. 108, 10 May 2002). Chapter 2 entitled 'Emissions' covers the duties and subject matters covered by art. 10 of D. Lgs. 4 August 1999 no. 372, comma 1 to implement art. 10 of D. Lgs. 4 August 1999 no. 372 , comma 5 and art. 6 of D.M. 23 November 2001, where comma 1 makes provision for MUD to be supplemented by the declarations on emissions that must be filed by factories subject to integrated environmental authorization under D. Lgs 4 August 1999 no. 372 "Implementation of Directive 96/61/EC relating to integrated prevention and reduction of pollution".
The analysis of *emissions* concerns information about any solid, liquid or gas introduced into the atmosphere coming from a plant that may produce atmospheric pollution. (Definition laid down in Italian law by art. 2, comma 4 of D.P.R. no. 203/88 to implement EC directives nos. 80/779, 82/884, 84/360 and 85/203 concerning laws on air quality relating to specific pollutants and pollution produced by industrial plants, in accordance with art. 15 of law no. 183, 16 April 1987). Atmospheric emissions can be divided into localized and diffuse, for localized emissions (i.e. from a specific point, often a chimney) the business must state: the pollutants contained in fumes giving names, their table and basic class (if they belong to a category covered by specific regulations contained in laws currently in force); the total amount emitted of each pollutant (expressed in terms of concentration levels, mass flow, etc.); the means to combat/reduce it and the efficiency of the technology employed; and provide broad overall indicators of pollution levels and sources. The purpose of these performance measurements is to verify compliance with legislation and to assess the efficiency and effectiveness of environmental management, and to highlight critical areas requiring intervention. More specifically, the relevant Italian legislation on this subject (in D.P.R. no. 203/88) lays down and defines some key concepts to assist accurate assessment of key environmental variables:

- atmospheric pollution - any change in the normal composition or physical state of atmospheric air conditions, due to the presence therein of one or more substances in such amounts and with such characteristics as to alter normal environmental conditions and the salubrity of the air as to constitute a danger or a direct or indirect prejudice to human health, compromising recreational activities and other legitimate uses of the environment, to alter biological resources and eco-systems and public and private material wealth (Definition laid down in art. 2 comma 1 of D.P.R. no. 203/88);
- emission ratings - such as the amount of pollutants emitted by reference to the production process, considered as a whole and split into its technological phases; expressed in terms of pollutant mass emitted, compared to the mass produced or raw material employed, or to other parameters that are appropriate to the production sector under review (Definition laid down in art. 2, comma 6 of D.P.R. no. 203/88);

- maximum emission levels - the concentration and/or the mass of pollutants in the emissions from plants in a given period of time that must not be exceeded (Definition laid down in art. 2 comma 8 of D.P.R. no. 203/88);
- best available technology - an appropriate tried and tested technological system that enables emission levels to be contained within and/or reduced to acceptable levels to safeguard health and the environment, provided that the application of such measures does not entail excessive costs (Definition laid down in art. 2 comma 7 of D.P.R. no. 203/88);
- guideline for the containment of emissions - criteria in line with technical advances relating to sectors of industry containing indications on: a) technological cycles, b) best available technology relating to systems for the containment of emissions, c) emission ratings with or without applying best available technology relating to systems for the containment of emissions. Minimum and maximum emission levels are identified on the basis of the abovementioned criteria (Definition laid down in art. 2 comma 5 of D.P.R. no. 203/88).

As an example the Italian law D.P.R. no. 203/88 in art. 3 comma 2 sanctions that guidelines for the containment of emissions as well as the minimum and maximum values for emissions are determined by an Environment Ministerial decree, whilst Regional authorities are responsible for setting emission levels on the basis of best available technology of guidelines and emission levels fixed at national level. It is clear then that it is first of all necessary to identify the values set at regional level (especially for new plants) in order to identify the key environmental variables in limits for emissions which apply to a specific plant, and, where these are not available, the only alternative is to refer to the limits set at national level. In addition, some specific measures relating to certain types of plant are in force at national level, for example D.M. no. 503/97 and D.M. no. 124/00 for incinerators of non hazardous and hazardous waste, or D.M. 05/02/98 and D.M. no. 161/02 for plants to recover materials and energy from waste, and these also set out the limits for emissions that must be referred to. D.M. 12/07/90 lays down more general guidelines and specifies in Attachment 1 the prescribed minimum and maximum limits for emissions for categories of pollutants or for specific substances that apply where not otherwise indicated in Attachment 2. Attachment 2 contains the minimum and maximum prescribed limits for emissions for certain pollutants that are characteristic of specific types of plants and/or production methods and which take precedence over the ones set out in Attachment 1, where the two differ, whereas the limits in Attachment 1, for parameters not expressly indicated by Attachment 2, remain valid. Attachment 3 deals with emissions for refineries, sites for combustion with a nominal thermal power greater than or equal to 50 MW, and plants for production of hydrocarbons and geothermal fluids to which apply exclusively the limits and rules set out in this Attachment. Emissions can be characterized as follows: by concentration, the ratio between the mass of pollutant emitted and the volume of gaseous effluent (e.g. mg/mc); by mass flow,

the mass of pollutant emitted in a time period (e.g. g/h); by emission ratings, the ratio between mass of pollutant emitted and a unit of measurement specific to the product designed or fabricated (e.g. kg/t; g/m); by other expressly indicated measures. The criteria to determine limits, if not otherwise indicated, are summarised in the following list:

1. in the case in which values for mass flow are stated, emission limits must be respected if the values for mass flow are reached or exceeded;
2. the values of emissions in Attachment 1, keeping the flow conditions indicated unchanged, represent minimum values, in these cases the maximum emission value is equal to double the indicated value;
3. if emission values in Attachments 2 and 3, keeping the flow conditions indicated unchanged, are expressed as a single numerical value this means that minimum and maximum values coincide;
4. emission values expressed as mass flows or as concentrations apply to one hour of plant operations in the most demanding operating conditions;
5. the limit values for emissions expressed as concentration levels and the reference volume of the oxygen content refer to the volume of gaseous effluent at normal physical conditions after detraction - where not expressly indicated - of the water vapour content. If the gaseous effluent in the oxygen content by volume differs from the one indicated in the reference value, then concentrations of emissions must be calculated using the following formula (1):

$$E = \frac{21 - O}{21 - O_M} * E_M \qquad (1)$$

where E_M = measured concentration, E = concentration, O_M = measured oxygen content, O = reference content for oxygen;

6. the oxygen content of gaseous effluent is the one deriving from the process;
7. limit values for emissions expressed in concentration relate to the amount of gaseous effluent not diluted more than is inevitable for technical or operating reasons. In cases where the gaseous effluent is diluted further then the concentrations of emissions must be calculated using the following formula (2):

$$E = \frac{E_M * P_M}{P} \qquad (2)$$

where P_M = measured flow, E_M = measured concentration, P = flow of undiluted gaseous effluent, E = concentration referred to flow P;

8. during the start-up and shutdown periods of plants the limit values for emissions do not apply;
9. the responsible authority, as an authorization centre, may establish specific rules besides the transitory periods in which limits of emissions do not apply.

Data is also to be collected concerning the *pollution of surface and underground bodies of water and in the soil and subsoil.* In Italy, law no. 319 of 10 May 1976 sets out the rules to protect water from being polluted, makes the State liable for setting out the general criteria and the methods to measure "surface and underground bodies of water". It is curious to note that there is no precise definition of the term "body of water" although similar terms are commonly accepted, even internationally. Nonetheless, "body of water" should be taken to mean: "any mass of water, regardless of its type, that presents hydrological, physical, chemical, biological characteristics, and is, or can be, used in one or more ways". In this respect, the water that must be protected from being damaged from a lowering of its quality, may be destined for, but not necessarily restricted to, the following purposes: 1) drinking; 2) agriculture; 3) industry; 4) maintaining aquatic life; 5) leisure activities; 6) navigation. The following classes of pollutants indicated by Eurostat are often referred to: BOD (biochemical oxygen demand) and COD (chemical oxygen demand) oxidants, nitrogen compounds, phosphoric compounds, solids in suspension, etc.. The information to be specified relates to individual pollutants and the amounts discharged in a one-year period, as well as the receptor: surface waters, soil, subsoil, underground water, waste water treatment plants. All these details are needed to reconstruct the cycle of water used in business.

Management of information is an essential part of running an environmental management system and for the adequate assessment of any eco-efficient redesign of the production cycle being considered; this is so that management decisions are based on confirmed data.

A key variable in managing relations with customers and relevant stakeholders is to design an *environmental marketing plan,* that will inform and differentiate the target market for which eco-efficient products are destined, educate customers on how to make use of value added services of an environmental nature that have been created during the design phase of the product (reuse of containers and/or parts of the products, recycling with the help of after sales service, etc) and involve them in the recovery of goods/assets.

E*nvironmental communications* addressed to the outside are designed to create a shared environmental culture. The actual form and content of such communications may differ according to their target audience: government and local government, banks, environmental groups, the general public, etc.

A critical part of the continuous learning processes that seek to raise consciousness of the environmental content and performance standards a product meets is the **management of human resources**. A definition of standards of performance is not

limited to the physical product but involves all the correlated activities in the production process, the means of production and a variety of aspects regarding the performance/efficiency of the business system. Management initiatives to establish and implement policies and objectives for environmental quality require Organization Development to support them, namely far-reaching intervention to improve problem solving processes and the renewal of the organization through a process of T group empowerment (Training Groups). Such education and training groups, which seek to forge satisfactory links between the properties/performance of products with the performance/efficiency/productivity of processes, identify the key environmental points of leverage on which to base continuous improvement and the underlying strategic direction of a business enterprise.

The installation of ***information management systems*** enables streams of data relating to key environmental resources (stock movements and flows) to be acquired over time. A business starting from the types of data illustrated in operations then integrating them with environmental indicators (benchmarks) and the costs incurred by business to pursue strategies and/or environmental operating plans can dynamically manage the environmental variable at the various levels in the firm's hierarchy. This support tool is required for the application of design methods to achieve eco-efficiency based on the assessment of key environmental resources, i.e. evaluation based on known data, by applying statistical tools (seven tools) to promote continuous environmental improvement in accordance with the Deming model or the PDCA cycle (UNI EN ISO 14004).

CONCLUSIONS

The key environmental variables briefly illustrated herein, which configure the peculiar characteristics of any business, provide back-up material for the assessment of operative decisions concerning environmental strategic control. Understanding gained via strategic environmental control of the processes underlying development and or running down of key environmental resources is an essential precondition for the implementation of a system of analysis and diagnosis based on continuous learning and an effectively formulated and implemented sustainable business strategy.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

GLOBAL DEVELOPMENT OF THE ENVIRONMENTAL VALUE CHAIN AND STRATEGIC ENVIRONMENTAL CONTROL

S Sparacia[1,*], A Milazzo[2], L Ciraolo[3]

ABSTRACT

The development of a sustainable environmental strategy must take into account the pervasive impact of the environmental dimension along the entire supply chain (Bianchi and Noci, 1997; Noci, 1997). The need for a business to collaborate with stakeholders, old and new, (Hartman and Stafford, 1998; White *et al*., 1996) most of all in cases in which it intends to develop radical environmental innovations requiring skills that are difficult to find within the business itself, involves defining the green system of values and how to develop this within a *green strategy network*. The network redefines and redesigns the strategies of the entire value chain of the sector. It is founded on cooperation with universities, research centres and/or other businesses, which may or may not be competitors, and that may even operate in other sectors for the development of environmental innovations.
Small and medium-sized enterprises are likely to benefit from joining a green strategy network as it may lessen the impact of financial burdens imposed through amendments made, in the sense of additional restrictions, to environmental standards and/or changes in stakeholder demands.

INDEX TERMS

Strategic management of the green network, environmental values, value chain.

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THE DEVELOPMENT OF THE VALUE CHAIN

The development of a system of environmental values[1] (Porter, 1985) by external routes along the value chain occurs through aggregation of specific activities or by establishing strong links with other businesses[2]. The types of collaboration agreements drawn up between firms to achieve development by external routes fall into two main categories that we have called *green equity* and *green non-equity*. The former type of agreements entail investment of risk capital by the business resorting to externalisation or to a reconfiguration of its assets in order to achieve greater eco-efficiency. There are a variety of ways in which this may be done, acquiring unrelated firms for example, or creating a number of spin-off companies in which the head company invests risk capital, or by setting up joint ventures, consortiums or cooperatives. In contrast, green non-equity-type agreements do not involve any outlay of risk capital. These agreements to collaborate may take on a variety of guises, such as the stipulation of voluntary agreements aimed at joint development of communication/marketing activities concerning environmental issues. Such forms of collaboration materialise through the deliberate construction of networks between businesses, e.g. Responsible Care[3]. The realization of a network is the outcome of a long learning process launched by a *mentor firm* possessing a proactive environmental formula. This mentor represents a point of reference for the network, it being the one to first involve the other businesses; initially by establishing two-way relations and subsequently by extending links in all directions (Lorenzoni, 1990). The mentor has the ability to acquire an overall view of the processes and of management activities that characterise the whole production and distribution supply chain. It can pick its partners, and coordinate them and thus assumes a position of *green leadership,* arising from partners' recognition of its competences.

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[1] The value system is the overall set of value chains of firms operating in the sector relevant to the business in question, n the words of Porter, "the value chain is not a collection of independent activities, but a system of interdependent activities connected by links within the value chain" Porter M., 1985.

[2] On this topic, see: Lorenzoni G., 1990. Lomi A., 1991. Marchini I., 1995. Boldizzoni *et al*.1993. In particular, regarding the objectives of relations between firms, Marchini makes a distinction between purely defensive goals (risk reduction, flexibility, neutralizing restrictions imposed by structural aspects of the sector) and proactive goals (generating synergy, efficient production, new technology, competitive advantage).

[3] Responsible Care an initiative launched in Canada in1984 and implemented in Europe in 1989 by the CEFIC. At present, 10,000 businesses worldwide participate in this programme, in Italy by 162 businesses and managed by Federchimica (1992), succeeded in fully involving businesses in charge of 383 factories scattered throughout Italy and also launched collaboration with state bodies by setting up a Committee for Chemical Development to capitalize on the important experience gathered in the field of environmental protection.

We have devised three different levels to reflect the evolutionary stages of the value chain for the management of key environmental variables as follows: (1) *casual gemmation (spin-off)*, (2) *preordained gemmation (spin-off)* and (3) *planned gemmation (spin-off)*. In the first the mentor firm establishes the initial links with other businesses through casual personal contacts in order to examine the advantages in terms of cost reductions and/or greater eco-efficiency of processes or in products. These interactions are viewed as short term and the mentor has no conscious plan to create an environmental network, and this is something that evolves gradually as the links formed spontaneously between enterprises become more consolidated. The second level often represents the natural progression of the previous one only that it takes a more long-term perspective. The casual links between firms become increasingly strengthened and regulated by common goals for eco-development. The third level is the most highly evolved state of green non-equity-type agreements between firms. In this case, the mentor firm chooses its partners not only on the grounds of their eco-efficiency but also on their ability to innovate, their entrepreneurial spirit, and their array of competences to fulfil the role that they may play as the green network grows. In such a situation, the partners and the mentor business are on an equal footing and the influence of the latter only tends to prevail in the strategic management of the green network and in acting as an interface between this network and the competition system. The relations working within a *green strategy network* are long-term agreements between diverse autonomous organizations working to achieve an environmental competitive advantage over competitors working outside of this network.

DYNAMICS CHARACTERISING THE GREEN STRATEGY NETWORK

The formulation and redesign of the strategies of the businesses making up the green strategy network are based on the following factors:

- an *integrated vision of key environmental resources*;
- on the ability to shape the portfolio of technologies and distinct competences characterizing the emerging markets of every single element in the value chain in order to meet expectations of stakeholders, reduce costs and/or improve quality and time to market;
- by redetermining the elements characterizing the strategic business area, in other words redefining the portfolio of products/services/customers/markets in the emerging environmental strategy. This strategy is strongly influenced by the expansion of the geopolitical market of reference, by the differences in the norms applying in these new emerging markets and also the different living standards and cultural and social organization reigning in these areas;
- by the changes in management procedures and grouping activities, by vertical or horizontal integration, to enable businesses to be more flexible as regards

their location and logistics. This will include considering the portfolio of suppliers available worldwide and looking at how restricted their production processes are by environmental considerations imposed.

The analysis of the supply chain is therefore the baseline for the definition of environmental characteristics of a product in line with the Quality Function Deployment (QFD) rationale and it is based on a *set of green values.*

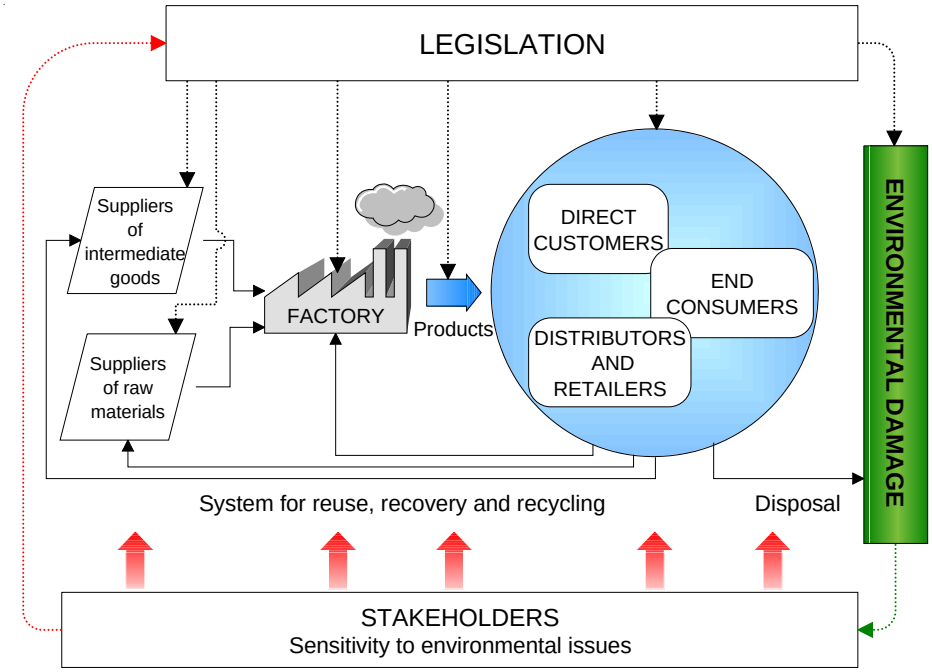

Figure 1. Environmental value chain

The analysis of the value chain to define the level of 'green' customer satisfaction[4] is something that cannot be instigated by the *customer*. It is a crucial mechanism for deciding what type of environmental performance to provide and how to manage the firm's own environmental value chain in relation to the competition system[5]

[4] Lorenzoni G., 1990. L'architettura di sviluppo delle imprese minori, Il Mulino, Milano.

[5] Customer satisfaction – can be considered in three respects. Firstly, the standard of environmental quality demanded, that is the characteristics the client asks for specifying the requisites for satisfaction so that the terms that need to be met are known. Secondly, the environmental quality expected, i.e. those aspects of environmental quality and of satisfaction the customer gives no thought to because they are taken for granted. Lastly, there is latent environmental quality, also known as "exciting" quality because when it is experienced the satisfaction derives from the fact that it was not known to exist.

(Porter, 1980) to stakeholders [6] and a broader system relating to the macro-environment (economic, political, social and cultural) with which the firm interacts (Coda, 1988). These are the factors that produce a single unit, a unit capable of influencing the success or failure of the business and the entire supply chain or industrial sector, because they influence strategic and operational decisions at all levels.

STRATEGIC ENVIRONMENTAL CONTROL ALONG THE VALUE CHAIN

The aim of strategic environmental control is to analyse the processes of creation, development, use and often the running down of environmental key resources. It is intended to help decisionmakers understand how to handle the current set of key environmental resources – tangible or intangible – so as to improve the firm's eco-results. Environmental key resources affect the eco-efficiency of the production factors employed and may result in the firm developing a tenable competitive advantage in the market in which it operates, thus carving out a Green SBA (Strategic Business Area; on this topic, see: Brunetti, 1990; Coda, 1984; Sorci and Vergara, 1990).

The management of key environmental resources affects the entire structure of the business as well as influencing others on the outside, in other words the whole supply chain. The development and management of a sustainable environmental strategy and strategic control applied to key environmental resources must take into account the pervasive impact of the environmental dimension along the entire supply chain (Bianchi and Noci, 1997; Noci, 1997) as well as the potential positive outcomes arising from the implementation and development of an integrated environmental strategy.

The need for a business to collaborate with stakeholders, old and new (Hartman and Stafford, 1998; White *et al.*, 1996), most of all in cases in which it intends to develop radical environmental innovations requiring competences that are difficult to find within the business itself, involves defining the environmental system of values as well as deciding how to develop this in the ***green strategy network***.

The reshaping and redesign of the strategy of the firms in a green strategy network causes all aspects contained in the entrepreneurial formula to be redefined and redesigned in order to install a proactive environmental strategy that is capable of picking up the weak signals of change in the economy or in society.

In a green strategy network, one formed by either informal, pre-ordained or planned 'gemmation' (spin-offs), each of the various key divisions of the businesses

[6] The competitive system is composed of five main "forces": 1) direct competitors, 2) suppliers, 3) customers, 4) firms offering substitute products and 5) those that could become competitors should they decide to enter the market segment of the enterprise. Porter 1980; Coda V. 1984, 1988, 1991.

in the network are grouped together so that the environmental aspects affecting these divisions can be jointly managed. The analysis tree (Figure 2) illustrates the key areas subject to joint environmental management: procurement; marketing and communication; sales; recovery or waste disposal of products; research and development; human resources; information systems.

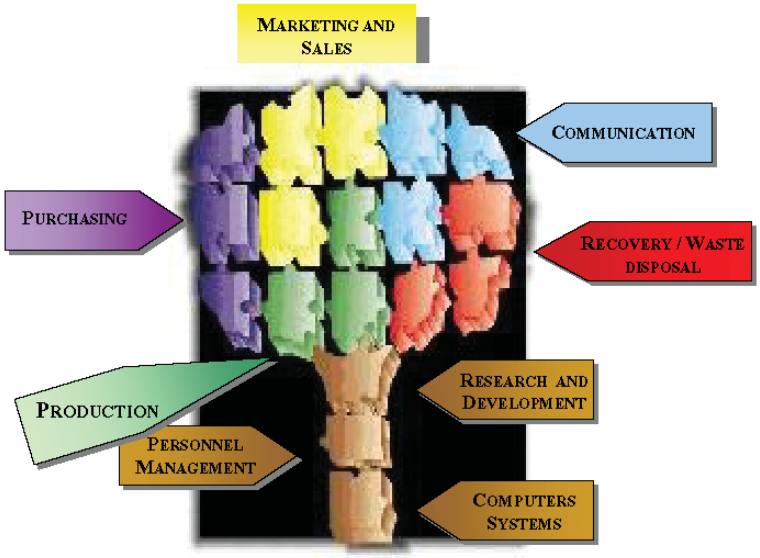

Figure 2. Tree of environmental key resources along the value chain of a green strategy network

The management of green networks depicted in the analysis tree highlights how the work of the Teams formed by staff members of the network businesses enables information and decision making to be stratified thus directly linked to the key environmental concerns of the individual areas illustrated. In this way the firm's hierarchy is rationalized and the business is structured and run to pursue effectively the environmental goals set and manage the key environmental variables identified. The need to map out the organizational hierarchy and the functions regarding environmental management issues dealt with by the Teams inserted at the various levels of the value chain traced provides a launching pad for an integrated environmental management system organized around core competences.

The identification of green "core competences" in a management of key environmental resources at all levels of the organizational hierarchy of the firms in the green network and relating to the areas shown in the analysis tree enables information retrieval to be optimised and thus the effectiveness of the decisions made in consequence, increasing the ability of network businesses to react to extremely variable environmental events By way of the green strategy network,

the value chain, a part of a system of values, acquires true operational elasticity and is thus able to meet dynamically (Forrester, 1968; Senge, 1990) the wide range of environmental demands imposed by the market / customers / stakeholders / relevant regulatory framework.

CONCLUSIONS

A green strategy network allows businesses to move more quickly and act rapidly on key environmental variables. Achieving excellence in the ability to act on key environmental resources is a critical factor for success in a competitive market nowadays. This factor is determined by the ability of environmental strategy to make a reactive response to changes in environmental regulations and to the weak signals of change in environmental satisfaction of customers and/or relevant stakeholders.

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The 14th International Conference
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Dubrovnik, CROATIA 6-10 October 2003

STRATEGIC ENVIRONMENTAL CONTROL

S Sparacia[1, *], A Milazzo[2], L Ciraolo[3]

ABSTRACT

The aim of this work is to define the concept of *strategic environmental control,* via the assessment of key environmental resources, in order to "decipher" the approach to environmental problems adopted by the strategic and operational management of businesses. The identification of key environmental resources and the learning processes that can be triggered are crucial factors in order to make a business reactive to the perception of weak signals of change in the environmental petitions raised by the market, society and institutions.

INDEX TERMS

Strategic and operational environmental control in business management.

THE ENVIRONMENTAL VARIABLE AND ENVIRONMENTAL MANAGEMENT SYSTEMS

The environment is a point of leverage[1] (and/or key resource[2]) that has specific characteristics compared to the other leverage points and/or key resources involved

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[1] Directional and operative points of leverage, are elements that may be manipulated and where the results generated by such intervention may be forecast over varying timespans and on the basis of a specific configuration hypothesised for the system in which the business must operate.

[2] Production factors that may lead a firm to develop a competitive advantage that is defensible in the market in which it competes

in strategic business management. This is because the environmental[3] impact of businesses is produced by many factors (multidimensional phenomenon) that cause changes in the environment[4]. These changes or environmental[5] aspects are determined by the interactions, direct or indirect, that occur not only during production activities but also in all stages in the life cycle of a product[6].
The implementation of environmental management systems in businesses on a voluntary basis, subsequently formalized nationally (e.g. British Standard 7750), at European level with EMAS (EC Regulation 1836/93 subsequently amended by no.761/2001) and worldwide with the ISO 14001:1996 standards, has made it clear to the public that businesses aim to safeguard the environment.
The ultimate aim of an environmental management system is continuous improvement[7] of environmental performance[8] meaning: "a process of improvement, year by year, in the results that can be measured by the environmental management system, being the results achieved by an organization's management of its significant environmental aspects on the basis of its policies[9] and its objectives[10] and its environmental targets[11]" (Source: UNI EN ISO 14001:1996; UNI EN ISO 14004:1997).
UNI EN ISO 14001:1996 and 14004:1997 define an EMS (Environmental Management System) at point 3.5 as: "the part of a system of general management that includes the organizational structure, planning activities, responsibilities, practices, and resources to design, implement, follow-up, review and keep environmental policy alive and active".
The systematic approach to Environmental Policy, of the type devised by Wilfredo Pareto, adopted by the Standards for codifying environmental management systems (Table 1), does not consider the environmental dimension a point of leverage (and/or key resource) with its specific characteristics that affect strategic business management nor how this same environmental management concerning points of leverage and/or key resources is heavily influenced by different stakeholders (Hunt et al., 1990; Rugman, 1998).

[3] Environmental impact, Source: UNI EN ISO 14050:1999 (1.13), 14001:1996 (3.4), 14004:1997 (3.4).

[4] Environment, Source: UNI EN ISO 14050:1999 (1.23), 14001:1996 (3.2), 14004:1997 (3.2).

[5] Environmental aspect, Source: UNI EN ISO 14050:1999 (1.10), 14001:1996 (3.3), 14004:1997 (3.3).

[6] Life cycle assessment (LCA), Source: UNI EN ISO 14040:1998, 14041, 14042, 14043.

[7] Continuous improvement, Source: UNI EN ISO 14001:1996 (3.1); 14004:1997 (3.1).

[8] Environmental performance, Source: UNI EN ISO 14001:1996 (3.8); 14004:1997 (3.8).

[9] Environmental policy, Source: UNI EN ISO 14001:1996 (3.9); 14004:1997 (3.9).

[10] Environmental goal, Source: UNI EN ISO 14001:1996 (3.7); 14004:1997 (3.7).

[11] Environmental target, Source: UNI EN ISO 14001:1996 (3.10); 14004:1997 (3.10).

Table 1. Comparison of standards for environmental management systems

System Element	ISO14000	EMAS	BS7750
Environmental Management System	4.0	ANNEX I, Part B	4.1
Preparatory Environmental Review	ANNEX A.4.2.1 (Guide)	Article 3, Paragraph b ANNEX I, Part C	ANNEX A.1.2 (Guide)
Environmental Policy	4.1	ANNEX I, Part A and D	4.2
Organisation and Personnel	4.3.1, 4.3.2	ANNEX I, Part B2 & D11	4.3
Environmental Effects/ Aspects	4.2.1, 4.2.2	ANNEX I, Part B3 & D2/3	4.4
Objectives and Targets	4.2.3	ANNEX I, Part A4	4.5
Environmental Management Programmes	4.2.4	ANNEX I, Part A5	4.6
Manual and Documentation	4.3.4, 4.3.5	ANNEX I, Part B5	4.7
Operational Controls	4.3.6, 4.3.7, 4.4.1, 4.4.2	ANNEX I, Part B4 & D6-7	4.8
Records	4.4.3	ANNEX I, Part B5	4.9
EMAS Audits	4.4.4	ANNEX I, Part B6, ANNEX II	4.10
Management Review	4.5	ANNEX I, Part B1	4.11
Environmental Statement	N/A	Article 5 and ANNEX V	N/A

The difficulty in formulating general rules that can assist management decision making regarding the strategic and operational management of environmental variables, and the related economic outcomes, triggers the need to develop the concept of a key environmental resource and that of strategic environmental control.

STRATEGIC ENVIRONMENTAL CONTROL AND KEY ENVIRONMENTAL RESOURCES

The aim of strategic control is to analyse the processes relating to the creation, development, use and, often even the running down, of a firm's *key resources*. It is intended to help decision makers understand which manoeuvres it should make in order to induce the current set of key resources to move in the desired direction. Strategic environmental control through the analysis of *key environmental resources* "deciphers" the approach to environmental problems adopted by the strategic and operational management of businesses. This approach identifies the entrepreneurial values (Coda, 1986) involved in formulating a "business

environmental strategy"[12] (Sparacia, *et al.* 2002) and the learning processes, relating to the key resources identified, in order to pick up (Hofer, *et al.* 1978) the weak signals of change in the environmental demands being emitted by the market and by society.

The definition we have assigned to k*ey environmental resources* is that they correspond, in environmental management terms, to those production factors, tangible or intangible, that significantly influence the eco-results of a business, inasmuch that the processes underlying survival, success or failure of a business system can be interpreted in the light of their dynamics.

The concept of key environmental resources can therefore also be traced back to those eco-efficient production factors that may lead a business to develop a tenable competitive advantage in the market in which it operates, thus carving out a Green SBA (Strategic Business Area; on this topic, see: Brunetti, 1990; Coda, 1984; Sorci and Vergara, 1990). The key environmental resource draws out factors, production and non, tangible or intangible that determine, on the basis of their dynamics, the processes underlying the survival, success or failure of a business system. In addition, one characteristic of the dynamics governing these factors is reactivity to environmental pressures coming not only from customers but also from stakeholders (State bodies, the local community, Green movements, public opinion). These factors originate, in quantitative terms, from the eco-results of a firm, and, in financial terms from the profitability of the business.

The concept of a key resource outlined above is similar in many ways to the concept of strategic asset activity which has been referred to by many academics who take the resource-based-view of a firm. Indeed, strategic activities represent a system of interdependent resources, either tangible or intangible, specific to the business system that enable a business to meet the expectations and needs of the various types of internal and external stakeholders (e.g. customers, employees, financial institutions, trade unions, political and government bodies) better than their competitors.

According to the resource-based-view (Amit, *et al*. 1993; Wernerfelt, 1984; Mahoney, *et al.* 1992; Teece, *et al.* 1997). of business, the higher earnings that a business may steadily achieve compared to its competitors may be explained in the light of its capability to create key resources with specific characteristics that give rise to distinctive competences, which in turn lead to a tenable competitive advantage and growth that is both stable and sustainable over time. Long term business development is highly influenced by the skill of a business to balance its exploitation of currently available key resources with the development of new strategic activities (Rugman*, et al.* 1998).

It is fairly rare to find that official company documents are able to spell out the qualitative and quantitative advantages in the set of key environmental resources currently available. The majority of key environmental resources cannot be

[12] Definition of environmental strategy in: proactive strategy, reactive strategy, passive strategy, adaptive strategy. Sparacia S., et al. 2002.

measured in monetary terms and some of them are made up of qualitative and/or physical variables. Nevertheless, it is extremely important for a business to understand how its portfolio of qualitative and quantitative competences tends to vary over time. This is because many phenomena, being not monetary values but qualitative or quantitative in nature, are not readily comprehensible if they are examined solely in relation to the figures in a balance sheet, in which key environmental factors are noticeable for their absence. In addition, there are the dynamic relations installed within a business system along its value chain, which compete to produce something unique, an entity that is able to influence the success or failure of a business and, at times, even the whole industrial sector concerned.

KEY ENVIRONMENTAL RESOURCES

The management of key environmental resources within the field of environmental management corresponds, therefore, to those production factors, tangible or intangible, that significantly influence the eco-results of a business, thereby affecting the processes underlying survival, success or failure of a business system. The main key environmental resources are processes (procedures), practices, materials or products to prevent pollution, reduce it or keep it under control and these include: recycling, waste treatment, changes to processes, control systems, the efficient use of resources and substitution of materials. This list is not exhaustive but represents the bare minimum of key environmental factors that need to be analysed to provide the foundations for strategic environmental control using a 'systems' approach (Forrester, 1968; Senge, 1990) taking account of the changing reality of the firm and/or the value chain of the production area involved (Figure 1).

RESEARCH AND DEVELOPMENT: Applying design techniques to achieve eco-efficiency.					
PERSONNEL MANAGEMENT: education and training to develop 'green' skills, incentive schemes					
Purchasing	Production	Marketing	Sales	Recovery	Communication
Substitution of high environmental impact products Cooperation with suppliers Use of eco-compatible transport	Internal recycling of discarded materials Minimising the consumption of energy and resources Integration	Marketing Mix defined so as to be consistent with environmental performance achieved Environmental reporting	Value added environmental services Product functionality also guaranteed in environmental terms	Cooperation with competitors and customers Waste disposal Items disposed of as refuse regarded as a last resort measure	Frequent exchange of views with public and the political system
COMPUTER SYSTEMS: use of information concerning environmental issues.					

Figure 1. Key environmental resources in a 'systems' approach to the firm

The key environmental variables briefly illustrated herein, which configure the peculiar characteristics of any business, can be made to interact by representing them as stocks and flows in a feedback loops via a simulator within a microworld (Figure 2), thereby obtaining simulations of scenarios.

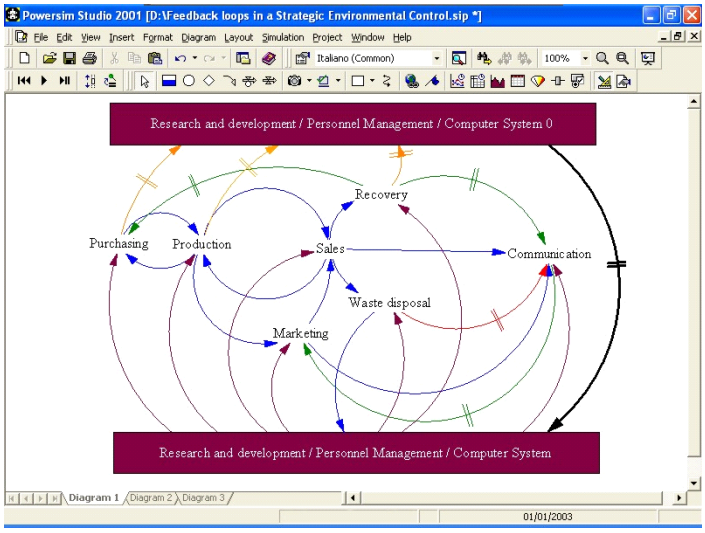

Figure 2. Feedback loops in Strategic Environmental Control.

These simulations are the outcomes of making changes to the key environmental variables which are input into the simulator and they provide back-up material for the assessment of operative decisions concerning environmental strategic control (Morecroft, 1985), (Figure 3).

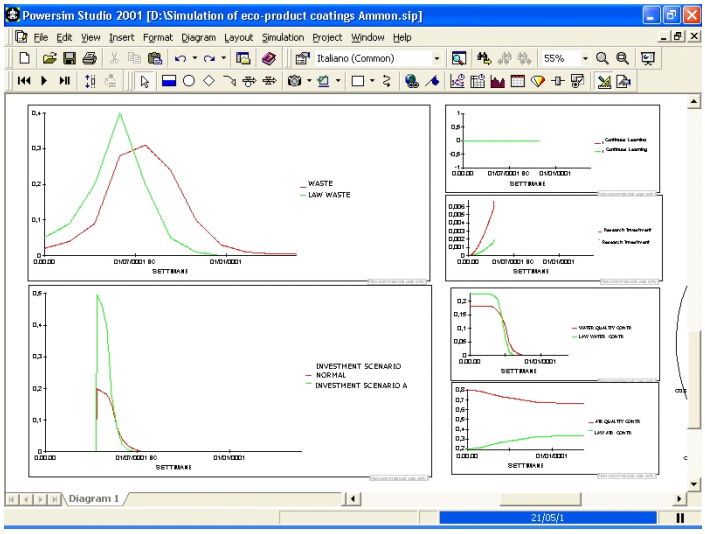

Figure 3. Simulation of specific key environmental variables for strategic control of a business

CONCLUSIONS

Understanding gained via strategic environmental control of the processes underlying development and or running down of key environmental resources is an essential precondition for the implementation of a system of analysis and diagnosis based on continuous learning and an effectively formulated and implemented sustainable business strategy. The use of simulation may aid the identification of the key variables and understanding of the potential scenarios.

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Dubrovnik, CROATIA 6-10 October 2003

SILAQ PROJECT - CROATIA

K Šega*, I Beslić, A Šišović, M Čačković and A Škrbec

ABSTRACT

The SILAQ Programme was developed in implementation of one of the four Sofia Initiatives on the application of the Environmental Action Plan in Central and Eastern European countries, which was adopted during the Third "Environment for Europe" ministerial conference in Sofia in1995. Bulgaria, Croatia, the Czech Republic, Hungary, Poland, Romania, Slovakia and Slovenia joined the Working Group.
In 2002 the PM sampling equipment was placed at disposal of the Croatian Ministry of Environment. The PM study in Croatia started in May and was completed in January 2003. Two Croatian institutions participated in the measuring campaign, Institute for medical research and Occupational Health (IMROH) and ANT, Zagreb.
Three different measuring campaigns were performed by IMROH.

1. Pollutant mass concentrations at Zagreb monitoring network sampling sites: PM_{10}, $PM_{2.5}$, sulphates, chlorides, nitrates, polycyclic aromatic hydrocarbons (PAH)
2. Pollutant mass concentrations at Zagreb crossroads: PM_{10}, $PM_{2.5}$, lead, cadmium, manganese, nirogen oxide, nitrogen dioxide, polycyclic aromatic hydrocarbons
3. Pollutant mass concentrations in the road tunnel "Tuhobić": PM_{10}, $PM_{2.5}$, lead, cadmium, manganese, carbon monoxide, nirogen oxide, nitrogen dioxide, polycyclic aromatic hydrocarbons

In this paper the results of the first measuring campaign are presented.
The investigation showed significant spatial and temporal differences of investigated air pollutant concentrations in Zagreb.

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INDEX TERMS

PM_{10}, $PM_{2.5}$, PAHs, chlorides, nitrates, sulphates

INTRODUCTION

The SILAQ Programme was developed in implementation of one of the four Sofia Initiatives on the application of the Environmental Action Plan in Central and Eastern European countries, which was adopted during the Third "Environment for Europe" ministerial conference in Sofia in1995. Bulgaria, Croatia, the Czech Republic, Hungary, Poland, Romania, Slovakia and Slovenia joined the Working Group. Bulgaria was appointed to chair the Working Group and the Regional Environmental Center for Central and Eastern Europe and its Local Office in Sofia were requested to coordinate the programme. This programme assisted the countries in learning more about their own problems and about each other. Specific and common problems were discussed jointly during the seminars. While utilising a relatively small amount of funds, the programme proved to be beneficial to the countries.
In Sofia, Bulgaria, during April 2000 the workshop entitled "High density areal PM sampling for air quality characterizations" was organized. Experts from Bulgaria, Croatia, Macedonia and Romania took part at training for planning studies and operating with portable MiniVol sampling equipment. The theory and practical exercises were organized .
In 2002 the PM sampling equipment was placed at disposal of the Croatian Ministry of Environment. The PM study in Croatia started in May and was completed in January 2003. Two Croatian institutions participated in the measuring campaign, Institute for medical research and Occupational Health (IMROH) and ANT, Zagreb. This paper present the preliminary results of the investigations performed by (IMROH).
During the December 2002 in Zagreb, Croatia, the regional meeting of the working group on characterization of particulate matter ($PM_{2.5}$/PM_{10}/TSP) pollution was organized in order to share the experience and results of the studies made in Croatia and to discuss the future usage of the equipment. Participants from Bulgaria, Croatia, Hungary, Macedonia, Romania and Slovenia took part in the meeting.

Three different measuring campaigns were performed by IMROH.

1. Pollutant mass concentrations at Zagreb monitoring network sampling sites: PM_{10}, $PM_{2.5}$, sulphates, chlorides, nitrates, polycyclic aromatic hydrocarbons (PAH)
2. Pollutant mass concentrations at Zagreb crossroads: PM_{10}, $PM_{2.5}$, lead, cadmium, manganese, nirogen oxide, nitrogen dioxide, polycyclic aromatic hydrocarbons
3. Pollutant mass concentrations in the road tunnel "Tuhobić": PM_{10}, $PM_{2.5}$, lead, cadmium, manganese, carbon monoxide, nirogen oxide, nitrogen dioxide, polycyclic aromatic hydrocarbons

In this paper the results of the first measuring campaign are presented.

POLLUTANT MASS CONCENTRATIONS AT SELECTED ZAGREB MONITORING NETWORK SAMPLING SITES

MATERIALS AND METHODS

Location and characteristics of sampling sites

Four sampling sites from local monitoring network were chosen for winter and summer sampling campaign:

- IMI – Ksaverska cesta, representing northern residential part of the town characterised by moderate traffic density and numerous green areas
- DOR – Dordiceva ulica, situated at city center characterised by high traffic density and individual heating (nowadays mainly natural gas)
- CRN - Ulica Baruna Filipovica, residential-industrial area in western part of the town, high traffic density
- PES - Getaldiceva ulica, residential-industrial, eastern part of the town

Measuring and sampling period

Samples were collected simultaneously over 24-hour sampling periods (noon to noon) during summer (June 2002 – July 2002) and winter measuring period (November 2002- January 2003).

Samplers

Eight samplers were used for this investigation. Each sampler could be used for total suspended particulate matter, PM_{10} or $PM_{2.5}$ fraction collection. Coarse particles are removed from the main air stream by means of inertial impactors. Particle samples are collected by final filtration. Upgrading the samplers they could be used for simultaneous particle and gas samples collection.Samplers are easily mounted on buildings, trees, piles etc. The main sampler characteristics are:

- Power supply: 220 V Ac or 12 V DC
- Air flow: 0.300 m^3h^{-1}
- Coarse particle fraction separation: inertial impaction
- Filter type: quartz, glass fibre

Sampling period programming:

- 6 different programs, start and end time (hh:mm)
- Day in the week: separate day, every day, weekend, working days

Sample analysis

Filters were preconditioned in dessicator for constant relative humidity 24 hour before, and again after sample collection. Sample weights were measured by Metler Toledo Microbalance. Acidic anions (chloride, nitrate and sulphate) were analysed using ion chromatography (Weiss, 1995). The analysis of PAH content

was performed by Varian Pro Star high-performance liquid chromatograph (HPLC) and a fluorescence detector with changeable excitation and emission wavelength, in order to optimise the selectivity and sensitivity for individual PAH species (Colombini, 1998).

RESULTS AND DISCUSSION

Summary statistics of pollutant concentrations, for both measuring periods, are presented in Tables 1-2. Number of samples, average concentration values, minimum and maximum concentration values are shown. Interquartile ranges were narrow compared to minimum–maximum range, showing grouping of the results around central concentration values.
In Table 3. concentration differences between the measuring sites, for both measuring periods are shown. It is obvious that the significant differences exit only during the summer period, while in winter concentrations are on the same level regardless to the measuring site location. In Table 4. seasonal differences in pollutant concentrations are presented.

Particulate matter

In Croatia, as well as in Europe (Air Quality Guidelines for Europe (2000), WHO Regional Publications, European Series, No. 91), no PM_{10} and $PM_{2.5}$ limit values are prescribed. The obtained results could only be compared to the proposed limit values of 50 μgm^{-3} for PM10 and 30 μgm^{-3} for $PM_{2.5}$ (CEC IP/97/853. Brussels, 8 October 1997: Commission proposes new air quality limit values). Taking into account that our results are grouped in summer and winter, and that they are not evenly spread along the year (lognormal mass concentration distribution is expected), we could only estimate that the average PM_{10} concentrations are around the limit value, while average $PM_{2.5}$ concentrations probably slightly exceed the limit value. Differences in particle concentration levels between the measuring sites are presented in Table 3. One-way anova showed that there is a difference at $p=0.05$ level during summer time for both particle fractions, while no significant difference was found during wintertime. These findings could be explained as the result of high traffic density as a predominating source during summer, while the contribution of traffic to particulate pollution, compared to other sources like space heating is lower during winter. One-tailed t-test showed statistically significant seasonal differences between summer and winter results (Table 4.), $PM_{2.5}$ concentrations at each sampling site. Significant seasonal differences for PM_{10} concentrations were found at two sampling sites, one related to traffic (DOR) and the other to the activity of local industry (PES). Higher particle concentrations occurred during winter measuring period, as it was expected. The largest difference was found at the measuring site located in eastern part of the town (PES).
Relationships between PM_{10} and $PM_{2.5}$ mass concentrations at all four sampling sites for both sampling periods are quite strong. This relationship is much stronger

during winter ($0.915<R<0.990$) than in summer ($0.546<R<0.800$), probably for two possible reasons:

a) Higher concentration levels measured during wintertime resulting in higher precision of measurement

b) Particle size distribution during winter shifted towards smaller particle size as a consequence of different particle sources (space heating) and different climatic conditions. For the same reason the slopes of the regression curves for winter period are much steeper, showing higher content of small particles.

Anion content in $PM_{2.5}$

Anion content was determined in high-risk particle fraction ($PM_{2.5}$). The results of measurements of acidic components (chlorides, nitrates, sulphates) in high – risk particle fraction $PM_{2.5}$ at four monitoring network sampling sites show no significant differences ($P>0.05$, ANOVA, one-way analysis of variance) in pollutant concentration levels between the measuring sites in winter period, while significant differences ($P<0.05$) were found for nitrates and sulphates in summer. Higher mass concentrations of all investigated anions were found in winter period, which may be due to greater emission of pollutants from space heating appliances and motor vehicle exhaust. The mass concentrations showed significant seasonal differences (one-tailed t-test), except for chlorides at sampling sites DOR and PES ($P>0.05$). More pronounced differences ($P<0.001$) were found for nitrates at all sampling sites, sulphates at the sampling site PES, and chlorides at the sampling site IMI.

PAH content in PM_{10}

PAH content was determined in inhalable (thoracic) particle fraction (PM_{10}). The following PAHs were measured: fluoranthene (Flu), pyrene (Pyr), benzo-b-fluoranthene (BbF), benzo-k-fluoranthene (BkF), benzo-a-pyrene (BaP) and benzo-ghi-perylene (BghiP). Data in Tables 1-2. show PAH mass concentrations for summer, and winter measuring period respectively. Summer concentrations were lower compared to the concentrations measured during winter. The PAH concentration values measured at the measuring site DOR were higher compared to the other measuring sites, especially for BghiP and BbF, probably as a consequence of high traffic density at this location. During wintertime the highest concentration values of all measured PAHs were found at the measuring site PES, residential-industrial, eastern part of the town. The concentration levels at other measuring sites were similar. Taking into account that our results are grouped in summer and winter, and that they are not evenly spread along the year (lognormal mass concentration distribution is expected), we could only estimate that BaP concentrations at the measuring sites DOR and PES were slightly higher compared to the limit value of 2 ng m^{-3} set by the Croatian law (Ordinance, 1996). The investigation showed significant spatial and temporal differences of investigated air pollutant concentrations in Zagreb. Concentrations were

Table 1. Pollutant concentrations during summer measuring period

PM10	PM2.5	Cl^-	NO_3^-	SO_4^{2-}	Flu	Pyr	BbF	BkF	BaP	BghiP
($\mu g\ m^{-3}$)					($ng\ m^{-3}$)					
				IMI						
35	35	35	35	35	34	34	34	34	34	34
13,4	6,3	0,00	0,11	0,41	0,028	0,012	0,038	0,025	0,010	0,030
292,8	55,1	1,94	1,68	17,24	0,273	0,310	0,648	0,255	0,294	0,509
41,0	**25,1**	**0,21**	**0,79**	**6,53**	**0,078**	**0,088**	**0,154**	**0,068**	**0,077**	**0,201**
				DOR						
24	21	21	21	21	24	24	24	24	24	24
23,8	0,0	0,02	0,22	1,28	0,008	0,005	0,070	0,029	0,030	0,143
69,4	46,7	6,83	1,45	16,63	0,267	0,330	0,524	0,330	0,558	0,792
41,8	**26,3**	**0,61**	**0,97**	**6,54**	**0,097**	**0,109**	**0,243**	**0,109**	**0,129**	**0,436**
				CRN						
24	24	24	24	24	24	24	24	24	24	24
15,5	11,6	0,00	0,17	0,61	0,012	0,012	0,065	0,030	0,022	0,054
65,1	53,1	2,78	1,73	14,24	0,313	0,242	0,340	0,168	0,276	0,576
42,1	**29,9**	**0,28**	**0,90**	**6,77**	**0,095**	**0,106**	**0,181**	**0,082**	**0,097**	**0,303**
				PES						
19	22	22	22	22	18	18	18	18	18	18
14,7	7,7	0,00	0,09	0,98	0,025	0,024	0,069	0,029	0,022	0,087
62,7	62,4	16,22	1,48	17,20	0,208	0,180	0,339	0,153	0,211	0,708
38,7	**23,8**	**0,87**	**0,72**	**5,52**	**0,094**	**0,088**	**0,158**	**0,079**	**0,094**	**0,251**

Table 2. Pollutant concentrations during winter measuring period

PM10	PM2.5	Cl^-	NO_3^-	SO_4^{2-}	Flu	Pyr	BbF	BkF	BaP	BghiP
($\mu g\ m^{-3}$)					($ng\ m^{-3}$)					
				IMI						
49	47	48	48	48	48	48	48	48	48	48
5,7	8,4	0,00	0,63	0,72	0,64	0,64	0,62	0,01	0,63	0,44
113,9	101,4	8,58	18,61	26,24	21,93	26,26	6,67	3,35	17,65	10,60
55,9	**49,3**	**1,01**	**6,28**	**9,59**	**3,54**	**3,68**	**2,26**	**1,05**	**3,11**	**2,90**
				DOR						
36	36	37	37	37	37	37	37	37	37	37
24,0	10,7	0,00	1,33	1,67	0,53	0,60	0,54	0,29	0,69	0,94
201,6	165,2	1,99	18,63	22,97	16,69	15,98	7,44	25,84	18,35	8,50
75,0	**52,9**	**0,55**	**6,76**	**9,65**	**3,83**	**3,91**	**2,55**	**1,88**	**4,02**	**3,44**
				CRN						
30	30	32	32	32	32	32	32	32	32	32
9,7	7,3	0,03	0,41	0,99	0,57	0,57	0,68	0,35	0,07	0,85
139,0	138,5	10,72	19,73	25,44	20,58	20,38	6,50	3,20	9,29	5,94
60,0	**55,0**	**1,00**	**7,11**	**10,60**	**4,20**	**4,40**	**2,52**	**1,34**	**3,52**	**2,90**
				PES						
25	25	25	25	25	25	25	25	25	25	25
25,6	19,2	0,07	1,75	2,07	0,29	0,47	0,87	0,40	0,60	1,00
298,0	266,5	2,58	34,10	34,51	58,95	61,19	15,10	7,98	26,94	15,91
96,5	**83,2**	**0,86**	**11,25**	**15,86**	**9,82**	**9,76**	**4,00**	**2,03**	**5,24**	**4,35**

Table 3. Differences in pollutant concentration levels between measuring sites

	Summer	Winter
PM10	+	
PM2.5	+	
Cl^-		
NO_3^-	+	
SO_4^{2-}	+	
Flu		
Pyr		
BbF	+	
BkF		
BaP		
BghiP	++	

$^{+}$ P<0.05 $^{++}$ P<0.01

Table 4. Seasonal differences of pollutant mass concentrations

	IMI	DOR	CRN	PES
PM10		+++		+++
PM2.5	+++	+++	+	+++
Cl^-	+++		+	
NO_3^-	+++	+++	+++	+++
SO_4^{2-}	+	++	+	+++
Flu	+++	+++	+++	++
Pyr	+++	+++	+++	++
BbF	+++	+++	+++	+++
BkF	+++	+++	+++	+++
BaP	+++	+++	+++	+++
BghiP	+++	+++	+++	+++

$^{+}$ P<0.05 $^{++}$ P<0.01 $^{+++}$ P<0.001

moderate, usually lower compared to prescribed limit values. It could be concluded that space heating, local industry and traffic are the main sources of air pollution. For better insight, and for comparison to the prescribed limit values, measurements should be performed all year round.

AKNOWLEDGEMENT

This investigation was performed under the auspices of the Regional Environmental Center for Central and Eastern Europe, Local Office in Sofia and the Ministry of Environmental Protection and Physical Planning, Republic of Croatia.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

ECOLOGICAL MONITORING IN GAS FIELD MOLVE

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ABSTRACT

Technological process of exploration, production, transport, processing and refining of the natural gas in the gas-condensate fields of Podravina, northwestern Croatia, has been conceived with the tendency to hinder in full environment pollution. In addition to this, by ecological monitoring the possible impact of the oil mining on the environment is being controlled. During the last twenty years, according to the Program on determination of the environment condition that has been implemented in cooperation with great number of researchers of different skills, the risks of the oil industry on human health and environment have been determined and by improvement of technological processes decreased. A great number of the scientific institutions and individuals take part in the preparation and implementation of ecological researches and analyses, processing and interpretation of results.

This paper comprises the part of these activities and ecological researches with a special emphasis on the air quality control. The results of the mean annual concentrations of the hydrogen sulphide and mercaptan in 1991, 1996 and 2002 were shown with the commentary about the decrease of the concentrations during 1996 and 2002 as compared to 1991; a part of results of research of mercury in the air from 1995 to 1997 and from 1999 to 2000 has also been shown.

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INDEX TERMS

Ecological monitoring, Ambient air, Oil & gas industry, Natural gas,

INTRODUCTION

At the beginning of exploitation of the natural gas, H_2S and Hg at the plants CPS Molve I and II have not been especially removed until 1992, but H_2S was released into atmosphere together with CO_2, while mercury was mostly retained in catchers of mercury on the cooling units. At annual production of $1.500x10^6$ m^3 in 1991, 1.427 tons/day of CO_2, with 477 kg/day of H_2S, respectively 0,089 kg/day of mercury were released into atmosphere. Temporary unpleasant smell of hydrogen sulphide and mercaptan in the plant and its surrounding, has initiated the need of their removal. (Špirić and Juranić, 1993) Therefore, the plant CPS Molve III has been designed in which two new units were constructed with emphasis to the environment protection. One of these economic and ecological units has been a cold section in which the separation of methane from other hydrocarbons is performed by application of aluminum heat exchangers. Demand for gas purity at the entrance into this unit is 50 times stricter for CO_2, ten times for H_2S, and even 5.000 times for Hg, in relation to MDK of these components in the air that are determined in 1993 by Rulebook on MDK in the atmosphere of the working area. On the ground of that we come to the conclusion that the safe work of this unit in the current period represents simultaneously the best monitoring of the environment condition. Otherwise, the risks and possible consequences, for instance only in the case of increase of mercury content at the entrance in this unit above 10 ng/m^3, could be more far-reaching than the emission of mercury itself into the environment. (Špirić, Juranić, Vađunec, *et al*., 1993)

Separation of mercury from natural gas is carried out by sulphur that is impregnated by active coal. An active coal is a micro porous material obtained from different materials (peat, wood, lignite), and has large active surface – up to 1.500 m^2/g. The process is performed so that at first comes to the physical adsorption in mezzopores and micropores; thereafter follows chemical reaction with sulphur into the stable compound – mercury sulphide HgS. At CPS Molve separation of mercury is realized in two stages. The first one that decreases the incoming mercury content in the gas from approximately 2.000 $\mu g/m^3$ to 0,12 $\mu g/m^3$, after that the gas comes into the other, the so called polish adsorber, in which the mercury, for the purpose of protection of the cryogenic section, is decreased to below 10 ng/m^3.

The second unit is a plant for separation of hydrogen sulphide and mercaptan from carbon dioxide but before its release into atmosphere. The process is carried out so that the current of the separated carbon dioxide at the plants CPS Molve I, II and III is brought into LO-CAT unit in which the separation of H_2S and a portion of mercaptan are carried out, after that follows their transformation into elemental sulphur, in the form of sulphur mud. The daily production of sulphur amounts about 400 kg. At annual production of gas of $1784,5x10^6$ m^3 of gas in

1996 the amounts of 1871 tons/day of CO_2, with 239 kg/day of H_2S and only 0,00851 kg/day of mercury were released into atmosphere.
During 1991, according to the program determined in advance, there started the comprehensive researches of pollutions of air, water, soil (chemical features and chemical pollutions, change of kind and content of pedo microflora, soil fauna), vegetation that is used for animal feed and forest vegetation, namely of all parts of environment and biosphere. A big multidisciplinary team of the researchers of Agricultural Faculty (4 scientists), Faculty of Veterinary Medicine (2) and Faculty of Forestry of the University of Zagreb, then of Institute for Medical Research and Industrial Medicine from Zagreb (11 scientists), Public Health Institute of Koprivnica-Kričevci county (3) and many others. The results of research are regularly, at least once a year, presented publicly to the local government, to journalists and to other interested parties. It can be said, that these researches have been in Croatia the only ones so far, and in the world rare comprehensive researches of the natural ecosystems made with the goal to determine the possible pollutions of the environment through emission from known sources. Namely, the presence of the possible pollutions were being initially determined in the air, then in the soil, soil fauna (rain worms), water and indicatory, respectively grass and forest vegetations or fauna – wildlife, in the wide area of the possible source of pollution – CPS Molve.
The measurements have been continued in a little altered form and have been still carried out, and from 2002 they are extended to the determination of the concentration of mercury in the urine of humans.

METHODS

On the ground of results of measurements of emission and meteorological indicators determined in 1991 the critical points of the emission were calculated and the locations of the measurement stations for detection of the specific pollutions in production of the natural gas in the gas field Molve were determined. The locations were selected in the vicinity of the wells Molve-9, 10, 11 and 12, and on them the samples of the chemical pollutions of the air (hydrogen sulphide, mercaptan and mercury) in 24-hour samples (Vađić, 1982; Vađić, Gentilizza, Hršak *et al*., 1980; Moore, Helwig and Graul, 1960) were determined.
The position of the measurement stations is shown in Figure 1. On the same measurement stations the samples of soil on three standard depths 0-3 cm, 10-15 cm and 40-50 cm, and of animal feed, have been taken. The continuing sampling of the radiation dose for determination of radioactivity has been carried out in the locations of Molve-9 and 10.
The samples for determination of water quality have also been taken. On the ground of collected and analyzed samples the results of the physical-chemical, bacteriological and saprobiological researches have been obtained that were carried out in the drinking water, ground waters, waste waters and watercourses.

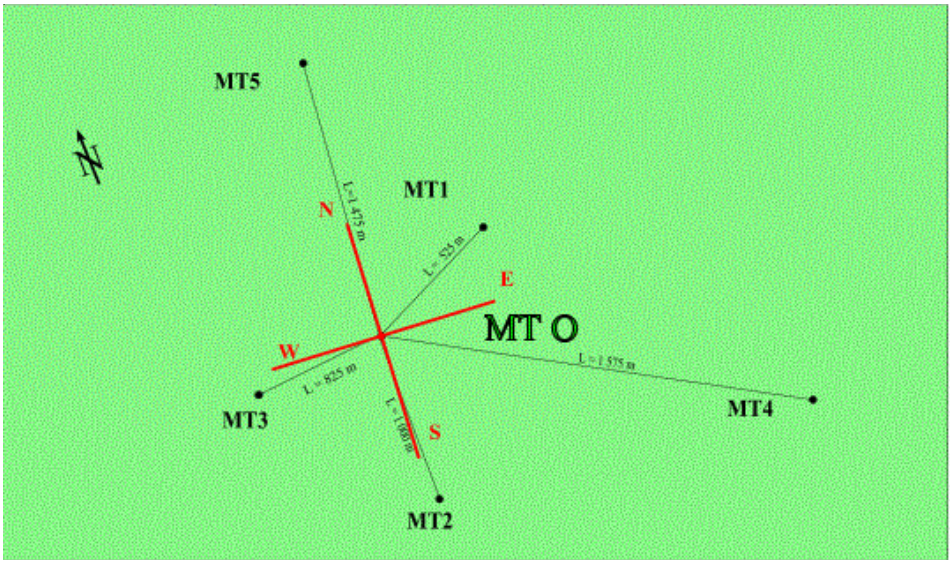

Figure 1. The position of the measurement stations

After construction of the modern processing plant for processing of the natural gas at the plant CPS Molve, with close technological system for removal of mercury from the natural gas in two stages (by active coal impregnated by sulphur), INA-Naftaplin defined and carries out continuing monitoring and determination of the mercury content in the air of the gas field Molve environment. Application of AFS-technique of mercury measurement that lasted for years provided experts of INA-Naftaplin with reliable results and mercury control in the processing currents and in the air of environment and enabled safe work during the production of the natural gas. The results of the air research in the environment of the production plants confirm the justification of the technology selection for mercury removal as well as measurement technique and its great efficiency (sensitivity, preciseness and reliability), and (also) prove presence of very low mercury concentrations that are not dangerous for people and environment and are considerably lower than maximum permissible. (Špirić, Vađunec, Popović *et al*., 1994)

Concentration of the total mercury is determined also in lampreys whose samples are taken in the area of CPS Molve, as well as in samples of wildlife (rabbit, roe-buck, crow, mallard, pheasant) that live in the larger area of Molve. For the need of these researches the mercury in muscles, liver, kidneys and brain of the mentioned wildlife is analyzed.

For immediate researches of the forest ecosystems the forest Gabajeva greda has been chosen which partly goes into gas field Molve, respectively it leans against it, and represents coherent forest surface the content of which has all characteristics that enable utilization of international guidelines for establishing the tested forest surfaces.

During 2002 the determination of mercury in the urine of workers of INA-CPS Molve was carried out, as well as of inhabitants of the village Molve and inhabitants of the village Kalnik as control group.

RESULTS AND DISCUSSION

In Table 1 is shown comparison of the mean annual 24-hour concentrations of hydrogen sulphide in the air measured during 1991, 1996 and 2002, and percentage concentration decrease during 1996 and 2002 as compared to 1991. In Table 2 are shown in the same way the results for mercaptans, and in Table 3 for mercury. The research results show that after building in of LO-CAT plant for removal of hydrogen sulphide and mercaptan as well as of adsorber for removal of mercury, it came to the considerable decrease of hydrogen sulphide, mercaptan and mercury concentrations on all four measurement stations.
During 2002 a further fall of mercaptan and mercury was measured, while hydrogen sulphide levels remained at similar levels.
The research results show that radioactive contamination of environment in the gas field Molve has not been increased due to operation of the gas wells.
Also, despite the increase of the gas production by 20 per cent during 1996 it did not come to an increase of the content of the chemical pollution in the water, soil,

Table 1. Comparison of mean annual 24-hour hydrogen sulphide concentrations in the air ($\mu g/m^3$) measured in 1991, 1996 and 2002

Measurement station	1991.	1996.	2002.	% decreases in 1996 as compared to 1991.	% decreases in 2002 as compared to 1991.
Molve-9	1.4	0.42	0.95	70,0	32.1
Molve-10	1.5	0.38	0.83	74.7	44.7
Molve-11	1.3	0.54	1.28	58.5	1.5
Molve-12	1.2	0.27	1.06	77.5	11.7

Table 2. Comparison of mean annual 24-hour concentrations of mercaptan in the air ($\mu g/m^3$) measured in 1991, 1996 and 2002.

Measurement station	1991.	1996.	2002.	% decreases in 1996 as compared to 1991.	% decreases in 2002 as compared to 1991.
Molve-9	2.4	2.20	0.64	8.3	73.3
Molve-10	3.9	2.15	0.56	44.9	85.6
Molve-11	3.3	2.41	0.98	27.0	70.3
Molve-12	3.1	2.80	0.73	9.7	76.5

Table 3. Results of mercury measurement in the air in Molve, in the period **A** (1995 – 1997) and **B** (1999-2000.)

	Mol-9		**Mol-10**		**Mol-11**		**Mol-12**		**CPS**	
	A	**B**	**A**	**B**	**A**	**B**	**A**	**B**	**A**	**B**
Minimum value (ng/m^3)	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1
Maximum value (ng/m^3)	14,7	27	26,9	11	36,1	15	18	10	56,2	20
Mean value (ng/m^3)	**5,7**	**9**	**5,0**	**4**	**5,4**	4	**3,7**	3	**10,6**	8

meadow and forest vegetation and game in comparison with condition from 1991. The decrease of biogenesis of the soil was determined but there is no evidence that the cause of this occurrence was the effect of emission from the plant CPS Molve. The results of the research of the content of the most important pollutions in the soil and vegetal material in agro ecosystems in the area of effects of CPS Molve made in 2002 within the program of the permanent monitoring of condition show that it came to the fall of the content of all analyzed pollutions in the soil, and that the content of heavy metals, sulphur and other biogenetic elements, as well as N: S relation in the vegetal material of plantain (*Plantago lanceolata*), is moving within tolerant values.

The mercury content in the tissue of wildlife can be considered as «normal».

In the forest Gabajeva greda a considerable improvement of the condition of the trees was determined, and so on the parts of the trees, where during the determination of the zero condition some damages were noticed, these damages were diminished.

The results of determination of the mercury concentration in the urine in the samples measured during 2002 showed an acceptable level of the exposure to mercury from the environment in all three groups of the respondents (workers of CPS Molve, inhabitants of Molve and Kalnik) and they were in accordance with valid international recommendations for general population (WHO, 1980; Hoet and Lauwerys, 1998).

Ecological monitoring and researches of the possible effects of the natural gas production on the health of people and environment are being continued with the same timing and scope in the next three-year period too.

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The 14th International Conference
AIR QUALITY - ASSESSMENT AND POLICY AT LOCAL, REGIONAL AND GLOBAL SCALES
Dubrovnik, CROATIA 6-10 October 2003

CITYDELTA: A MODELLING INTER-COMPARISON EXERCISE IN 8 EUROPEAN CITIES

Ph Thunis* and C Cuvelier

ABSTRACT

As a contribution to the modelling activities in the CAFE programme of the DG-Environment of the European Commission, an open model inter-comparison exercise has been launched by the JRC-IES in collaboration with EMEP, IIASA and EUROTRAC to explore the present (1999) and future (2010) urban air quality predicted by different atmospheric chemistry-transport dispersion models. The different emission-reduction scenarios investigated in this project as well as the range of responses resulting from this model inter-comparison will used in the cost-effectiveness analysis of CAFE with the aim to balance Europe-wide emission controls against local measures. This exercise proposes therefore a common understanding of the benefits and limitations of regional emission control against local measures.
The model inter-comparison focuses on ambient levels of particulate matter and ozone in urban areas. It addresses health-relevant matrices of exposure (e.g., long-term concentrations) to fine and coarse particles as well as to ozone. Comparisons are currently conducted for 8 European cities: Berlin, Copenhagen, Katowice, London, Marseille, Milan, Paris and Prague and involve the active participation of more than 15 modelling groups in Europe. Each of them was asked to perform a long-term validation simulation for a 300x300 km area around each city: a six months run for Ozone and a full year run for PM, and a number of (NO_x,VOC,$PM_{2.5}$ and PM_{coarse}) emission-reduction scenario simulations for the year 2010.

INDEX TERMS

Urban air quality, Model intercomparison exercise, 2010 emission scenarios, Regional versus local air quality.

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INTRODUCTION

An open model inter-comparison exercise (CityDelta) has been launched by the JRC-IES in collaboration with EMEP[1], IIASA[2] and EUROTRAC[3] to explore the present (1999) and future (2010) urban air quality predicted by different atmospheric chemistry-transport dispersion models. The model inter-comparison focuses on long term ambient levels of particulate matter (12 months) and ozone (6 months) in 8 European cities: Berlin, Copenhagen, Katowice, London, Marseille, Milan, Paris and Prague.

CityDelta[4] aims at providing guidance on how urban air-quality could be implemented in a Europe-wide evaluation of the cost-effectiveness of emission control strategies. CAFE (Clean Air For Europe) expects information from integrated assessment models on a cost-effective balance between emission control measures that should be taken at the European/Community level and measures that should be best left to the local city Authorities. For this integrated assessment task the central questions are:

- What is the influence of local versus regional emission control on health-relevant indicators for fine particles (PM_{10}, $PM_{2.5}$) and ozone in urban air?
- How regional model predictions differ from predictions obtained with finer resolved models?
- What is the range of agreement between different photochemical-dispersion models on the level of responses to emission changes?
- What is the range of variability in air quality among cities in response to similar changes in emissions?

These questions suggest CityDelta to focus on the interpretation of various deltas (in emissions, among models, among cities or across scales), the final aim being to provide recommendations on how to include urban air-quality into integrated assessment modelling.

In this paper, the CityDelta methodology is presented focusing on the necessary model input data and on the interpretation procedure. Preliminary conclusions are drawn based on a first set of results.

METHODOLOGY

Comparability among model results is ensured only if models are run in similar conditions. To achieve this purpose, same emissions and meteorological year (1999) were imposed to all participating models. Regarding the emissions, the inventories which were provided at both the local (city) and regional (EMEP-TNO[5]) scales have been merged to cover a 300 x 300 km^2 domain over which results were requested (Figure 1). The EMEP Eulerian model[4] has been used to provide boundary conditions for all city domains.

In parallel with the inter-comparison, an evaluation of model performances against monitoring data is carried out for the 1999 base case. Monitoring data (O_3, NO_2, NO, PM_{10} and eventually $PM_{2.5}$) for the different cities have been compiled with the help of local organizations and made available to the CityDelta participants. Emission scenarios for 2010 have been prepared by IIASA with emission reductions specific to each country, pollutant and activity sector. The emission scenarios include:

a) the 2010 CLE (Current Legislation) scenario

b) additional NO_x reductions to MFR (Maximum Feasible Reduction) level

c) additional NO_x reductions to (MFR+CLE)/2 level

d) additional VOC reductions to MFR level

e) Combined MFR VOC and NO_x reductions

f) PM_{coarse} reduced to MFR level

g) $PM_{2.5}$ reduced to MFR level

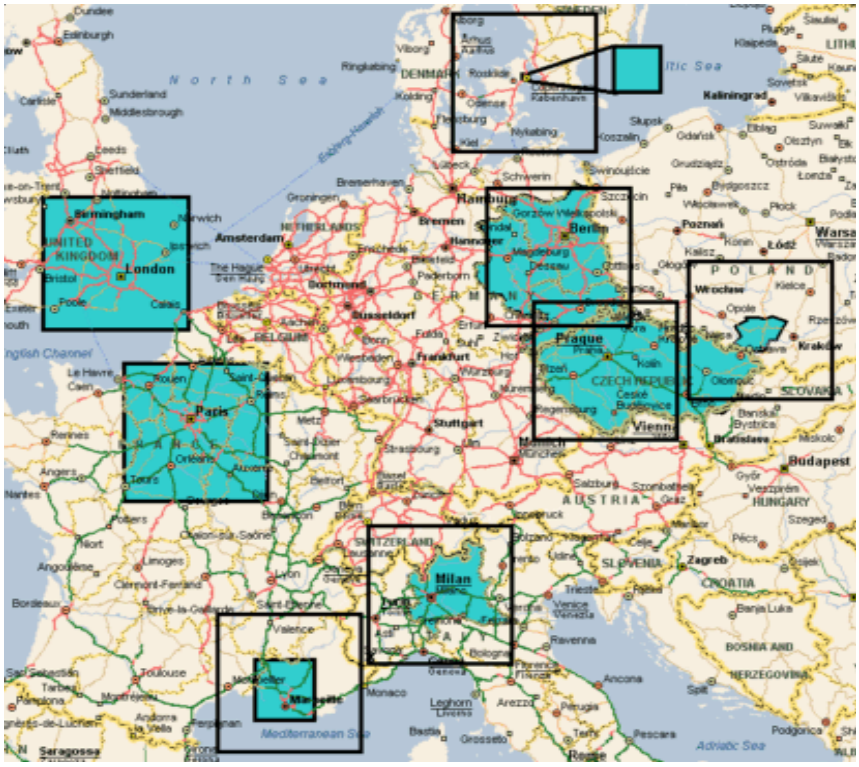

Figure 1. Spatial coverage of the local high resolution emission inventory (grey shaded area) within the computational domain of 300x300 km^2 indicated by the solid squares around each city.

About 15 European modelling groups are participating in this exercise (see table 1). Of course, each group did not perform simulations over the whole set of CityDelta cities and emission scenarios but many participated on multiple cities and with different model resolutions.
After submission by each modelling group of results to the JRC-IES for processing, a subset of the full dataset was used to perform the intercomparison of the results. A graphical interpretation tool has been made available by JRC-IES to the CityDelta community with which each participating group could evaluate its own results and compare them to others. The tool is flexible enough to guarantee a visualisation of various types of indicators. Usage of a common tool also facilitates the discussions between CityDelta participants. This graphical tool currently includes applications to visualize a) the monitoring data, b) the emissions, c) the evaluation of the model results at monitoring sites, d) the model answers to emission reductions and e) a 2-D visualisation for time-averaged indicators.

Table 1. List of participating modelling groups in the CityDelta exercise. For each city and model, the letters OP indicate either Ozone (O) or PM (P) simulations. The three last columns indicate the spatial resolution at which models are run.

Contact Person	Model	Paris	London	Prague	Katow	Milan	Berlin	5 km	10 km	50 km
M. Bedogni	***CAMX***					O		x		
R. Berkowicz	***THOR***		OP		OP		OP	x	x	x
F. Brocheton	***MOCAGE***	O	O	O	O	O	O			x
	MOCAGE	O				O			x	
L. Volta	***CALGRID***					O		x		
N. Moussiopoulos	***OFIS***	OP	OP	OP		OP	OP			
	MUSE	O	O	O		O	O		x	
G. Pirovano	***STEM***					O		x		
R. Stern	***REM3***						OP	x		
G. Schaedler	***MCCM***				OP		OP	x		x
C. Honore	***CHIMERE***	OP	OP	OP	OP	OP	OP			x
	CHIMERE	OP	OP	O		OP	OP	x		
L. Tarrason	***EMEP***	OP	OP	OP	OP	OP	OP			x
J. Brechler	***SMOG***			O				x	x	
B. Denby	***EPISODE***						O		x	
P. Builtjes	***LOTOS***	OP					OP	x	x	x
C. Philippe	***TRANSCHIM***	O		O				x	x	
O. Hellmuth	***MUSCAT***						OP		x	
F. De Leeuw	***EUROS***	O			O	OP			x	
C. Borrego	***CAMX***		OP					x		

DISCUSSION

The fourth City-Delta workshop took place in Valencia in April 2003 with a main objective being the interpretation of preliminary results. More than 220 6-months

gas-phase and 90 yearly aerosol-phase simulations were available at that date. Although preliminary, a few conclusions have been drawn regarding modelled long term ozone. In general, fine scale resolution model results (5 and 10 km) did not show a significant improvement compared to coarse ones (50 km) and the variability looked larger among different models with similar resolution than across scales with similar models. All models exhibited difficulty in reproducing the night time behaviour, showing a clear overestimation. On the other hand, NO_2 predictions versus measurements were significantly improved with finer resolutions. The variability among model results was much more marked in some cities than others as is illustrated from the figure below.
Regarding PM, models generally showed a clear underestimation of long-term mean concentrations and some difficulties in reproducing the seasonal variations of the measurements.

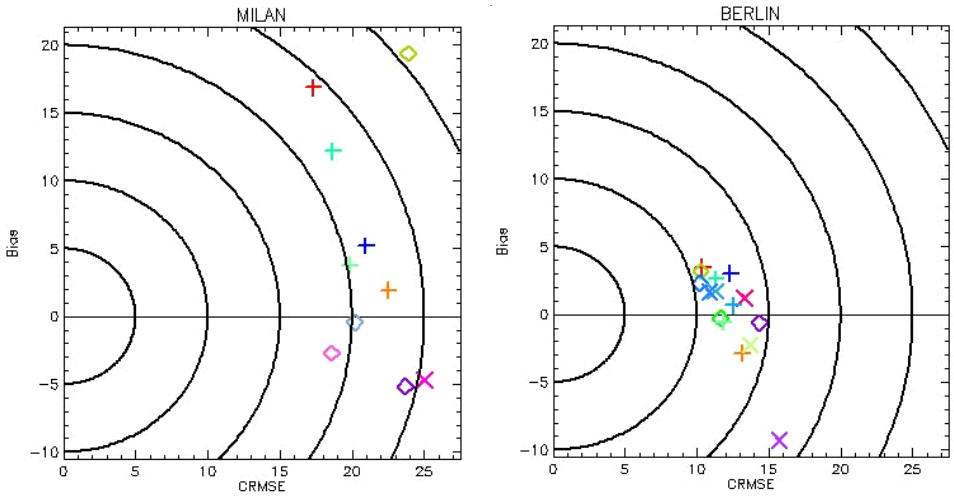

Figure 2. Modelled 6 months averaged O3 concentrations in terms of bias and Centred Root Mean Squared error (CRMSE). The distance between the symbol and the circles origin provides the Root Mean Squared Error. Model resolutions are either 5 km (%), 10 km(x) or 50 km (+)

CONCLUSIONS

In collaboration with IIASA, EMEP and EUROTRAC (TNO-MEP), the JRC-IES has launched in February 2002 a contribution to the CAFÉ programme of the DG_Environment in the area of air quality modelling. One of the objectives is to explore the present (1999) and future (2010) urban air quality predicted by different atmospheric chemistry-transport dispersion models. The activity is health-driven and the focus of the project is restricted to the long-term exposure to O_3, and PM (fine coarse). An other objective of CityDelta is to investigate the

impact of various types of emission-reductions (CLE and MFR scenarios for VOC, NO_x, $PM_{2.5}$, PMcoarse) on levels of ozone and PM for 8 European cities. For these cities monitoring data has been made available by the city authorities and high-resolution emission inventories were set up. After pre-processing by the JRC-IES all input data has been made available to the 20 participating modelling groups, who produced a large number of results on various spatial resolutions ranging from 3 km up to 50 km.

A general methodology was developed by JRC-IES to allow all modelling participants to visualize and analyse not only their own results but also to make intercomparisons with the results provided by other groups. The graphical visualisation tool allows the intercomparison of results for the base year (1999) and the intercomparison of the differences (deltas) among the model results in terms of spatial resolutions, model formulations, cities, and emission-reductions for the year 2010.

The 4th CityDelta workshop in Valencia (April 2003) concluded in a lack of PM results. Also a number of inconsistencies in the emission inventories have been identified. This was the reason to launch a follow-up of CityDelta with a specific focus on the impact of PM emission-reductions taking into account the consistency of the emission inventories for the various resolutions (i.e. high-resolution for city emissions, and 50 km resolution for the EMEP emissions). The first results of this CityDelta follow-up will be discussed at the 5th CityDelta workshop in Matera (October 2003) with the final CityDelta conclusions to be expected by the beginning of 2004.

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4 CityDelta homepage: http://rea.ei.jrc.it/netshare/thunis/citydelta

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The 14th International Conference
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Dubrovnik, CROATIA 6-10 October 2003

AIR QUALITY IN CROATIA MONITORING AND CATEGORIZATION AT REGIONAL SCALE

V Vadjić*

ABSTRACT

Monitoring of air quality in urban and industrial areas in Croatia has started in Zagreb during the 60s and it was organised by the Institute for Medical Research and Occupational Health and regional authority. Since the early seventies air pollution monitoring has been gradually introduced in other Croatian towns by regional Institutes of Public Health together with the regional authorities. All regional monitoring networks use the same methodology for air quality monitoring and are connected in one common network. Today this is the only monitoring network which exists in Croatia. This network has plenty of manually operated stations and only a few automatic stations. Reorganization and harmonization of the regional network is expected in the future. Automatic equipment will be gradually introduced to replace the manually operated one. The first automatic monitoring station in State monitoring network was established in Zagreb in 2003. In accordance with the Ordinance on locations of permanent air monitoring stations in the national network (Ordinance, 2002) 22 automatic stations for continuous monitoring of air pollution are expected to be installed in the State monitoring network till the end of 2007. The stations will be located in towns, industrial areas, national parks and islands.There are also some local monitoring stations in Croatia for monitoring specific air pollutants in industrial areas, gas fields and near waste dumps. Global indicators of air quality in Croatia are monitored by Meteorological and Hydrological Service.
During 2002 the surveillance of air quality was provided in 39 Croatian towns. This paper describes an ongoing air quality surveillance in regional network with respect to the results of sulphur dioxide, smoke, total suspended particulate matter, metals lead, cadmium and manganese in total suspended particulate

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matter, PM_{10}, nitrogen dioxide, ozone and polycyclic aromatic hydrocarbons measurements in seven the largest Croatian towns. The results refer to the entire monitoring period in each town where the surveillance was performed. Only SO_2 and smoke were measured in all seven towns and air quality greatly improved over the years of measuring. Air in Croatian towns was moderately polluted with SPM, $PM_{10,}$ NO_2 and BaP. Levels of lead, cadmium and manganese in SPM and ozone were very low during the whole surveillance period. Croatian towns follow trends similar to those of other European countries.

INDEX TERMS

Limit values, metals, nitrogen dioxide, ozone, PAH, recommended values, smoke, sulphur dioxide, total suspended particulates

INTRODUCTION

The surveillance of air quality in Croatia started in Zagreb in 1962 with the measurement of deposited matter (DM). A network for SO_2 and smoke measurement was organized in 1965, for total suspended particulate matter (TSP) and for its heavy metals content in 1972, for NO_2 in 1994, for ozone in 1996, for PM_{10} in 1998, and for polycyclic aromatic hydrocarbons (PAH) in 2000. The continuous surveillance in Zagreb was organized by the Institute for Medical Research and Occupational Health and regional authority. The Institute participates in the QA/QC audit within the GEMS/AIR Programme of the WHO. Since the early seventies, air pollution monitoring has been gradually introduced in other Croatian towns by regional Institutes of Public Health and regional authorities. During 2002 the monitoring of air quality was provided in 39 Croatian towns. Figure 1 shows the air quality regional network in the urban areas of Croatia.

Air quality is currently assessed by comparing annual means and the 98th percentile values with recommended (RV) and limit (LV) values stipulated by the Law on Air Quality Protection in Croatia (Law, 1995, p. 1452) and the Ordinance on Recommended and Limit Air Quality Values (Ordinance, 1996, p.4198). The Law on Air Quality Protection in Croatia gives three categories of air quality:

1st category - clean air (the concentration levels of air pollution are below RV)

2nd category - moderately polluted air (the concentration levels of air pollution are over RV and below LV)

3rd category - polluted air (the concentration levels of air pollution are over LV).

This paper desribes the measurement of general and specific pollutants in Croatian towns included in the air quality surveillance programme. The results refer to the entire surveillance period. The presented data were obtained from only one

measuring site in each town, either the only one, or the one in the most polluted area in each town. The categorization of towns according to air quality parameters stipulated by the Law on Air Quality Protection in Croatia and the Ordinance on Recommended and Limit Air Quality Values is also presented.

MATERIAL AND METHODS

Sulphur dioxide samples were collected from approximately 2 m^3 of ambient air into hydrogen peroxide solution (ISO-4219, 1979) over 24 hours. The mass concentration of SO_2 was determined by titration with sodium tetraborate (ISO-4220, 1984) and by ion chromatography (UNEP/WHO, 1994).
Smoke samples were collected on Whatman No. 1 filter paper using a volumetric apparatus (BS 1747, 1969). The sampler volume amounted to approximately 2 m^3 of air. Mass concentrations were determined by the reflectometric method.

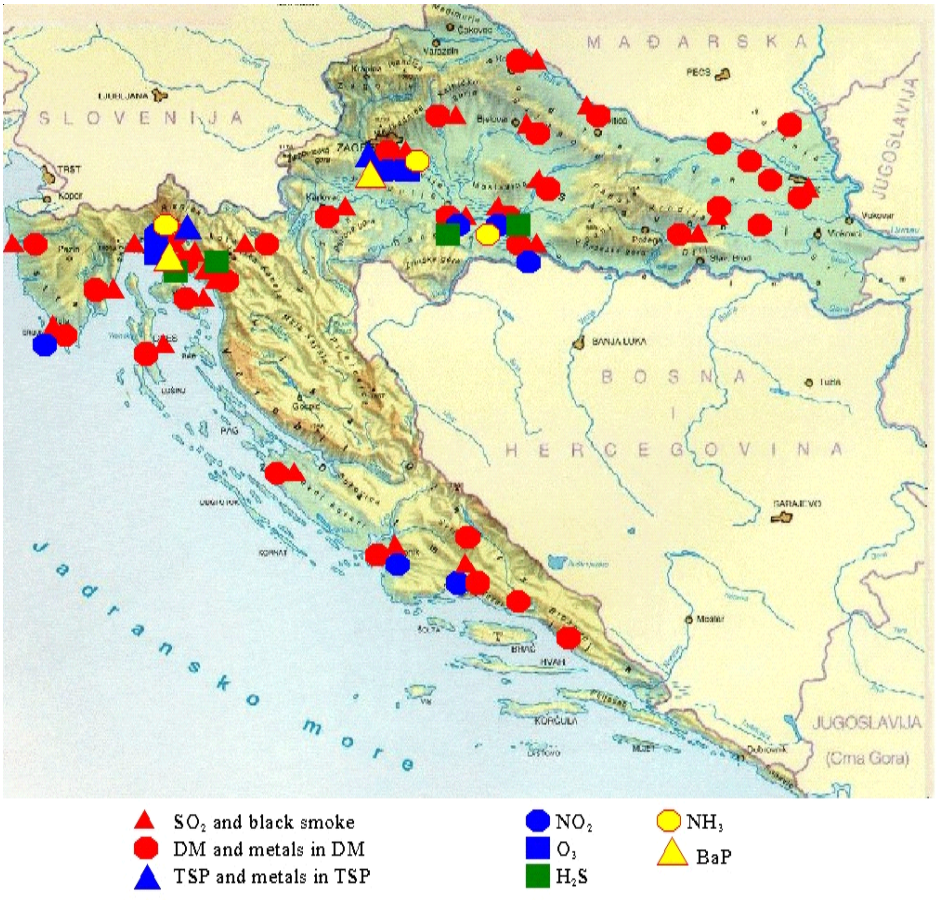

Figure 1. Air quality regional network in the urban areas of Croatia

TSP samples were collected on membrane filters by means of a pump providing approximately 200 m^3 of air during 24 hours. The mass concentraion of TSP was determined gravimetrically. Flame atomic absorption spectrophotometry method was used to determine the content of heavy metals - lead, cadmium and manganese in the same samples.
PM_{10} samples were collected on glass fibre filters using Ingenieurbuero Sven Lockel, Volume Sampler LVS 3 from approximately 55 m^3 of air in 24 hours. The mass concentration of PM_{10} was determined gravimetrically.
Samples were kept in the deep freeze at -18 °C, wrapped in aluminium foil for PAH analyses. They were extracted with cyclohexane in an ultrasonic bath for one hour, separated from undissolved parts by centrifugation and evaporated to dryness. Then they were redissolved in acetonitrile and analysed with a high-performance liquid chromatograph (HPLC) and a fluorescence detector. A detailed procedure for the preparation and analysis of samples has been described earlier (Šišović, 1991, p. 235). Samples were analyzed for the following PAH: fluoranthene (Flu), benzo-b-fluoranthene (BbF), benzo-k-fluoranthene (BkF), benzo-a-pyrene (BaP), dibenzo-ah-anthracene (DahA), and benzo-ghi-perylene (BghiP).
The air samples of NO_2 were collected by passive sampling on filter papers impregnated with triethanolamine. The mass concentration of NO_2 was determined by the spectrophotometric method (Pauković, 1987, p. 17), but they were also monitored using automatic chemiluminiscence instruments.
The concentrations of ozone were determined continuously on UV absorption principle by means of automatic monitors.

RESULTS AND DISCUSSION

Air quality was categorized with respect to recommended (RV) and limit (LV) air quality values given in Croatian Law on Air Quality Protection and the Ordinance on Recommended and Limit Air Quality Values, as shown in Table 1. The Law and the Ordinance will be soon regulate into accordance with European standards.

Table 1. Recommended (RV) and limit (LV) air quality values ($\mu g/m^3$)

Pollutant	Measuring period	Average	RV		LV	
		Time (hours)	Annual mean	RV_{98}	Annual mean	LV_{98}
SO_2	1 year	24	50	125	80	250
Black smoke	1 year	24	50	125	80	250
TSP	1 year	24	75	120	150	350
Pb in TSP	1 year	24	1		2	
Cd in TSP	1 year	24	0.01		0.04	
Mn in TSP	1 year	24	1		2	
NO_2	1 year	24	40	60	60	120
O_3	1 year	24		110		150
PM_{10}	1 year	24	50	70		
BaP*	1 year	24	0.2	1	2	10

* - ng/m^3

Table 2. shows the categorization of seven towns in Croatia with respect to SO_2 concentration levels. The air in Zagreb, Rijeka, and Pula was very polluted in the sixties, seventies, and eighties, that is, the air quality was of the 3rd category. In the other four towns the levels of SO_2 were lower and the air quality was of the 2nd or the 1st category. The decreasing trend for SO_2 started in the eighties and continued through the nineties so the air quality rose to the 2nd and then subsequently to the 1st category in all towns.

Table 2. Categorization of Zagreb, Split, Osijek, Sisak, Karlovac, Rijeka and Pula with respect to the SO_2 levels

Years	1st category C<RV	2nd category RV<C<LV	3rd category C>LV
1965.			■
1966.			■
1967.			■
1968.			■
1969.			■
1970.			■
1972.			■
1973.			■ ○
1974.			■ ○
1975.	●		■ ○
1976.	● □ ▲	▽	■ ○
1977.	● ▲	□ ▽	■ ○
1978.	● □ ▲	▽	■ ○
1979.	● □ ▲ ▽		■ ○
1980.	● □ ▲	□ ▽	■ ○
1981.	● □ ▲ ▽	■	○
1982.	● □ ▲ ▽	■	○ X
1983.	● □ ▲ ▽	X	■ ○
1984.	● □	▲ ▽ X	■ ○
1985.	● □ ▽	▲ X	■ ○
1986.	● ▽	□ ▲	■ ○ X
1987.	● □ ▲ ▽		■ ○ X
1988.	● □ ▲ ▽		■ ○ X
1989.	● □ ▲ ▽	■ X	○
1990.	● □ ▲ ▽ X	■	○
1991.	● □ ▲ ▽	■ ○ X	
1992.	● □ ▲ ▽	■ X	○
1993.	● □ ▲ ▽	■ X	○
1994.	■ ● □ ▲ ▽ X	○	
1995.	■ ● □ ▲ ▽ X	○	
1996.	■ ● □ ▲ ▽ X	○	
1997.	■ ● □ ▲ ▽ ○ X		
1998.	■ ● □ ▲ ▽ ○ X		
1999.	■ ● □ ▲ ▽ ○ X		
2000.	■ ● □ ▲ ▽ ○ X		
2001.	■ ● □ ▲ ▽ ○ X		
2002.	■ ● □ ▲ ▽ ○ X		

■ - Zagreb ●- Split □ - Osijek ▲- Sisak ▽ - Karlovac ○- Rijeka X - Pula

According to the levels of smoke the air quality in all seven towns was similar to categories determined for SO_2 (Table 3). The decreasing trend for smoke was stronger than for SO_2 in Zagreb and air quality shifted to the 1st category in the eighties. The levels in Karlovac were in the 2nd category until 1996 and the levels of smoke in Rijeka are still of the 2nd category.

Table 3. Categorization of Zagreb, Split, Osijek, Sisak, Karlovac, Rijeka and Pula with respect to the black smoke levels

Years	1st category C<RV	2nd category RV<C<LV	3rd category C>LV
1965.			■
1966.			■
1967.			■
1968.			■
1969.			■
1970.			■
1972.			■
1973.			■ ○
1974.			■ ○
1975.	●		■ ○
1976.	● □ ▲	▽	■ ○
1977.	● □ ▲		■ ▽ ○
1978.	● □ ▲	▽	■ ○
1979.	● □ ▲	■ ▽	○
1980.	● □ ▲	▽	■ ○
1981.	● □ ▲	■ ▽	○
1982.	■ ● □ ▲▽ X		○
1983.	● □ ▲ X	■ ▽	○
1984.	● □ ▲ X	■ ▽	○
1985.	● □ ▲ X	■ ▽	○
1986.	● □ ▲ X	■ ▽	○
1987.	■ ● □ ▲ X	▽	○
1988.	■ ● □ ▲ X	▽	○
1989.	■ ● □ ▲ X	○	▽
1990.	■ ● □ ▲ X	▽ ○	
1991.	■ ● □ ▲ X	▽ ○	
1992.	■ ● □ ▲ ▽ X	○	
1993.	■ ● □ ▲ X	▽ ○	
1994.	■ ● □ ▲ X	▽ ○	
1995.	■ ● □ ▲ X	▽ ○	
1996.	■ ● □ ▲ X	▽ ○	
1997.	■ ● □ ▲ ▽ X	○	
1998.	■ ● □ ▲ ▽ X	○	
1999.	■ ● □ ▲ ▽ X	○	
2000.	■ ● □ ▲ ▽ X	○	
2001.	■ ● □ ▲ ▽ X	○	
2002.	■ ● □ ▲ ▽ X	○	

■ - Zagreb ●- Split □ - Osijek ▲- Sisak ▽ - Karlovac ○- Rijeka X - Pula

Table 4. shows the categorization of Zagreb and Rijeka air with respect to levels of total suspended particles (TSP) and metal content in TSP. The air quality in Zagreb with respect to the levels of TSP was of the 3rd category at the beginning of the monitoring during the seventies. In the nineties the air quality improved to the 2nd category. The levels of TSP in Rijeka were, with some variations, of the 2nd category. The levels of Pb, Cd, and Mn in TSP were very low and the air quality in this respect was of the 1st category during the whole monitoring period. The surveillance for NO_2 started in Rijeka in 1980, in Pula in 1990, in Zagreb in 1994, in Sisak in 1998 and in Split in 2002 (Table 5). The results showed that the air quality in Zagreb and Rijeka was of the 2nd category, in Pula, Sisak and Split was of the 1st category during the whole monitoring period.

Table 4. Categorization of Zagreb and Rijeka with respect to levels of TSP and metals in TSP

Years	1st category C<RV	2nd category RV<C<LV	3rd category C>LV
1972.	● ▣		■
1973.	● ▣		■
1974.	● ▣		■
1975.	● ▣		■
1976.	● ▣		■
1977.	▣	●	■
1978.	● ▣		■
1979.	● ▣		■
1980.	● ▣	■ □	
1981.	□ ● ▣	■	
1982.	□ ● ▣	■	
1983.	● ▣	■ □	
1984.	● ▲ ▣	□	■
1985.	● ▲ ▣	■	
1986.	● ▲ ▣		■
1987.	● ▲ ▣	■	
1988.	● ▲ ▣		■
1989.	● ▲ ▣	■	
1990.	● ▲ ▣	■	
1991.	□ ● ▲ ▣	■	
1992.	□ ● ○ ▲ ▽ ▣	■	
1993.	● ▲ ▣	■	
1994.	● ○ ▲ ▽ ▣	■ □	
1995.	● ○ ▲ ▽ ▣	■ □	
1996.	● ○ ▲ ▽ ▣	■ □	
1997.	● ○ ▲ ▽ ▣	■ □	
1998.	● ○ ▲ ▽ ▣	■ □	
1999.	● ○ ▲ ▽ ▣	■ □	
2000.	● ○ ▲ ▽ ▣	■ □	
2001.	● ○ ▲ ▽ ▣	■ □	
2002.	● ○ ▲ ▽ ▣	■ □	

■ - TSP Zagreb ●- Pb Zagreb ▲- Cd Zagreb ▣ – Mn Zagreb
□ - TSP Rijeka ○- Pb Rijeka ▽ - Cd Rijeka

The surveillance for NO_2 started in Rijeka in 1980, in Pula in 1990, in Zagreb in 1994, in Sisak in 1998 and in Split in 2002 (Table 5). The results showed that the air quality in Zagreb and Rijeka was of the 2nd category, in Pula, Sisak and Split was of the 1st category during the whole monitoring period.

Table 5. Categorization of Zagreb, Split, Sisak, Rijeka and Pula with respect to the NO_2 levels

Years	1st category C<RV	2nd category RV<C<LV	3rd category C>LV
1980.		○	
1981.		○	
1982.	○		
1983.		○	
1984.		○	
1985.		○	
1986.		○	
1987.		○	
1988.		○	
1989.		○	
1990.	X	○	
1991.	X	○	
1992.	X	○	
1993.	X	○	
1994.	X	■ ○	
1995.	X	■ ○	
1996.	X	■ ○	
1997.	X	■ ○	
1998.	▲ X	■ ○	
1999.	▲ X	■ ○	
2000.	▲ X	■ ○	
2001.	▲ X	■ ○	
2002.	▲ X ●	■ ○	

■ - Zagreb ●- Split ▲- Sisak ○- Rijeka X - Pula

Ozone was monitored only in Zagreb and in Rijeka. Ozone levels had been of the 1st category since the beginning of measurement in 1996 in Zagreb and in 2001 in Rijeka (Table 6).

A measuring site for PM_{10} was established in 1998 only in Zagreb. The concentration levels of PM_{10} were of the 2nd category since the beginning of measurement in 1998 (Table 7).

The PAH monitoring started in 2000 in Zagreb and in 2001 in Rijeka. Ordinance on Recommended and Limit Air Quality Values presents RV and LV for BaP only. The concentrations of BaP were of the 2nd category during the whole monitoring period (Table 8).

Table 6. Categorization of Zagreb and Rijeka with respect to the O_3 levels

Years	1st category C<RV	2nd category RV<C<LV	3rd category C>LV
1996.	■		
1997.	■		
1998.	■		
1999.	■		
2000.	■		
2001.	■ ○		
2002.	■ ○		

■ - Zagreb ○- Rijeka

Table 7. Categorization of Zagreb with respect to the PM_{10} levels

Years	1st category C<RV	2nd category RV<C<LV	3rd category C>LV
1998.		■	
1999.		■	
2000.		■	
2001.		■	
2002.		■	

■ - Zagreb

Table 8. Categorization of Zagreb and Rijeka with respect to the BaP levels

Years	1st category C<RV	2nd category RV<C<LV	3rd category C>LV
2000.		■	
2001.		■ ○	
2002.		■ ○	

■ - Zagreb ○- Rijeka

CONCLUSIONS

Air quality in Croatia is presently within tolerable limits for SO_2 and smoke. It used to be rather poor in Zagreb and Rijeka in the 60s and 70s, and it improved in the 80s, primarily because coal was replaced by gas and liquid fuel and because district heating was introduced in densely populated districts. Further reduction

of air pollution was observed in Zagreb and Rijeka recently, which may be attributed to the reduced industrial activity as a consequence of Serbian aggression in Croatia in the 90s. Levels of Pb and Cd in TSP and ozone in Zagreb and Rijeka and Mn in TSP in Zagreb and NO_2 in Pula, Sisak and Split were within tolerable limits for the whole period of surveillance.

Concentrations of TSP in Zagreb were of the 3rd category in the 70s. From 1989 the TSP concentrations shifted to the 2nd category while NO_2, PM_{10} and BaP concentrations remained of the 2nd category from the beginning of measurements in Zagreb and Rijeka. Concentrations of TSP in Rijeka were, with some variations, of the 2nd category.

With respect to SO_2 , smoke, metals Pb, Cd, and Mn in TSP, and ozone, air quality in Croatia is presently of the 1st category (clean air) and with respect to TSP, PM_{10}, NO_2 and BaP it is of the 2nd category (moderately polluted air).

Reorganization and harmonization of the regional network is expected in the future. Automatic equipment will gradually be introduced to replace the manualy operated one. Monitoring of TSP, metals Pb, Cd and Mn in TSP and NO_2 is expected to start in all larger towns. Ozone measuring is also expected to start along the coast and VOC started with monitoring in Zagreb in 2003.

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Dubrovnik, CROATIA 6-10 October 2003

PARTICLE NUMBER CONCENTRATIONS FROM RURAL TO URBAN SITES IN SWITZERLAND

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ABSTRACT

In Switzerland, particulate matter is controlled by legal standards concerning the mass of PM_{10}. Therefore, PM_{10} is routinely measured at many sites covering different levels of pol-lution. Additionally, $PM_{2.5}$ is measured at some sites. To characterise the smallest fraction of particulate matter, routine measurements of the total particle number concentration were started in spring 2003. In a preliminary project, particle number concentrations were meas-ured at four sites from January 2000 through April 2002. The instrument used, TSI type 3022A, counts particles in the range between 7 nm and 3 μm. At a site near a highway particle number concentrations are 9 times higher than at a rural site and 5 times higher than at an ur-ban background site. This clearly confirms that emissions of motor vehicles are dominated by ultrafine particles and are responsible for high ambient particle number concentrations. The mass concentrations of PM_{10} and $PM_{2.5}$ however, are only slightly higher in the vicinity of roads. This is well explained by the fact that the nanoparticles in fresh exhaust gases grow rapidly by coagulation. The resulting particles, as well as the coarser ones, can have a long lifetime in the atmosphere and contribute to a fairly homogeneous background of PM-mass concentrations. The particle measurements near a highway were stratified according to wind direction and weekday. The results confirm that motor vehicles are responsible for a large part of ultrafine particles in ambient air and that mainly heavy-duty vehicles emit ultrafine parti-cles. The particle number concentrations correlate well with the concentrations of nitrogen oxides, but less with particle mass concentrations like PM_{10} or $PM_{2.5}$.

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INDEX TERMS

Particulate matter, particle number, ultrafine particles.

INTRODUCTION

In Switzerland, the Swiss Air Pollution Monitoring Network (NABEL) and networks of local authorities measure air pollutants at sites of different pollution level, ranging from remote Alpine sites to locations at the kerbside of roads with heavy traffic. The compliance with the national air quality standards is controlled and the longterm changes of the air pollutants are monitored (BUWAL, 2001). For particulate matter, only legal standards concerning the mass of PM_{10} are set. However, many medical studies show that PM_{10}-mass alone is presumably not sufficient to explain health effects. Mainly the ultrafine particles originating from combustion processes are of great concern for human health. Therefore, an additional physical and chemical characterisation of ambient particulate matter is desired. Corresponding measurements of particle properties were performed for shorter periods, but are usually not measured in air quality monitoring networks. A comprehensive summary of European measurements of particulate matter is given in (Putaud et al., 2002). That study shows that a regional background largely affects both PM_{10} and $PM_{2.5}$ mass concentrations. The $PM_{2.5}/PM_{10}$ ratio was found to be fairly constant at a given site, but to vary between sites. Measurements of particle size distribution show a most persistent mode around 100 – 200 nm at all sites. In areas with heavy traffic smaller particles around 20 – 30 nm dominate. Data from a mobile measurement laboratory confirm these findings for Switzerland (Bukowiecki et al., 2002).

To obtain better characterisation of ambient aerosols in Switzerland on a long-term basis, as a first step measurements of $PM_{2.5}$ mass concentration were started at some sites. This was also done in view of the discussion of introducing $PM_{2.5}$ as a new air quality standard in the EU. To further improve our knowledge of the physical characterisation of particulate matter in ambient air, a monitoring of PM_1, $PM_{2.5}$, PM_{10} and particle number concentration (PNC) was started in spring 2003 at five stations of the national network NABEL. The goal is to obtain longterm series of the physical characterisation of aerosols, allowing to study the relationships between various particle properties, concentrations of gaseous pollutants and meteorological parameters and to detect possible trends in the particle parameters. In a preliminary project, the particle number concentrations were measured at four sites from January 2000 through April 2002 with two instruments. These measurements allow a description of particle number concentrations in Switzerland and a discussion of their relationship to other air quality data.

METHODS

The particle mass concentrations are measured in the NABEL network with Digitel DA80H samplers with daily filter change for daily mean values and with continuously operating betameters Eberline FH62 I-R. The betameters are in operation since end of 2001. They are calibrated by means of gravimetric measurements performed every fourth day. The par-ticle number concentrations are measured with a condensation particle counter, type TSI 3022A. The lower cut-off of the instrument is about 7 nm; the upper cut-off is defined by the inlet and is about 3 μm at the NABEL stations. Since spring 2003, five particle counters are routinely operated at sites of the NABEL network.

During the preliminary project two particle counters were operated in two-month blocks at four NABEL stations. The selected sites cover different pollution levels. Table 1 gives a brief description of the sites, more detailed information can be found in the technical report of the NABEL network (EMPA, 2000).

The two particle counters were simultaneously operated at the station pair Basel and Payerne and at the station pair Zürich and Härkingen. The times of operation can be found in the final report of the project (Gehrig and Fischer, 2002). Data were measured with a time resolution of ten minutes. The subsequent statistical evaluations were conducted with calculated half-hourly means.

Table 1. Characterisation of the four sites with measurements of particle number concentra-tion. In brackets are the station codes used in tables and figures.

Basel (BAS)	Suburban, at border of city on a hill
Zürich (ZUE)	Urban background, in a park, backyard situation
Härkingen(HAE)	Kerbside, 20m north of highway
Payerne (PAY)	Rural background

RESULTS AND DISCUSSION

At each of the four stations particle number concentration was measured on about 300 to 400 days from January 2000 to April 2002. Table 2 gives a summary of the daily mean values of particle counts, particle mass concentrations and concentrations of various gaseous com-pounds.

At each site the measurement periods covered all seasons. To check the representativity of the campaign periods, the averages of PM_{10} mass concentrations during the campaigns are compared to the averages of all days over the whole period from January 2000 to April 2002 (Table 3). The good agreement of the campaign means and the whole period means indicates that the campaigns represented the ambient aerosol load well.

A Student-t test of the averages from Table 1 shows that the particle number concentrations are significantly ($p<0.001$) different from site to site. However,

Table 2. Averages of daily mean values from January 2000 to April 2002 for days only with valid values of the particle number concentration (PNC).

		BAS	HAE	PAY	ZUE
Number of days		374	405	339	309
PNC	P/cm^3	11452	86880	9797	18314
PM10	$\mu g/m^3$	20.4	28.6	19.6	24.3
PM2.5	$\mu g/m^3$	15.5		14.6	18.5
NOx	ppb	17.7	79.0	9.6	35.5
NO	$\mu g/m^3$	6.5	72.0	3.1	20.4
NO2	$\mu g/m^3$	22.9	36.3	13.2	34.7
CO	mg/m^3		0.55	0.26	0.53
Ratio of concentrations					
PNC/PM10		560	3033	501	754
PNC/PM2.5		740		671	993
PNC/NOx		649	1100	1018	516
PNC/NO		1755	1207	3203	899
PNC/NO2		500	2395	741	528
PNC/CO			157441	37107	34811

Table 3. Averages of daily mean values for all days from January 2000 to April 2002.

		BAS	HAE	PAY	ZUE
PM10	$\mu g/m^3$	22.5	27.4	20.6	24.4
PM2.5	$\mu g/m^3$	17.6		15.7	18.2

PM_{10} and $PM_{2.5}$ mass concentrations are not significantly different ($p>0.05$) at Basel and Payerne. Thus, at sites not immediately affected by strong emission sources the PM_{10} and $PM_{2.5}$ mass concentrations are dominated by a regional background which is more uniform in space than particle number concentration. Only one of the sites, Härkingen (HAE), is directly exposed to road emissions, as it is located in immediate vicinity of a highway with a traffic volume of about 70,000 vehicles per day. At Härkingen much higher concentrations of particle number and NO are observed than at the other three sites. Also the ratios PNC/PM_{10}, PNC/NO_2 and PNC/CO are much higher at Härkingen, indicating that PM_{10}, NO_2 and CO concentrations are spatially more uniform than particle number concentration.

In Figure 1 the mean weekly cycle of the particle number concentrations is shown, in Figure 2 the weekly cycle of PM_{10} mass concentration. All sites show a smaller number of particles during weekends than on weekdays. It cannot be decided

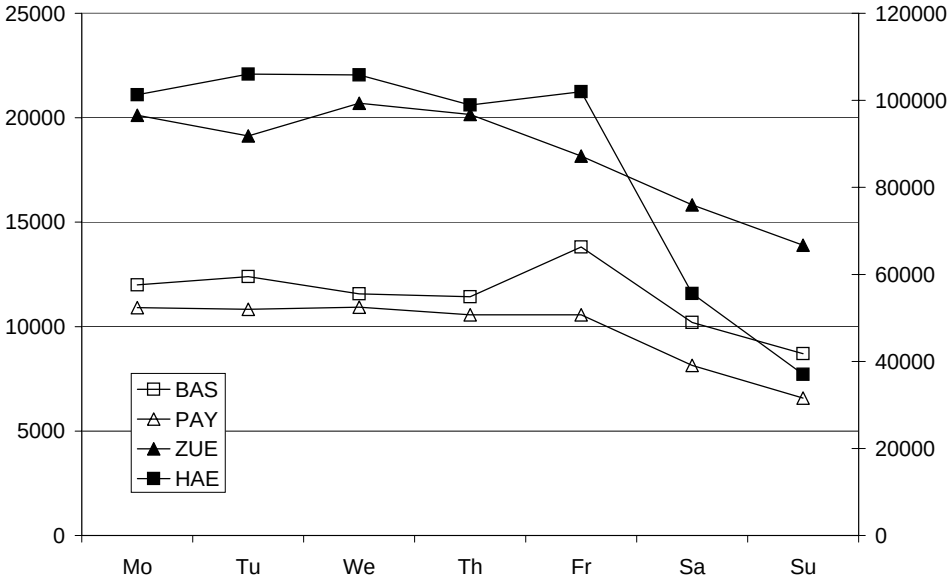

Figure 1. Average particle number concentrations on each day of the week for Basel, Payerne and Zürich (left scale) and Härkingen (right scale).

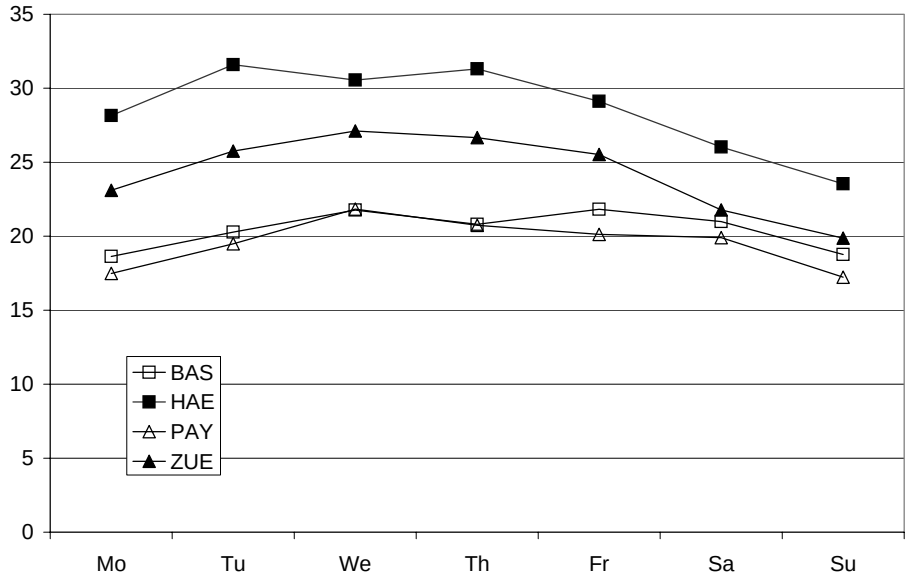

Figure 2. Average PM_{10} mass concentrations on each day of the week.

whether this is caused by the lower industrial activity or the reduced heavy-duty traffic during weekends. The strongest reduction on weekends is seen at Härkingen, where particle number concentration drops on Sundays to less than half of the weekday value. From Monday to Friday about 13,000 heavy-duty vehicles per day pass by the station Härkingen, on Sunday only 2,000. This strongly affects the particle number concentrations but hardly the PM10 mass concentration. PM_{10} values are highest in the middle of the week, indicating a delayed build-up of PM_{10} mass concentration with increased industrial activity and traffic volume starting from Monday on.

The half-hourly means of particle number concentrations correlate well with the concentrations of gaseous pollutants (Figure 3). Particle number concentrations are better correlated with the concentrations of NO, NO_x and NO_2 than with particle mass concentrations. Only at Zürich a high correlation with CO is seen. This may be due to the higher CO-emission factors of motor vehicles in an urban traffic situation compared to a highway situation. At the station in Härkingen correlation with NO and NO_x is very high. This is explained by the fact that both NO and particle number concentration are primary pollutants of motor vehicles. Both concentrations decay with increasing distance from the source as NO gets oxidised and particles coagulate.

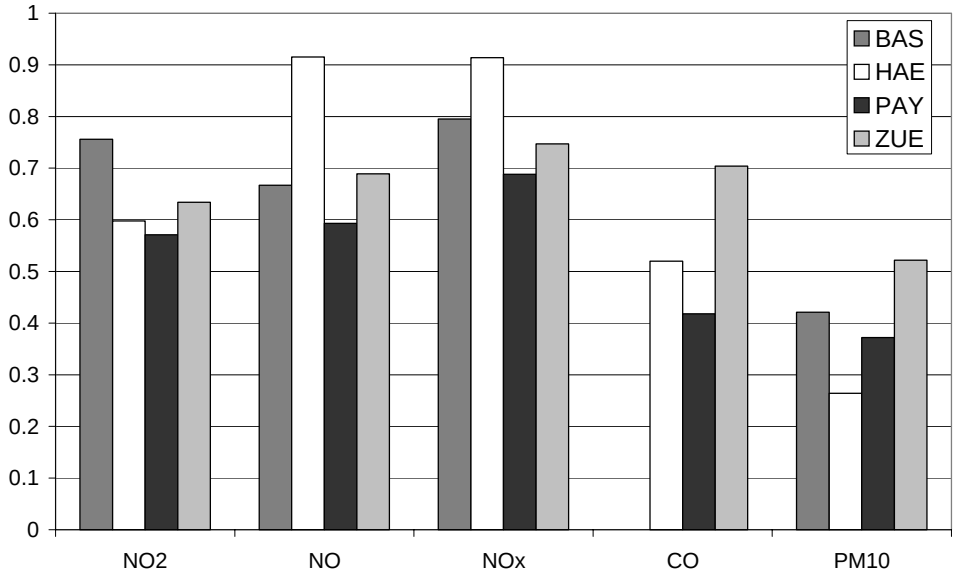

Figure 3. Correlation coefficients of half-hourly means of particle number concentration with other parameters.

Stratifying data according to the half-hourly wind direction can identify the influence of the highway on the pollution level at Härkingen. The highway runs nearly in east-west direction. Therefore, a sector with southerly winds (135°-225°)

and a sector with northerly winds (315°–45°) were compared. For southerly winds, the station is leeward of the highway. All measured pollutants have markedly higher concentrations for wind from the sector south (Table 3). The ratio of the concentrations for southerly and northerly winds for particle number concentration is very similar that for NO, whereas NO_2, CO and PM_{10} show similar ratios on a lower level. Thus, particle number concentration is closer related to NO than to PM_{10} mass concentration. For southerly winds the particle number concentration is strongly correlated to the number of heavy-duty vehicles passing by the station.

Table 3.Averages of half-hour mean concentrations at Härkingen with winds from the highway (sector south) and without influence of the highway (sector north). The last column gives the correlation *r* of particle number concentration and number of heavy-duty vehicles.

	NO ($\mu g/m^3$)	NO_2 ($\mu g/m^3$)	CO (mg/m^3)	PNC ($1/cm^3$)	PM10 ($\mu g/m^3$)	*r*
Sector south	107.8	40.2	0.698	128957	34.7	0.802
Sector north	17.9	24.5	0.383	22956	27.1	0.112
Ratio south/north	6.0	1.6	1.8	5.6	1.3	7.2

CONCLUSION AND IMPLICATIONS

Mean particle number concentrations for different sites in Switzerland ranging from rural (about 10,000 Part./cm^3) to kerbside near a highway (about 90,000 Part./cm^3) were determined over a two-year measurement period. The analysis of weekday dependence and of the relationship to gaseous compounds clearly shows that high particle number concentrations are caused by emissions of motor vehicles and mainly by heavy-duty traffic.

The operation of particle counter turned out to be possible in a monitoring network. Since spring 2003, particle counters started their continuous operation at five sites. Together with new PM_1 mass concentrations, these measurements will provide data for a more detailed characterisation of the physical properties of particulate matter.

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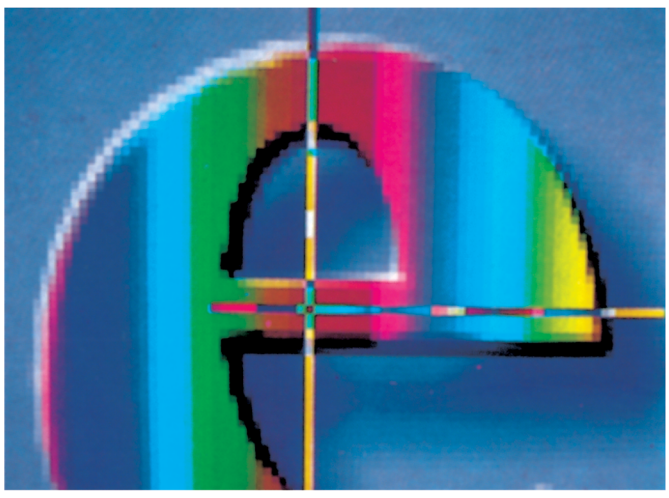
Dubrovnik, 2003



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ISBN 953-6609-03-7