Izdavač
HRVATSKO UDRUŽENJE ZA ZAŠTITU ZRAKA
Zagreb, Ksaverska c. 2

Za izdavača
Dr.sc. Gordana Pehnec

Urednik
Dr.sc. Krešimir Šega

Tehnički urednici
Dr.sc. Ivan Bešlić
Dunja Lipovac

Recenzenti
Znanstveno-stručni odbor

Kompjutorski slog
mtg-topgraf d.o.o., Velika Gorica

Tisak
mtg-topgraf d.o.o., Velika Gorica

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♦European Federation of Clean Air – EFCA

OSMI HRVATSKI
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ZAŠTITA ZRAKA '13

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KAZALO

Tema 2 – Emisije onečišćenja u atmosferu

Tema 3 – Onečišćenje vanjske atmosfere – imisije

Tema 4 - Razvoj i provjera mjernih metoda

Tema 5 - Procjena izloženosti i učinci na zdravlje i okoliš

Tema 6 – Azbest u zraku

Tema 7 – EFCA sekcija "Carbon in particles"

Posteri

UVODNA RIJEČ

Osnovne teme VIII. Hrvatskog znanstvenog-stručnog skupa pod nazivom "Zaštita zraka '13" u organizaciji Hrvatskog udruženja za zaštitu zraka su:

1. Upravljanje kvalitetom zraka – inspekcija i nadzor
2. Emisije onečišćenja u atmosferu
3. Onečišćenje vanjske atmosfere – imisije
4. Razvoj i provjera mjernih metoda
5. Procjena izloženosti i učinci na zdravlje i okoliš
6. Azbest u zraku
7. EFCA sekcija "Ugljik u česticama"

I ovaj puta, velik broj prijavljenih sudionika skupa te 57 prijavljenih izlaganja prikazanih u ovom zborniku sažetaka, pokazuju velik interes stručne javnosti kao i važnost tematike onečišćenja zraka za našu zajednicu. Posebno želimo naglasiti sekciju "Ugljik u Česticama" koju organiziramo pod pokroviteljstvom Europske federacije udruženja za čisti zrak i zaštitu okoliša (European Federation of Clean Air and Environmental Protection Associations - EFCA, http://www.efca.net/efca2/).

Uz navedeno, pozitivna iskustva s prethodno održanih skupova, predstavljaju razloge naše vjere u uspjeh i ovog skupa. Svim učesnicima želimo uspješna izlaganja, plodonosne rasprave, korisne izmjene iskustava te ugodno druženje.

Vladimira Vađić i Krešimir Šega

UVODNA RIJEČ

The main topics of the 8th Croatian scientific and professional Meeting "Air Protection '13", organized by the Croatian Air Pollution Prevention Association (CAPPA), are:

1. Managing air quality – inspection and control;
2. Pollution emission into the atmosphere;
3. Outdoor air pollutants – immisions;
4. Developing and test measuring of methods;
5. Estimating exposure and impact on health and the environment;
6. Asbestos in the air;
7. EFCA section "Carbon in particles "

Once again, the relatively high number of participants and as much as 57 presentations in the Meeting's Book of Abstracts demonstrate the great interest of our colleagues, as well as the importance of the topic of air pollution for our society. We would like to especially point out the topic of "Carbon in particles", which is to be presented under the auspices of the European Federation of Clean Air and Environmental Protection Associations (EFCA, http://www.efca.net/efca2/).

In addition to the above mentioned topics, positive experiences from previous meetings give us reason to believe in the success of this year's Meeting. We wish all of the participants successful presentations, fruitful discussions, useful exchange of experiences, and a pleasurable gathering.

Vladimira Vađić i Krešimir Šega

Uvodna predavanja

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40 GODINA HRVATSKOG UDRUŽENJA ZA ZAŠTITU ZRAKA

Ključne riječi: *EFCA, HUZZ, IUAPPA, pregled aktivnosti, skupovi*

Hrvatsko udruženje za zaštitu zraka (HUZZ) je dobrovoljna, neprofitna udruga koja okuplja fizičke i pravne osobe sa sjedištem u Republici Hrvatskoj radi zaštite i promicanja ciljeva zajedničkih strukovnih interesa s područja zaštite zraka od onečišćivanja. Počeci rada HUZZ-a vezani su uz osnivanje Jugoslavenskog društva za čistoću zraka 1973. godine. Jugoslavensko društvo za čistoću vazduha osnovano je u Zagrebu na inicijativu hrvatskih stručnjaka iz tog područja te je imalo sjedište u Sarajevu, a članice Društva bile su republičke sekcije. Reorganizacijom 1983. godine republičke sekcije prerasle su u republička Društva za zaštitu zraka ujedinjena u Savez Društava za čistoću vazduha Jugoslavije. Raspadom Jugoslavije, od 1991. godine Društvo djeluje kao samostalno udruženje sa ciljem zaštite zraka na području Hrvatske. Na Skupštini 1993. godine Društvo za zaštitu zraka Hrvatske promijenilo je svoj naziv u ime koje nosi i danas – Hrvatsko udruženje za zaštitu zraka. Hrvatska je 1992. godine postala samostalna država, primljena je u Ujedinjene nacije, a iste godine Hrvatsko udruženje za zaštitu zraka na svjetskom kongresu u Montrealu, Kanada, primljeno je u Internacionalnu uniju za zaštitu zraka (IUAPPA) kao punopravan član. Europska federacija za čisti zrak (EFCA) osnovana je 1997. godine, a naše Udruženje član je EFCA od 1998. godine. Udruženje je u tijekom svog rada organiziralo brojne stručne sastanke u raznim gradovima Hrvatske. 1997. godine organiziralo je prvi nacionalni skup o zaštiti zraka te se od tada skup redovito održava svake dvije godine. Zajedno s IUAPPA-om HUZZ je bio i organizator međunarodnog skupa "The 14th International Conference Air Quality – Assessment and Policy at Local, Regional and Global Scales u Dubrovniku 2003. godine. Također, svake druge godine Udruženje organizira stručni seminar u inozemstvu. Članovi HUZZ-a pružali su također i stručnu pomoć pri izradi zakonskih propisa iz područja kvalitete zraka. Povodom 40. godišnjice Udruženja dan je pregled osnovnih aktivnosti HUZZ-a u protekla četiri desetljeća kao i osoba koje su obilježile njegov rad.

[1] Institut za medicinska istraživanja i medicinu rada, Ksaverska cesta 2, Zagreb

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Pehnec, G.[1]

THE 40TH ANNIVERSARY OF THE CROATIAN AIR POLLUTION PREVENTION ASSOCIATION

Keywords: *EFCA, HUZZ, IUAPPA, review of activities, meetings*

The Croatian Air Pollution Prevention Association (CAPPA) is a volunteering, non-profit organization that gathers members from the Republic of Croatia in order to protect and promote common professional goals in the field of air protection. CAPPA traces its origin back to the foundation of the Yugoslavian Association for Clean Air in 1973. The Yugoslavian Association for Clean Air was established in Zagreb by Croatian experts from the field of air protection. Its headquarters were located in Sarajevo and its membership was divided into republic sections. After reorganization in 1983, the Republic Sections became Republic Associations for Air Protection, united within the Yugoslavian Union of Air Protection Associations. When Croatia declared independence from Yugoslavia in 1991, the Croatian Republic Association started to act as an independent unit. At a general meeting in 1993, the Association changed its name to the Croatian Air Pollution Prevention Association, as it is called today. In 1992, Croatia became an independent state and a member of the United Nations. That same year, at the World Clean Air Congress in Montreal, Canada, CAPPA was admitted into the International Union of Air Pollution Prevention and Environmental Protection Association (IUAPPA). The European Federation of Clean Air (EFCA) was founded in 1997 and our Association has been its member since 1998. CAPPA has organized many professional meetings across Croatia. In 1997, CAPPA hosted the first national conference on air protection and from then, the conference is organized regularly every two years. In 2003 together with IUAPPA, the Association organized The 14th International Conference on Air Quality – Assessment and Policy at Local, Regional and Global Scales in Dubrovnik. Furthermore, every two years, CAPPA also organizes workshops abroad. CAPPA members regularly offer professional help during the preparation of air pollution protection legislation. On the occasion of the 40th anniversary of CAPPA, this paper gives an overview of the most important activities of CAPPA during the four decades, as well as the persons that marked its history.

[1] Institute for Medical Research and Occupational Health, Ksaverska c. 2, Zagreb

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Šega, K.[1] i Bešlić, I.[1]

PRORAČUN POKAZATELJA PROSJEČNE IZLOŽENOSTI PREMA DIREKTIVI 2008/50/EC ZA RAZDOBLJE 2001. – 2012.

Ključne riječi: *$PM_{2.5}$, pokazatelj prosječne izloženosti, cilj smanjenja izloženosti na nacionalnoj razini, zahtijevana razina izloženosti*

Procijenjene su vrijednosti koncentracija frakcija lebdećih čestica $PM_{2.5}$ i pokazatelja prosječne izloženosti (PPI) u atmosferi Zagreba. Rezultati procjene određeni su na osnovi vrijednosti koncentracija izmjerenih u razdoblju 1999.-2012. Trendovi su bili silazni i iznosili su -0.464 μg m^{-3} god^{-1} za koncentracije te -0.430 μg m^{-3} god^{-1} za PPI. Rezultati modela pokazuju da će granične vrijednosti koncentracija za prvu i drugu predviđenu fazu vjerojatno biti zadovoljene. Vrijednosti PPI propisani za cilj smanjenja izloženosti na nacionalnoj razini i zahtijevana razina izloženosti neće biti zadovoljene u roku, već vjerojatno nekoliko godina kasnije.

[1] Institut za medicinska istraživanja i medicinu rada, Ksaverska c. 2, Zagreb, Hrvatska

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Šega, K.[1] and Bešlić, I.[1]

ASSESSMENT OF AVERAGE EXPOSURE INDICATOR FOLLOWING THE DIRECTIVE 2008/50/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL FOR 2001-2012 PERIOD

Keywords: *$PM_{2.5}$, average exposure indicator, national exposure reduction target, exposure concentration obligation value*

Following the DIRECTIVE 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe, $PM_{2.5}$ particle fraction concentrations and average exposure indicator (AEI) for Zagreb atmosphere were assessed. Results were predicted for future period based on concentration data for 1999-2012 period.
Both trends are negative, with slopes -0.464 μg m^{-3} $year^{-1}$ and -0.430μg m^{-3} $year^{-1}$for concentrations and average exposure indicator respectively. Model shows that concentration limit values for Stage 1 and Stage 2 could be met, while national exposure reduction target and exposure concentration obligation values for AEI will not be reached in due time, but probably several years later.

[1] Institute for Medical Research and Occupational Health, Ksaverska c. 2, 10000 Zagreb

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OSIGURAVANJE KVALITETE I VALIDACIJA METODA IZ PODRUČJA ISPITIVANJA KVALITETE ZRAKA I EMISIJE IZ STACIONARNIH IZVORA

Ključne riječi*: validacija, aspekti validacije, tipsko odobrenje, izjava o prikladnosti metode*

Prema zahtjevima točke 5.4.5 norme HRN EN ISO/IEC 17025 (Opći zahtjevi za osposobljenost ispitnih i umjernih laboratorija) uspješno provedena validacija je objektivni dokaz da je neka ispitna metoda, kao definirana i usvojena procedura koja vodi do ispitnog rezultata, prikladna za uporabu. Preduvjet validacije jest precizno određena svrha i područje ispitne metode.
Validacija ispitne metode najčešće sadrži sljedeće aspekte:

- *Specifičnost / selektivnost*
- *Točnost*
- *Preciznost (ponovljivost, obnovljivost i međupreciznost)*
- *Područje (opseg) – kontinuirana skala unutar koje je metoda primjenjiva i točna*
- *Mjerna rezolucija (prostorna, vremenska i sl.)*
- *Funkcijska prilagodba (najčešće za linearnost) u svrhu interpolacije*
- *Robusnost – neosjetljivost na potencijalne varijabilne parametre*
- *Utjecaj matrice (kod analitičkih mjerenja)*
- *Primjenjivost za predikcije i analize trendova*
- *Granica detekcije – najmanja koncentracija koja se može detektirati*
- *Granica kvantifikacije – najmanja količina koja se može kvantificirati*
- *Mjerna nesigurnost*
- *Međulaboratorijske usporedbe*
- *Ostale vrste sistemskih analiza*

Osnova validacije pri određivanju masenih koncentracija plinovitih onečišćujućih tvari u vanjskom zraku je pravovaljano tipsko odobrenje (type approval) automatskog analizatora. Za određivanje masenih koncentracija lebdećih čestica osnova validacije je u upotrebi referentnih sakupljača ili provedena ekvivalencija ne-referentnog uređaja s referentnim sakupljačem. Validacija određivanja sastava lebdećih čestica provodi se uobičajenim postupcima validacije analitičkih metoda.
Kod ispitivanja emisije iz stacionarnih izvora validacija većine metoda provodi se provjerom radnih karakteristika analizatora (linearnost, ponovljivost, granica detekcije) i provjerom odziva analizatora na nula i mjerno područje (span) vrijednost prije i nakon svakog mjerenja pomoću referentnih tvari.
Za pojedine metoda validacija se provodi uzorkovanjem slijepe probe i određivanjem učinkovitosti apsorpcije. Analitički dio se validira uobičajenim postupcima.
Validacija metode se mora podrobno dokumentirati i mora sadržavati izjavu da je metoda prikladna za namijenjenu uporabu.

[1] Institut za medicinska istraživanja i medicinu rada, pp 291, Ksaverska cesta 2, HR-10001 Zagreb, Republika Hrvatska, franic@imi.hr, ibeslic@imi.hr

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QUALITY ASSURANCE AND VALIDATION OF METHODS IN THE FIELD OF AIR QUALITY TESTING AND STATIONARY SOURCE EMISSIONS

Key words: *validation, validation aspects, type approval, suitability statement*

According to the requirements of chapter 5.4.5 of HRN EN ISO/IEC 17025 Norm (General requirements for the competence of testing and calibration laboratories) successfully completed validation is objective evidence that a test method, as defined and adopted procedure leading to the test result, is suitable for use. Prerequisite of validation is the precisely defined purpose and scope of the test method.

Validation of test method usually comprises the following aspects:

- *Specificity / selectivity*
- *Accuracy*
- *Precision (repeatability, reproducibility and intermediate precision)*
- *Span – continuous scale within which the method is applicable and correct*
- *Measurement resolution (spatial, temporal, etc.)*
- *Curve fitting, (typically for linearity) for interpolation purpose*
- *Robustness – the insensitivity to potential variable parameters*
- *The impact of the matrix (for analytical measurements)*
- *Applicability for prediction and trend analysis*
- *Detection limit – the lowest concentration that can be detected*
- *The limit of quantification – the minimum amount that can be quantified*
- *Measurement uncertainty*
- *Interlaboratory comparisons*
- *Other types of system analyses*

Type approval of automatic analyser is the validation base for determination the mass concentration of gaseous pollutant in ambient air. Using the reference sampler or providing the equivalence testing of non-referent devices assures the validation of method for determination the mass concentration of particulate matter. Validation of methods for the determination of the composition of particulate matter is carried out by standard procedures for validation of analytical methods.

Contentment of assigned performance characteristics for automatic analysers is validations assurance of automatic method for monitoring the stationary source emission. Furthermore, checking the analyser response to zero and span value, before and after each measurement with reference materials, fulfils the requirements for validation.

For some methods validation is performed by sampling blanks and determining the efficiency of absorption. The analytical part is validating according to usual procedures.

Validation of methods must be thoroughly documented and must include a statement that the method is suitable for its intended purpose.

[1] Institute for Medical Research and Occupational Health, PO Box 291, Ksaverska cesta 2, HR-10001 Zagreb, Republic of Croatia e-mail: franic@imi.hr, ibeslic@imi.hr

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van Kuijk, A.[1] and Groen, R.[1]

PILOT PROJECT AIR QUALITY MONITORING SYSTEM IN TBILISI, GEORGIA

Keywords: *ambient air quality, particulate matter, automated monitoring stations, air quality modelling*

The project 'Air quality monitoring in Tbilisi, Georgia' aims at establishing an integral pilot urban background air quality monitoring system in the City of Tbilisi, Georgia, as well as a sustainable local capacity to operate and maintain the system, local awareness on the importance of air quality and policy recommendations to improve air quality and further expand the system of air quality monitoring in Georgia in the future. The air quality monitoring system consist of two independent state-of-the-art methods, which are complementing each other: measuring and modelling air quality. Fully automated measurements of PM_{10}, $PM_{2.5}$, NO_x, O_3, CO, SO_2 as well as relevant meteorological parameters, are logged and transferred to the recipient (Georgian National Environmental Agency). The air quality model ADMS-Urban is prepared by compiling emission inventory (EMIT) of all Tbilisi emission sources (road network, households, industrial sites, airport). Staff is trained and assisted during 1 pilot year. The monitoring data will provide a quantitative base for the compliance to European and national legislation with respect of air quality, but this requires a full scale implemented AQ monitoring system (in future). First of all the results will give an indication of the air quality in Tbilisi and will be used for public awareness and policy awareness. The project advises and supports the recipient with the possibilities of how the results can be used for communication, policy assessments and taking measures.

[1] Witteveen+Bos Consulting Engineers, The Netherlands, P.O. Box 233, 7400 AE, Deventer. *www.witteveenbos.com*

Tema 1
Upravljanje kvalitetom zraka – inspekcija i nadzor

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Vađić, V.[1] i Zovko, N.[1]

E-REPORTING

Ključne riječi: *e-reporting, kvaliteta zraka, izvješćivanje, razmjena informacija, okoliš*

Europska Komisija 12. prosinca 2011. godine donijela je provedbenu Odluku 2011/850/EU o utvrđivanju pravila za provedbu Direktiva 2004/107/EZ i 2008/50/EZ Europskog parlamenta i Vijeća o obvezama država članica Europske Unije u pogledu izvješćivanja o procjeni i upravljanju kvalitetom zraka kao i o uzajamnoj razmjeni informacija o mrežama i postajama, te mjerenjima kvalitete zraka, na onim postajama koje se između postojećih odaberu u svrhu uzajamne razmjene informacija.
Kako bi se racionalizirala količina informacija koje se objavljuju, što je više moguće povećala korist od tih informacija, te smanjilo administrativno opterećenje, informacije moraju biti dostupne u standardiziranom strojno čitljivom obliku i u skladu sa zahtjevima Direktive 2007/2/EZ o uspostavljanju Infrastrukture za prostorne informacije u Europskoj zajednici (INSPIRE).
Odluka 2011/850/EU također poznata i kao Implementing Provisions on Reporting (IPR) zamjenjuje tri odluke: Odluku Vijeća 97/101/EZ o uspostavljanju uzajamne razmjene informacija i podataka iz mreža i pojedinačnih postaja za mjerenje onečišćenja zraka, Odluku Komisije 2004/224/EZ o utvrđivanju postupaka za podnošenje informacija o planovima ili programima u vezi s graničnim vrijednostima određenih onečišćujućih tvari u zraku i Odluku Komisije 2004/461/EZ o utvrđivanju upitnika za podnošenje godišnjeg izvješća o procjeni kvalitete zraka.
U svrhu utvrđivanja nadležnog tijela i okvira za provedbu Odluke Komisije 2011/850/EU u svibnju 2013. godine donesen je Pravilnik o uzajamnoj razmijeni informacija i izvješćivanju o kvaliteti zraka (NN 57/13). Ovim Pravilnikom propisani su način, rokovi, sadržaj i format podataka za uzajamnu razmjenu informacija i izvješćivanje o procjenjivanju i upravljanju kvalitetom zraka. Također sukladno Pravilniku nadležno tijelo za provedbu Odluke Komisije 2011/850/EU je Agencija za zaštitu okoliša (AZO).
Za razmjenu informacija i izvješćivanje o procjenjivanju i upravljanju kvalitetom zraka koriste se podaci o koncentracijama onečišćujućih tvari dobivenih mjerenjima na stalnim mjernim mjestima određenih propisom kojim se uređuje popis mjernih mjesta za praćenje onečišćujućih tvari u zraku, te podaci dobiveni indikativnim mjerenjima, tehnikama modeliranja i objektivnom procjenom. Te podatke potrebno je dostaviti u informacijski sustav zaštite zraka u elektroničkom obliku koristeći formate i protokole koje Agencija objavljuje na svojim internetskim stranicama.
Način, rokovi, sadržaj i format dostavljanja navedenih informacija u repozitorij podataka koji je uspostavljen od Europske komisije u suradnji s Europskom agencijom za zaštitu okoliša biti će prikazana u ovome radu.

[1] Agencija za zaštitu okoliša, Zagreb, Hrvatska

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E-REPORTING

Keywords: *e-reporting, air quality, reporting, exchange of information, environment*

The European Commission 12 December 2011 adopted the Implementing Decision laying down rules for Directives 2004/107/EC and 2008/50/EC of the European Parliament and of the Council establishes rules regarding the Member States' obligations to report on the assessment and management of ambient air quality as well as the reciprocal exchange of information and the measurements of air quality, obtained from those stations that are selected for the purpose of reciprocal exchange from amongst existing stations.

To streamline the amount of information made available, maximise the usefulness of such information and to reduce the administrative burden, information must be available in a standardised, machine-readable form and in line with the requirements of Directive 2007/2/EC establishing an Infrastructure for Spatial Information in the European Community (INSPIRE).

Decision 2011/850/EU also known as Implementing Provisions on Reporting (IPR) replaces three decisions: Council Decision 97/101/EC of establishing a reciprocal exchange of information and data from networks and individual stations measuring ambient air pollution, Commission Decision 2004/224/EC laying down arrangements for the submission of information on plans or programmes in relation to limit values for certain pollutants in ambient air and Commission Decision 2004/461/EC laying down a questionnaire to be used for annual reporting on ambient air quality assessment. In purpose to establish the competent authority and framework for the implementation of Commission Decision 2011/850/EU in May 2013th is adopted Ordinance on the reciprocal exchange of information and reporting on air quality (OG 57/13). Ordinance prescribed manner, deadlines, content and format of the data for the reciprocal exchange of information and reporting on the assessment and management of ambient air quality. According to the Ordinance, Croatian Environment Agency (CEA) is the competent authority for the implementation of Commission Decision 2011/850/EU.

Data used for the exchange of information and reporting on the assessment and management of ambient air quality are data on concentration level of specific pollutant obtained by fixed measurements points regulating with the regulation for the list of fixed measurement points for air pollutants monitoring, as well as data obtained by indicative measurements, modelling techniques and objective estimation. These data have to be submitted to the Air Quality Information System in electronic form using the formats and protocols that the Agency publishes on its website.

Manner, deadlines, content and format for submitting the information in the data repository that has been established by the European Commission in cooperation with the European Environment Agency will be presented in this paper.

[1] *Croatian Enviroment Agency, Zagreb, Croatia*

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Davila, S.[1], Bešlić, I.[1] i Šega, K.[1]

USPOREDBA CAQI METODE ZA IZRAČUNAVANJE INDEKSA KVALITETE ZRAKA I HRVATSKE LEGISLATIVE

Ključne riječi: *CITEAIR, CAQI, granična vrijednost, PM10*

Ocjena kvalitete zraka u Republici Hrvatskoj na godišnjoj razini definirana je s tri kategorije kvalitete zraka do 2010. godine, odnosno dvije kategorije od 2011. godine s obzirom na broj prekoračenja satnih i/ili dnevnih graničnih vrijednosti te s obzirom na prekoračenje godišnje granične vrijednosti. Navedeni način prikazivanja kvalitete zraka u skladu je s CAFE direktivom 2008/50/EC te je namijenjen stručnoj javnosti i zakonodavstvu. U svrhu prilagodbe ocjene kvalitete zraka široj javnosti, u mnogim zemljama Europske Unije i svijeta kvaliteta zraka na dnevnoj i godišnjoj razini većinom se prikazuje pomoću indeksa kvalitete zraka. Zbog različitog definiranja indeksa kvalitete zraka, kako u Europskoj uniji tako i u svijetu, međusobna usporedba ocjene kvalitete zraka nije bila moguća. Od 2004. godine započeo je projekt CITEAIR kojem je jedan od zadataka bio definiranje jedinstvenog indeksa kvalitete zraka kojeg bi koristile gotovo sve članice Europske unije u svrhu međusobne usporedbe kvalitete zraka. Kao rezultat projekta nastao je CAQI (Common Air Quality Index) model za izračunavanje indeksa kvalitete zraka. Do kraja 2011. godine većina zemalja Europske unije i preko 90 gradova prihvatilo je CAQI model izračuna indeksa kvalitete zraka. CAQI model koristi pet kategorija za prikazivanje kvalitete zraka od vrlo niskog do vrlo visokog indeksa. Indeks može poprimiti vrijednosti od 0 do 100, time da niži indeks odgovara boljoj kvaliteta zraka. Indeks kvalitete zraka može se računati za satne, dnevne i godišnje vrijednosti. Ukupni indeks za pojedino mjerno mjesto je najviši izračunati indeks od svih onečišćujućih tvari koje se mjere na tom mjernom mjestu. Dnevni i godišnji indeks računaju se kao prosječne vrijednosti satnog indeksa za određeno mjerno mjesto.
U radu će se prikazati usporedba Uredbom definirane kategorizacije kvalitete zraka s indeksom kvalitete zraka određenim CAQI modelom u gradu Zagrebu.

[1] Institut za medicinska istraživanja i medicinu rada, Ksaverska cesta 2, Zagreb

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Davila, S.[1], Bešlić, I.[1] i Šega, K.[1]

COMPARISON OF CAQI METHOD FOR CALCULATING THE AIR QUALITY INDEX WITH CROATIAN LEGISLATION

Keywords: *CITEAIR, CAQI, limit value, PM10*

Assessment of the air quality in Croatia on annual basis is reduced from three categories till the year 2010 to two categories since 2011 due to the number of hourly and/or daily excess of limit values. This method of presenting air quality is in according to the European CAFE directive 2008/50/EC used for professional and legislative purposes. Countries of the European Union and worldwide assess air quality on daily and annual basis using air quality index which is more appropriate for informing general public. Due to the large number of different air quality indexes it was impossible to compare them among each other. Since the year 2004 CITEAIR project started, in order to create a unique air quality index which would be used by almost all members of the European Union for the purpose of mutual comparison of air quality. The project resulted in CAQI (Common Air Quality Index) model preparation for the air quality calculation. By the end of 2011 the majority of European Union countries and over 90 cities accepted CAQI model. CAQI model uses five categories of air quality ranging from very low to very high index. The index can take values from 0 to 100, assuming: lower the index, better the air quality. Air quality index can be calculated for hourly, daily and annual values. The total index for each measuring site is the highest calculated index for all the pollutants measured on specific site. Daily and annual indexes are calculated as the average of the hourly values of the index for that measuring site. Results of the comparison between air quality categories and air quality index for Zagreb data will be presented.

[1] Institute for Medical Research and Occupational Health, Ksaverska cesta 2, Zagreb

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Avirović, G.[1], Živković, N.[1] i Leaković, S.[1]

EMISIJA STAKLENIČKIH PLINOVA IZ PROIZVODNJE GNOJIVA – UTJECAJ PROPISA I AKTIVNOSTI USKLAĐIVANJA

Ključne riječi: *besplatne emisijske jedinice, didušikov oksid, dušična kiselina, proizvodnja amonijaka, trgovanje emisijama, ugljikov dioksid*

Industrija gnojiva prema podacima Međunarodnog udruženja proizvodnje gnojiva (International Fertilizer Industry Association – IFA) na izravni i neizravni način doprinosi globalnoj emisiji stakleničkih plinova i to sa oko 0,93 % kroz proizvodnju, 0,07 % kroz distribuciju i sa oko 1,5 % kroz primjenu gnojiva. Od industrije općenito se očekuje da doprinese globalnim naporima smanjenja emisije stakleničkih plinova, a energetski intenzivne aktivnosti (kao što je proizvodnju dušičnih gnojiva) predmetom su posebne pozornosti. Proizvodna postrojenja pri proizvodnji mineralnih gnojiva u Petrokemiji d.d. u Kutini su, pored emisije specifičnih plinovitih onečišćujućih tvari u zrak (amonijak, dušikovi oksidi, sumporov dioksid, plinoviti fluoridi, kao HF) i emisije krutih čestica (sirovine i gotovi proizvodi), i izvori emisije stakleničkih plinova i to: didušikova oksida (N_2O) i ugljikova dioksida (CO_2). U ukupnoj emisiji u zrak iz Petrokemije d.d., u 2012.g., jednako kao i ranijih godina, najzastupljeniji su staklenički plinovi s ukupnim učešćem od oko 99 %. U proizvodnji gnojiva Petrokemije d.d. emisije stakleničkih plinova primarno su povezane s procesima proizvodnje energije i amonijaka (emisija CO_2) i dušične kiseline (emisija N_2O). Od siječnja 2013.g. hrvatska industrija gnojiva jednako kao i europska industrija gnojiva postaje obveznikom sheme trgovanja emisijama Europske Unije (EU Emission Trading Scheme). Sukladno nacionalnim odnosno europskim propisima i ciljevima smanjenja emisije stakleničkih plinova u Petrokemiji d.d., osim prioritetnog ulaganja u modernizaciju tehnologije, proveden je niz aktivnosti implementacije sustava izračuna preliminarno dodijeljenih besplatnih emisijskih jedinica, temeljeno na "benchmark" razinama, te praćenja i izvješćivanja o emisijama. Opisan je tijek aktivnosti koje je Petrokemija provela u postupku usklađivanja s propisanim obvezama prema EU ETS kao i mjere smanjivanja emisije stakleničkih plinova. Ukazano je na mogući negativni utjecaj ove legislative na poslovanje Petrokemije d.d.

1 *Petrokemija d.d. tvornica gnojiva, Aleja Vukovar 4, 44320 Kutina, HRVATSKA*

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Avirović, G.[1], Živković, N.[1] and Leaković, S.[1]

GREENHOUSE GAS EMISSIONS FROM FERTILIZER PRODUCTION – EFFECT OF REGULATIONS AND COMPLIANCE ACTIVITIES

Keywords: *free allowances, nitrous oxide, nitric acid, ammonia production, emissions trading, carbon dioxide*

According to the data of International Fertilizer Industry Association, fertilizer industry contributes directly and indirectly to the global greenhouse gas emissions with around 0.93% through production, 0.07% through distribution and with about 1.5% through the application of fertilizers. The industry in general is expected to contribute to global efforts to reduce greenhouse gas emissions, and the energy-intensive activities (such as the production of nitrogen fertilizers) are subject to special attention. In addition to the specific emissions of gaseous (ammonia, nitrogen oxide, sulphur dioxide, gaseous fluorides as HF) and particulate pollutants (raw materials and final products) into the air in the production of mineral fertilizers in Petrokemija, Plc. Kutina, production facilities are the sources of greenhouse gases that include nitrous oxide (N_2O) and carbon dioxide (CO_2). In 2012, same as in previous years, the most common in the total emissions from the Company are greenhouse gases with a total share of about 99%. In the production of fertilizers of Petrokemija, Plc. greenhouse gas emissions are primarily associated with the processes of energy and ammonia production (CO_2 emissions) and nitric acid production (N_2O emissions). Since January 2013, Croatian fertilizer industry as well as the European fertilizer industry has become liable to the European Emissions Trading Scheme (EU ETS). In line with the national and European regulations and the goals to reduce greenhouse gas emissions, next to priority investments in modern technology, Petrokemija, Plc. conducted a series of activities in implementation of calculating preliminary allocated free allowances system, based on the "benchmark" levels, and monitoring and reporting emissions. This paper describes the course of activities carried out by Petrokemija in the process of compliance with the stipulated obligations under the EU ETS, as well as measures to reduce greenhouse gas emissions. It points to the possible negative impact of this legislation on the Company business.

[1] Petrokemija, Plc. Fertilizer Company, Aleja Vukovar 4, 44320 Kutina, CROATIA

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Tarnik, T.[1] i Topić, Ž.[2]

HRVATSKA ELEKTROPRIVREDA U EUROPSKOM SUSTAVU TRGOVANJE EMISIJSKIM JEDINICAMA STAKLENIČKIH PLINOVA (EU-ETS)

Ključne riječi: *energetika, ugljikov dioksid, trgovanje emisijskim jedinicama*

Republika Hrvatska uključila se prvi puta u Europski sustav trgovanja emisijskim jedinicama stakleničkih plinova EU ETS (engl. European Union Emission Trading Sheme), na početku trećeg razdoblja trgovanja koje je započelo 1.1.2013. i traje do 31.12.2020. godine. Treće razdoblje trgovanja ima znatno stroža pravila u odnosu na prethodna dva razdoblja. Za sektor energetike najznačajnija razlika očituje se u činjenici da više nema dodjele besplatnih emisijskih jedinica za emitiranje ugljikovog dioksida (CO_2) koji nastaje kao posljedica izgaranja fosilnih goriva za proizvodnju električne energije, osim nekih izuzetaka koje se ne odnose na RH. Obveznici trgovanja mogu kupovati emisijske jedinice na državnim dražbama, na burzama te putem bilateralnih ugovora s partnerima. Za pokrivanje obveze emitiranja stakleničkih plinova i predaje u Registru stakleničkih plinova Europske Unije, obveznici trgovanja moraju otvoriti Račun operatera postrojenja na koji predaju emisijske jedinici u količini koja odgovara verificiranim emisijama stakleničkih plinova do 30. travnja tekuće godine za prethodnu kalendarsku godinu. Na cijenu emisijskih jedinica utječe niz čimbenika: omjer ponude i potražnje na tržištu, meteorološke i ekonomske prilike te političke odluke. Osnove upravljanja rizicima u procesu upravljanja portfeljem emisijskih jedinica uglavnom su iste kao i za druge vrste robe i sirovina, s tom razlikom što je tržište emisijskih jedinica stvoreno i upravljano politički, a njegova baza su nematerijalizirane emisijske jedinice, za razliku od fizičke robe. Uključivanjem RH u EU ETS, Hrvatska elektroprivreda zbog obavljanja djelatnosti uslijed koje se emitira CO_2, ima obvezu kupiti na tržištu emisijske jedinice stakleničkih plinova koje nastaju kao posljedica izgaranja fosilnih goriva iz termoenergetskih postrojenja ulazne toplinske snage >20 MW. Obveza kupnje emisijskih jedinica predstavlja novi varijabilni trošak koji je potrebno uključiti u proizvodnu cijenu energije. U ovom radu dan je prikaz zakonskih obveza i rokovi provedbe obveza u okviru EU ETS-a, opisan je proces pripreme Hrvatske elektroprivrede za uključivanje u EU ETS te su navedeni izazovi kojim će HEP biti izložen tijekom trećeg razdoblja trgovanja.

[1] Hrvatska elektroprivreda d.d., Sektor za održivi razvoj i unaprjeđenje kvalitete, Ulica grada Vukovara 37 Zagreb, [2] Metroalfa d.o.o. Karlovačka cesta 4L Zagreb

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Tarnik, T.[1] and Topić, Ž.[2]

CROATIAN POWER COMPANY IN EUROPEAN UNION EMISSION TRADING SYSTEM (EU-ETS)

Keywords: *power company, carbon dioxide, emission trading system*

Republic of Croatia has joined for the first time in the European emission trading system GHG EU ETS (European Union Emission Trading Scheme), at the start of the third trading period, which began 01/01/2013 and lasts until 31/12/2020 year. Third trading period has much stricter rules than the previous two periods. For the power sector the most significant difference is in the fact that there is no allocation of free allowances for carbon dioxide (CO_2) emission, which occurs as a result of burning fossil fuels for electricity production, with some exceptions that are not related to Republic of Croatia. Operators can buy emission allowances on government auctions, exchanges and through bilateral agreements with partners. To cover obligations GHG emissions and surrender in the Register of greenhouse gas emissions of the European Union, operators must open an account to surrender emission allowances in an amount corresponding verified greenhouse gas emissions by 30 April of the current year for the previous calendar year. The price of emission units affected by a number of factors: the ratio of supply and demand in the market, weather and economic conditions, and policy decisions. Fundamentals of risk management in the process of portfolio management allowances are generally the same as for other types of goods and raw materials, with the exception that the market of allowances created and managed politically, and its base are dematerialized allowances, unlike physical goods. The inclusion of the EU ETS, Croatian Electricity Company of activities performed due to emitted CO_2, has the obligation to buy the market allocation of greenhouse gas emissions from the combustion of fossil fuel power plant thermal input> 20 MW. The obligation to purchase allowances represents a new variable cost which should be included in the generation cost of energy. This paper gives an overview of the legal obligations and deadlines for implementation of the obligations under the EU ETS, described the process of preparing the Croatian Power Company for inclusion in the EU ETS and are given challenges that Croatian Power Company will be exposed during the third trading period.

[1] Hrvatska elektroprivreda d.d., Sektor za održivi razvoj i unaprjeđenje kvalitete, Ulica grada Vukovara 37 Zagreb, [2] Metroalfa d.o.o. Karlovačka cesta 4L Zagreb

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Rožman B.[11] i Vujanović, M.[2]

SUSTAV TRGOVANJA EMISIJAMA STAKLENIČKIH PLINOVA

Ključne riječi: *trgovanje emisijama, emisije, stakleнički plinovi, ETS, cap and trade, CO2*

Svrha i cilj trgovanja emisijama stakleničkih plinova (eng. Emission Trading System- ETS) u pojedinoj državi usko je povezana s obvezom smanjenja emisije te zemlje, odnosno s izvršenjem obveza prema Kyoto protokolu. ETS je u EU započeo 2005 na principu "cap and trade". Pod "cap" se podrazumijeva ograničenje ukupnog iznosa emisija stakleničkih plinova iz postrojenja, koje je obveznik ETS. Unutar emisijskog ograničenja, obveznici sustava primaju dodijeljene emisijske jedinice koje mogu prodavati ili kupovati od onih kojima nisu potrebne. Ograničena ukupna količina emisijskih jedinica osigurava njihovu vrijednost. Na kraju svake godine pojedino postrojenje je obavezno predati količinu emisijskih jedinica kako bi pokrili svoje stvarne emisije. Ukoliko obveznik ETS smanji emisije tada svoj "višak" jedinica može prodati postrojenju koje nema dovoljno emisijskih jedinica za pokrivanje stvarnih emisija ili ih može iskoristiti za vlastite buduće potrebe.

Od 1.1.2005. do 31.12.2007. godine trajalo je prvo razdoblje trgovanja (probno razdoblje) čija je svrha bila priprema za mehanizam međunarodnog trgovanja emisijama stakleničkih plinova u skladu s Kyoto protokolom. U siječnju 2008. godine počelo je drugo razdoblje trgovanja koje je trajalo do 31.12.2012. godine. Treće razdoblje počelo je u siječnju 2013. i trajat će do 2020. godine.

Koncept sustava trgovanja emisijama temelji se na učinkovitoj optimizaciji troškova smanjenja emisija. Količina ukupnih dodijeljenih emisijskih jedinica će se tijekom vremena smanjivati pa će do 2020. biti dodijeljeno 21% manje emisijskih jedinica nego 2005. godine.

ETS je obavezan u svim članicama EU i danas je implementiran u 31 državi (27 članica EU, Island, Lihtenštajn, Norveška i Hrvatska). Sustav obuhvaća elektrane, tvornice s izgaranjem, rafinerije, željezare, cementare, vapnare i šire. Od 2012. godine u ETS su uključeni i zrakoplovni operatori a od 2013. godine sustav je proširen na petrokemijsku industriju, proizvodnju amonijaka i aluminij. Također su uključeni i drugi plinovi, a sve u cilju jačanja ETS u trećem razdoblju trgovanja od 2013. do 2020. godine.

EU je u ETS uvela novčanu vrijednost emisijskih jedinica CO2 i pokazala kako je moguće trgovati emisijama stakleničkih plinova te istovremeno postići planirana smanjenja emisija postrojenja. Za treće razdoblje trgovanja uvedene su promjene u aukciji emisijskih jedinica kako bi se još više povećala efikasnost sustava.

[1] Agencija za zaštitu okoliša, Trg maršala Tita 8, 10000 Zagreb
[2] Fakultet strojarstva i brodogradnje, Ulica Ivana Lučića 1, 10000, Zagreb

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Rožman B.[1] and Vujanović, M.[2]

EMISSION TRADING SYSTEM

Keywords: *emissions trading, emissions, greenhouse gases, ETS, cap and trade, CO2.*

The purpose and aim of emissions trading (Emission Trading System ETS) in each country is closely connected with the obligation to reduce emissions of the country, with the execution of obligations under the Kyoto protocol. In 2005 the EU started with ETS on the principle of "cap and trade". Under the "cap" is meant limit of the total amount of greenhouse gas emissions from the installations, which is subject of ETS. Within the emission limits, mandatory participants receive allocated emission allowances which they can sell or buy from those that have insufficient. Limited the total quantity of allowances provide their value. At the end of each year an installation is required to submit the amount of allowances to cover their actual emissions. If the ETS's mandatory participants reduce emissions then its "surplus" units can be sell to the installations which does not have enough allowances to cover their actual emissions, or they can use them for their own future needs. The first trading period (trial period) was from 1.1.2005 to 31.12.2007. Its purpose was to prepare a mechanism for international emissions trading under the Kyoto Protocol. The second trading period started on January 2008, which lasted until 31.12.2012. The third period began in January 2013 and will last until 2020 year.

The concept of ETS is based on optimizing emission reductions on the cost effective way. The amount of the total allocated allowances will decline over the time, so by 2020 will be allocated 21% less allowances than on 2005.

ETS is mandatory in all EU Member States and now it is implemented in 31 countries (27 EU member states, Iceland, Liechtenstein, Norway and Croatia). The system includes power stations, combustion plants, refineries, steel mills, cement industry, lime-and beyond. In 2012 ETS also involved the aircraft operators and from the 2013 the system was extended to the petrochemical industry, the production of ammonia and aluminium. With the aim of strengthening the ETS in the third trading period, from the 2013 to the 2020 other gases are also included.

The EU ETS introduced the financial value of CO2 emission allowances and showed that it is possible to trade with greenhouse gas emissions and at the same time achieve the planned emission reduction in the installation. Changes in the auction of allowances were introduced in the third trading period in order to further increase the efficiency of the system.

[1] Croatian Environment Agency, Trg maršala Tita 8, 10000 Zagreb
[2] Faculty of Mechanical Engineering and naval Architecture, Ulica Ivana Lučića 1, 10000, Zagreb

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Roksa, I.[1]

UTJECAJ IPPC DIREKTIVE I DIREKTIVE O INDUSTRIJSKIM EMISIJAMA NA RAD TERMOELEKTRANE SISAK VEZANO UZ EMISIJE ONEČIŠĆUJUĆIH TVARI U ZRAK

Ključne riječi: *IPPC Direktiva, IE Direktiva, emisije onečišćujućih tvari u zrak, najbolje raspoložive tehnike*

IPPC Direktiva (Direktiva o cjelovitom sprječavanju i nadziranju onečišćenja) je postavila niz obveza za izdavanje dozvola i kontrolu industrijskih postrojenja primjenom najbolje raspoloživih tehnika (NRT-a) te je iz iste prenesena obveza ishođenja objedinjenih uvjeta zaštite okoliša (okolišne dozvole) u Zakon o zaštiti okoliša (NN 110/07) i Uredbu o postupku utvrđivanja objedinjenih uvjeta zaštite okoliša (NN 114/08).

Direktiva o industrijskim emisijama (IE Direktiva) objedinjuje zakonske propise iz područja zaštite okoliša za industrijska postrojenja u jedan dokument te u potpunosti zamjenjuje IPPC Direktivu od 07. siječnja 2014. godine. Smanjenje štetnog utjecaja na okoliš i nadalje se postiže okolišnim dozvolama, ali uz niže granične vrijednosti emisija u zrak koje su dostižne primjenom najboljih raspoloživih tehnika (NRT-a). Odredbe IE Direktive vezane uz emisije u zrak iz industrijskih postrojenja prenesene su u hrvatsko zakonodavstvo u Uredbu o graničnim vrijednostima emisija onečišćujućih tvari u zrak iz nepokretnih izvora (NN 117/12).

Termoelektrana Sisak je termoenergetsko postrojenje nazivne toplinske snage veće od 50 MW te za nastavak rada mora ishoditi Rješenje o objedinjenim uvjetima zaštite okoliša (okolišnu dozvolu). Okolišnom dozvolom će se propisati granične vrijednosti emisija onečišćujućih tvari u zrak do i nakon isteka prijelaznog razdoblja (nakon 31.12.2017.) koje su u skladu s primjenom najboljih raspoloživih tehnika (NRT-a).

U ovom radu prikazan je pregled aktivnosti na provedbi obveza IPPC Direktive i IE Direktive u Termoelektrani Sisak vezano uz emisije onečišćujućih tvari u zrak, analiza graničnih vrijednosti emisija onečišćujućih tvari u zrak povezanih sa primjenom IPPC Direktive i IE Direktive te prijedlog mjera potrebnih za usklađivanje postrojenja s navedenim direktivama.

Smanjivanje emisija onečišćujućih tvari u zrak iz Termoelektrane Sisak kako bi se uskladile s vrijednostima emisija dostižnim primjenom najboljih raspoloživih tehnika (NRT-a) je uvjet za nastavak rada Termoelektrane Sisak nakon isteka prijelaznog razdoblja.

[1] HEP-Proizvodnja d.o.o., Termoelektrana Sisak, Ulica braće Bobetko 40, 44010 Sisak

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Roksa, I.[1]

IMPACT OF THE IPPC DIRECTIVE AND THE INDUSTRIAL EMISSIONS DIRECTIVE ON CONTINUING OPERATION OF THE THERMAL POWER PLANT SISAK WITH RESPECT TO THE EMISSIONS OF AIR POLLUTANTS

Keywords: *IPPC Directive, IE Directive, emissions of air pollutants, best available techniques*

IPPC Directive (Integrated Pollution Prevention and Control Directive) established a set of general obligations for issuing permits and regulating industrial plants using the best available techniques (BAT), and it served to provide integrated environmental requirements (environmental permit) included in the Environmental Protection Act (OG 110/07) and the Regulation of Procedures for Establishing Integrated Environmental Requirements (OG 114/08).

Industrial Emissions Directive (IE Directive) combines industrial plant regulations regarding environmental protection in one document and replaces the IPPC Directive, effective January 07, 2014. Reduction of the effects on the environment continues to be achieved through environmental permits. However, the maximum allowed emission levels are lower and need to be met by using the best available techniques (BAT). IE Directive regulations regarding emissions from industrial plants were codified in the Croatian legislation by the Regulation of emission limit values for air pollutants from stationary sources (NN 117/12).

TE Sisak is a thermal power plant with rated thermal input higher than 50 MW. To continue operation, it has to obtain the integrated environmental requirements (the environmental permit). The Environmental permit will include emission limit values for air pollutants until and after the transition period (after December 31, 2017), which comply with the best available techniques (BAT).

This presentation reviews TE Sisak activities regarding the implementation of the IPPC Directive and the IE Directive requirements for emissions of air pollutants. It also presents analysis of emission limit values for air pollutants following the IPPC Directive and IE Directive, as well as the proposals for implementing measures in response to these directives.

Reducing emissions of air pollutants to meet the emission values using best available techniques (BAT) is necessary for continued operation of TE Sisak after the end of the transition period.

[1] HEP-Proizvodnja d.o.o., Termoelektrana Sisak, Ulica braće Bobetko 40, 44010 Sisak

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UTJECAJ DIREKTIVE O INDUSTRIJSKIM EMISIJAMA NA RAD POSTROJENJA TE-TO ZAGREB

Ključne riječi*: rješenje o objedinjenim uvjetima zaštite okoliša, najbolje raspoložive tehnike, emisije u zrak*

TE-TO Zagreb je termoenergetsko postrojenje nazivne toplinske snage veće od 50 MW te za nastavak rada mora ishoditi Rješenje o objedinjenim uvjetima zaštite okoliša (tzv. okolišnu dozvolu) sukladno Uredbi o postupku utvrđivanja objedinjenih uvjeta zaštite okoliša (NN 114/08) i Zakonu o zaštiti zraka (NN 130/11). Obveza ishođenja objedinjenih uvjeta zaštite okoliša prenesena je u Uredbu i Zakon iz Direktive o cjelovitom sprječavanju i nadziranju onečišćenja (Integrated Pollution Prevention and Control Directive 2008/1/EZ) tzv. IPPC Direktive.

Direktiva 2010/75/EU o industrijskim emisijama (IED- Industrial Emissions Directive) objedinjuje zakonske propise iz područja zaštite okoliša za industrijska postrojenja u jedan dokument te u potpunosti zamjenjuje IPPC Direktivu od 07. siječnja 2014. godine. IED se naziva i novom IPPC direktivom jer se smanjenje štetnog utjecaja na okoliša i nadalje postiže okolišnim dozvolama zasnovanim na najbolje raspoloživim tehnikama -NRT (eng. BAT – Best Available Techniques), ali i novim, sada nižim, sektorskim graničnim vrijednostima emisija u zrak. Uvođenje Direktive o industrijskim emisijama ima za cilj objediniti glavnu regulativu glede zaštite okoliša za industrijska postrojenja u jedan zakonski dokument, uskladiti granične vrijednosti emisija u zrak za velike termoenergetske uređaje i postrojenja s vrijednostima emisija dostižnih primjenom najbolje raspoloživih tehnika te unaprijediti jasnoću propisa glede ishođenja objedinjenih uvjeta zaštite okoliša, praćenja emisija i izvješćivanja. Odredbe Direktive o industrijskim emisijama, a koje su vezane uz emisije u zrak iz industrijskih postrojenja, prenesene su u hrvatsko zakonodavstvo u Uredbu o graničnim vrijednostima emisija onečišćujućih tvari u zrak iz nepokretnih izvora (NN 117/12).

U ovom radu prikazana je analiza Direktive o industrijskim emisijama s pojašnjenjem svih obveza koje se odnose na postrojenje TE-TO Zagreb te prijedlozima mjera potrebnih za usklađivanje termoenergetskog postrojenja TE-TO Zagreb s istom. Isto tako, napravljena je usporedba graničnih vrijednosti emisija u zrak povezanih s primjenom Uredbe o postupku utvrđivanja objedinjenih uvjeta zaštite okoliša (NN 114/08) i Direktive o industrijskim emisijama 2010/75/EU.

[1] HEP –Proizvodnja d.o.o., Ulica grada Vukovara 37, Zagreb
[2] HEP-Proizvodnja d.o.o., TE-TO Zagreb, Kuševačka 10a, Zagreb

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Babačić, M.[1] and Begović, M.[2]

TE-TO ZAGREB – IMPACT OF THE INDUSTRIAL EMISSIONS DIRECTIVE

Keywords: *decision on integrated environmental protection, the best available techniques, air emissions*

TE-TO Zagreb is electricity generation plant the rated thermal input exceeding 50 MW, and to continue the work must obtain a decision on integrated environmental protection (the environmental permit) in accordance with the Regulation on the procedure for determining integrated environmental protection (NN 114/08) and the Law on Air Protection (NN 130/11). The obligation to obtain integrated environmental protection was transferred to a statute from the Integrated Pollution Prevention and Control Directive 2008/1/EC so called IPPC Directive.

IED – Industrial Emissions Directive 2010/75/EU combines legislation concerning environmental protection for industrial plants in a single document, and completely replaces the IPPC Directive from 07th January 2014. IED is called and the new IPPC directive as reduce the impact on the environment and still achieves environmental permits based on the best available techniques-BAT, but also a new, far lower, emission limit values in air. The introduction of the Industrial Emissions Directive aims to consolidate the main legislation concerning environmental protection for industrial plants in one legal document, adjust the emission limit values for air conditioners and large thermal power plants with emission values achievable using best available techniques and to improve the clarity of the regulations in terms of obtaining the integrated environmental monitoring and reporting of emissions. The provisions of the Industrial Emissions Directive, which are associated with air emissions from industrial plants, were transferred to the Croatian legislation in the Decree on the limitation of emissions of air pollutants from stationary sources (NN 117/12).

This paper presents an analysis of the Industrial Emissions Directive with an explanation of all obligations relating to power plant TE-TO Zagreb and proposed measures necessary to comply power plant TE-TO Zagreb with the same. Also, a comparison is made for emissions to air associated with the application of the Regulation on the procedure for determining integrated environmental protection (NN114/08) and Industrial Emissions Directive 2010/75/EU.

[1] HEP –Proizvodnja d.o.o., Ulica grada Vukovara 37, Zagreb
[2] HEP-Proizvodnja d.o.o., TE-TO Zagreb, Kuševačka 10a, Zagreb

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Živković, N.[1] i Avirović, G.[1]

ZAHTJEVI REFERENTNOG DOKUMENTA O OPĆIM PRINCIPIMA MONITORINGA U POSTUPKU ISHOĐENJA "OKOLIŠNE DOZVOLE"

Ključne riječi: *objedinjeni uvjeti, okolišna dozvola, referentni dokument monitoringa, uvjeti monitoringa, check-lista*

Petrokemija d.d. tvornica gnojiva u Kutini prema svojim djelatnostima je operater-obveznik utvrđivanja objedinjenih uvjeta zaštite okoliša ili "okolišne dozvole". Prema propisima utvrđeni objedinjeni uvjeti zaštite okoliša ili "okolišna dozvola" moraju sadržavati odgovarajuće zahtjeve za monitoring emisija uz navođenje prikladne metodologije i učestalosti mjerenja, postupka vrednovanja i obvezu dostave podataka potrebnih za ocjenu usklađenosti nadležnom tijelu. U posebnoj točki propisanog obrasca (OZ-IPPC) putem kojega se podnosi zahtjev za izdavanje okolišne dozvole kroz petnaest točaka, za svaku sastavnicu okoliša (zrak, voda, tlo), operater mora detaljno opisati mjerno mjesto, primijenjene analitičke metode i metode uzorkovanja, učestalost mjerenja/uzorkovanja, uvjete mjerenja/uzorkovanja, metode bilježenja, obrade i pohrane podataka te navesti podatke o laboratoriju koji mjerenje provodi uz očitovanje o njegovom statusu akreditiranog laboratorija. Europska komisija je kao pomoć nadležnom tijelu koje izdaje "okolišnu dozvolu" ali i operaterima koji podliježu obvezi njena ishođenja izradila referentni dokument o općim principima monitoringa u vezi sa zahtjevima praćenja industrijskih emisija na izvoru. U referentnom dokumentu detaljno se obrazlažu svi aspekti monitoringa, a graničnim vrijednostima emisija koje se utvrđuju okolišnom dozvolom pridružuju se uvjeti monitoringa. Iako je najveći dio principa monitoringa iz referentnog dokumenta ugrađen u nacionalne propise koji reguliraju ovo područje njegova vrijednost kao vodiča je neupitna. Posebno interesantna su poglavlja koja opisuju kako postupati s mjernim nesigurnostima, ovisnost vremena usrednjavanja i učestalosti mjerenja o tipu proizvodnog procesa koji se prati, postupanje s rezultatima ispod granice detekcije i "outliner-ima" te pristup monitoringa od direktnog mjerenja i praćenja tzv. surogat parametara do bilanciranja i izračuna emisija. U radu je prikazana sukladnost između propisanih zahtjeva mjerenja emisija u zrak i referentnog dokumenta o monitoringu. Izrađena je "check-lista" za ocjenu sukladnosti sa zahtjevima referentnog dokumenta o monitoringu koja predstavlja koristan alat za operatera, ovlaštenika i nadležno tijelo koje donosi "okolišnu dozvolu".

[1] Petrokemija d.d. tvornica gnojiva, Aleja Vukovar 4, 44320 Kutina, HRVATSKA

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REQUIREMENTS FOR REFERENCE DOCUMENT ON THE GENERAL PRINCIPLES OF MONITORING IN THE PROCESS OF OBTAINING "ENVIRONMENTAL PERMIT"

Keywords: *integrated requirements, environmental permit, reference monitoring document, monitoring condition*

Petrokemija, Plc. Fertilizer Company is according to its activities an operator liable to obtain integrated requirements for environmental protection or "environmental permit". According to the regulations, the established integrated environmental requirements or "environmental permit" shall include appropriate requirements for monitoring emissions with specifying appropriate methodology and measurement frequency, the evaluation process and an obligation to submit the data needed to assess compliance to the competent authority. In a separate item of the prescribed form (OZ-IPPC), through which the application for environmental permit is submitted, with fifteen points for each environmental component (air, water, soil), the operator must describe in detail the measurement site, the applied analytical and sampling methods, frequency of measurement/sampling, measurement/sampling conditions, methods of recording, processing and storage of data, and provide information on the laboratory that carried out the measurements with a statement on its status as an accredited laboratory. To assist the competent authority that issues the "environmental permit" and also the operators who have to obtain it, the European Commission prepared a reference document on the general principles of monitoring in connection with the requirements for monitoring industrial emissions at source. The reference document explains in detail all aspects of monitoring, emission limit values and monitoring conditions. Although most of the principles of monitoring from the reference document are already incorporated in the national legislation regulating this area, its value as a guide is unquestionable. Especially interesting are the chapters that describe how to handle the measurement uncertainties, the dependence of the averaging time and measurement frequency on the type of production process that is monitored, handling results below the detection limit and "outliners" as well as the approach of monitoring from the direct measurement and monitoring of the so-called surrogate parameters to balancing and calculating emissions. This paper presents the compliance between regulatory requirements of emission into air measurements and the reference document on monitoring. As the same information must be listed for environmental monitoring (air quality), there will be a problem in the evaluation of pollutants that are monitored but for which there is no longer a prescribed limit (e.g. fluorides). Check-list for the assessment of conformity with the requirements of the reference document on monitoring was made, which is a useful tool for operators, authorized consulting organization and competent authorities that brings environmental permit.

[1] Petrokemija, Plc. Fertilizer Company, Aleja Vukovar 4, 44320 Kutina, CROATIA

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VAŽNIJE RAZLIKE IZMEĐU STARIH I NOVIH IZDANJA NORMI ZA MJERENJE PLINOVITIH ONEĆIŠĆUJUĆIH TVARI U ZRAKU

Ključne riječi: *nove norme za plinovite onečišćujuće tvari u zraku, tipsko odobrenje, mjerna nesigurnost*

Krajem 2012. Hrvatski zavod za norme izdao je nova izdanja hrvatskih normi HRN EN 14626:2012, HRN EN 14211:2012, HRN EN 14212:2012, i HRN EN 14625:2012 koje zamjenjuju stare norme iz 2006. godine. Cilj rada je opisati najvažnije promjene u novim izdanjima normi za određivanje koncentracija CO, NO/NO_2, SO_2, i O_3 u zraku referentnim metodama, s posebnim naglaskom na poglavlja koja se odnose na ispitne laboratorije. Značajnije promjene učinjene su u preciznijem definiranju i odjeljivanjem poglavlja koja se odnose na proizvođače instrumenata, na laboratorije koji provode testove za tiska odobrenja te na ispitne laboratorije koji provode mjerenja na terenu. Uvedene su nove definicije mjeriteljskih pojmova koje se navode u posebnom odlomku.

U novim izdanjima normi detaljnije je objašnjena svrha i smisao tipskog odobrenja (type approval), tko ga smije izdavati i provoditi testove radnih karakteristika te se navode obvezujuće norme za proizvodnju i kontrolu proizvodnje mjernih instrumenata. Promijenjeni su kriteriji prolaznosti za neke od testova radnih karakteristika iz Tablica 1, uvodi se izračun granice detekcije a procedure i zahtjevi za referentnim materijalom za neke testove su neznatno promijenjeni.

Najveće izmjene provedene su u poglavlju koje se odnosi na kontrolu kvalitete. U redovnoj kontroli kvalitete uvodi se obaveza izvođenja testa ponovljivosti na nul (zero) i span plinu i linearnosti (lack of fit) na zero plinu, te su promijenjeni pojedini kriteriji prolaznosti. Dozvoljava se produživanje intervala kalibracije ukoliko se potvrdi stabilnost sustava za provjeru odziva, navodi se formula za korekciju mjernih podataka nakon kalibracije te mogućnost promjene mjernog područja ukoliko se ukaže potreba. Nadalje, navedena je nova i vrlo korisna shema postupanja s podatcima u slučaju prekoračenja granica prihvatljivosti.

Bitno je naglasiti da je primijenjen liberalniji pristup pri izračunu mjernih nesigurnosti te je dopušteno izračunavati mjernu nesigurnost kao sastavnog dijela ciljane kvalitete podataka i bez podataka iz tipskog odobrenja ali u skladu sa zahtjevima EN ISO 20988. Također su uvedene neke promjene pri izračunu pojedinih sastavnica mjerne nesigurnosti te je uvedena nova sastavnica mjerna nesigurnost zero plina.

[1] Ekonerg Koranska 5 Zagreb
[2] Institut za medicinska istraživanja i medicinu rada Ksaverska cesta 2, Zagreb
[3] Veleučilište Velika Gorica, 10 410 Velika Gorica, Zagrebačka c. 5, Hrvatska

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SOME IMPORTANT DIFFERENCES BETWEEN OLD AND NEW CROATIAN STANDARDS FOR AMBIENT AIR QUALITY

Keywords: *new standards, air quality, type approval, quality control, combined standard uncertainty*

By the end of 2012 Croatian standards institute has issued new Croatian standards 1426, 14211, 14212 and 14625 to replace same standards from 2006. Aim of this paper is to describe some most important changes between these new and old standards for CO, NO/NOx, SO2 and O3 in ambient air, with emphases on chapters dedicated for testing laboratories. Some important changes in new standards are better explanation of dedications of chapters concerning roles of equipment manufacturers, testing laboratories and laboratories that are performing type approval tests, and introduction of some new metrological definitions.

Also, new standards more detailed explain the purpose and goals of type approval tests and who can do tests for type approval and who can issue type approval. Standards concerning manufacturing and control of manufacturing of type-approved instruments for ambient air are also given. In type approval testing chapters, some performance criterions and some referent materials for tests specifications are changed, also calculation of lower detection limit is introduced.

Biggest changes are in chapters dedicated to testing laboratories. In continues quality control for field measurements performance of repeatability standard deviation test on zero and span gas as well as lack of fit test are introduced. In addition, some performance criterions for QA tests are changed. Possibility of prolongation of calibration intervals in certain circumstances is explained and formulas for measuring data correction are introduced. New and very useful scheme for validation of data in cases of poor QC results is also introduced.

It is important to emphasize that annexes concerning calculations of uncertainty are no more normative, so uncertainties on limit value now can be calculated without data from type approval tests but still have to be according to EN ISO 20988. There are also some changes in calculation of uncertainties on limit value consisting of some new standard uncertainties in combined standard uncertainty budget i.e. standard uncertainty of zero air.

[1] EKONERG-Energy and Environmental Protection Institute, 10 000 Zagreb, Koranska 5,
[2] Institute for Medical Research and Occupational Health Ksaverska cesta 2, Zagreb
[3] University of Applied Sciences Velika Gorica, 10410 Velika Gorica, Zagrebačka c. 5, Croatia

Tema 2
Emisije onečišćenja u atmosferu

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Čretnik, J.[1] i Šlibar, M.[1]

AUTOMATSKI MJERNI SUSTAVI ZA ČESTICE

Ključne riječi: *čestice, praćenje emisije čestica, AMS za čestice, tehnike mjerenja čestica*

Zaštita okoliša je sve važnija u našem društvu. Osim opće svijesti ljudi i tvrtki, zaštita okoliša je tražena zakonom. Među ostalima, veliki izvori emisije su dužni uspostaviti stalno praćenje emisija. Mjerenja emisija zahtijevaju EU direktive i nacionalno zakonodavstvo, posebno stalno praćenje velikih izvora emisija. Jedan od parametara, važnih za kakvoću okolnog zraka, ali kojeg je teško mjeriti stalno, su čestice. Postoji nekoliko različitih principa mjerenja čestica automatskim mjernim sustavima (AMS), koji imaju dobre i loše strane za različite aplikacije.

Zahtjevi za automatske mjerne sustave su vrlo složeni. Postojeća razina kvalitete AMS u cijeloj Europi pa i u samim pojedinačnim zemljama je vrlo različita. Za poboljšanje i ujedinjenje praćenja emisija u Europi, CEN je izdao tri standarda za osiguranje kvalitete AMS.

Prilikom obavljanja umjeravanja AMS za čestice, postoji nekoliko problema, koje treba uzeti u obzir. Nedostatak referentnih materijala, koji se mogu koristiti za umjeravanje AMS, je najvažniji. Dakle, za većinu AMS za čestice potrebno je izvoditi umjeravanje sa standardnom referentnom metodom (SRM), da bi se dobio izlaz masne koncentracije čestica. U slučaju čestica SRM je ručna gravimetrijska metoda, određena standardima.

Ovaj rad se bavi dostupnim mjernim principima AMS za čestice, osnovnim zahtjevima za osiguranje kvalitete AMS za čestice i ručnim tehnikama za umjeravanje to jest kalibraciju AMS za čestice.

Mjerenje čestica je složen zadatak, bilo da se obavlja ručno ili automatski. Za točno automatsko mjerenje, odabir pravog AMS, koji je primjeran za svrhu, je prvi i najvažniji zadatak. Niti jedna druga akcija ne može ispraviti pogrešan izbor AMS. Da bi se moglo izvesti taj izbor, nužno je dobro poznavanje samog procesa. To uključuje, između ostalog, sam proces izvora onečišćenja, radne uvjeta, procesni plin, uvjete i svojstva čestica.

Ljudske aktivnosti imaju veliki utjecaj na okoliš; stoga je vrlo važno, da se upotrebljavaju najbolje dostupne tehnike, uključujući i praćenje. Višestruke prednosti praćenja može se postići samo ako su podaci pouzdani i usporedivi, a oni su dobiveni iz programa praćenja odgovarajuće kakvoće.

[1] RACI d.o.o., Tehnološki park 24, SI-1000 LJUBLJANA, SLOVENIJA

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Čretnik, J.[1] and Šlibar, M.[1]

AUTOMATED MEASURING SYSTEMS FOR PARTICULATE MATTER

Keywords: *particulate matter, dust emission monitoring, particulate matter AMS, dust measurement techniques.*

Environment protection is more and more important in our society. Apart from general consciousness of people and companies, environment protection is requested by law. Among others, large emission sources are obliged to establish permanent emission monitoring.
Emission measurements are required by EU directives and national legislations, especially continuous monitoring of large pollution sources. One of the parameters, important for ambient air quality, yet difficult to measure continuously, is particulate matter. Several different measurement principles for particulate matter automated measurement systems (AMS) exist, which have their pro's and con's for different applications.
For automated measuring system the requirements are very complex. The existing quality level of AMS throughout Europe and in particular countries is very different. To improve and unify emission monitoring in Europe, CEN has issued three standards for quality assurance of AMS.
When performing calibration of AMS dust, there are several issues to be observed. Lack of reference materials, which could be used for calibration of the AMS is the most important one. Therefore, for most AMS for particulate matter a calibration with a standard reference method (SRM) is necessary to get a mass concentration output. In case of particulate matter SRM is a manual gravimetric method, determined by standards.
This paper deals with available measurement principles for particulate matter AMS, basic quality assurance requirements for AMS and manual techniques for calibration of particulate matter AMS. Measurement of particulate matter is a complex task, whether it is performed manually or automatically. For an accurate automated measurement, choosing a correct AMS, that is fit-for-purpose, is the first and the most important task. No other action can correct the wrong choice of the AMS. To be able to perform this choice, good knowledge of the process is necessary. This includes, among others, plant process, operating conditions, process gas conditions, and particulate matter characteristics.
Human activities have great influence on the environment; therefore it is very important that the best available techniques are used, including the monitoring. Multiple benefits of monitoring can be achieved only if the data are reliable and comparable and they have been obtained from an appropriate quality monitoring program.

[1] RACI d.o.o., Tehnološki park 24, SI-1000 LJUBLJANA, SLOVENIA

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Zgorelec, Ž.[1], Bilandžija, D.[1], Mesić, M.[1], Reis, I.[2], Jurišić, A.[1] i Šestak, I.[1]

EMISIJE CO_2 IZ OBRADIVOG POLJOPRIVREDNOG TLA

Ključne riječi: *ozima pšenica, gnojidba, CO_2 fluks, disanje tla*

Održiva poljoprivreda podrazumijeva uspješno gospodarenje poljoprivrednim resursima kako bi se udovoljilo sve većim ljudskim potrebama za hranom, vlaknima i energijom, ali uz istodobno održavanje kvalitete okoliša i zaštitu prirodnih resursa. Središnje mjesto u zaštiti pripada upravo tlu kao važnom segmentu poljoprivrednog ekosustava. Ukupna količina ugljika u tlu na globalnoj razini gotovo je tri puta veća od one u nadzemnoj biomasi. Terestička sekvestracija ugljika proces je kojim agronomska i šumarska praksa mogu utjecati na uklanjanje ugljika iz atmosfere. Sekvestracija usporava brzinu klimatskih promjena povećanjem količine uskladištenog ugljika u biljnom materijalu i tlu, održavanjem postojećih količina ugljika u biljnom materijalu i tlu, i smanjenjem emisija stakleničkih plinova: ugljikovog (IV) oksida, metana i dušikovog (I) oksida iz tla. Pravilnim gospodarenjem poljoprivrednim tlom (obrada, gnojidba, navodnjavanje,…) može se presudno utjecati na emisiju CO_2 iz tla. U RH najveći doprinos u emisiji stakleničkih plinova prema sektorima imaju energetika i poljoprivreda. Tako npr. prema Izvješću o stanju okoliša RH (2007) i podacima Agencije za zaštitu okoliša, poljoprivreda kao sektor doprinijela je sa 12,1 % u emisiji stakleničkih plinova u 2004. g. što nije zanemarivo. Zbog nedostatka istraživanja i vlastitih nacionalnih podataka, a vezanih za tematiku disanja tla (CO_2 emisiju ili fluks) u realnim agroklimatskim uvjetima provodi se istraživanje u Zapadnoj Panonskoj poljoprivrednoj podregiji RH, na rubu granice s Parkom prirode Lonjsko polje. U vegetacijskoj 2012. g. utvrđen je utjecaj mineralne gnojidbe (N+P+K) na emisiju CO_2 iz tla tijekom uzgoja ozime pšenice (sjetva/žetva=05.11.11./11.07.12.). Pokus je postavljen još 1996. g. s ciljem utvrđivanja utjecaja gnojidbe dušikom na prinos ratarskih kultura, te kvalitetu podzemne i površinske vode (prvenstveno NO_3^-). Istraživanje je 2011. g. prošireno i na praćenje utjecaja na atmosferu (emisija CO_2). Pokus se sastoji od 10 tretmana (svaki u 4 ponavljanja) koji se razlikuju u primijenjenim dozama dušika (od 0 do 300 kg/ha), ukupna veličina pokusa je gotovo 4,5 ha, tip tla je drenirani Pseudoglej ravničarski distrični, dok prosječna nadmorska visina pokusa iznosi 97,2 m. Područje je karakteristično za umjerenu kontinentalnu klimu sa srednjom godišnjom temperaturom od 10,7 °C i srednjom godišnjom količinom oborine od 865 mm. Od listopada 2011. do studenog 2012. provedeno je 10 mjerenja. Srednje godišnje vrijednosti CO_2-C fluksa kretale su se od 9,8 kg/ha×dan određenih na varijanti br. X (crni ugar-obrada bez sjetve) do 31,4 kg/ha×dan zabilježenih na varijanti br. V sa primijenjenih 200 kg N/ha.

[1] Sveučilište u Zagrebu Agronomski fakultet, Svetošimunska cesta 25, 10000 Zagreb
[2] Student diplomskog studija Agroekologija

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Zgorelec, Ž.[1], Bilandžija, D.[1], Mesić, M.[1], Reis, I.[2], Jurišić, A.[1] and Šestak, I.[1]

CO_2 EMISSIONS FROM ARABLE AGRICULTURE SOIL

Keywords: *winter wheat, fertilization, CO_2 efflux, soil respiration*

Sustainable agriculture implies successful management of agricultural resources in order to meet growing human needs for food, fiber and energy, but at the same time maintaining the quality of the environment and protection of natural resources. Central place in the protection belongs to the soil as an important segment of the agricultural ecosystem. The total amount of carbon in the soil at the global level is nearly three times higher than those in the surface biomass. Terrestrial carbon sequestration is the process by which agronomic and forestry practices can affect the removal of carbon from the atmosphere. Sequestration slows down the speed of climate change by increasing the amount of carbon stored in plant material and soil, maintaining the existing amount of carbon in plant material and soil, and reducing emissions of greenhouse gases: carbon (IV) oxide, methane and nitrogen (I) oxide from the soil. Agricultural soil management (tillage, fertilization, irrigation, ...) can have a crucial influence on the emission of CO_2 from the soil. In the Republic of Croatia the greatest contribution in greenhouse gas emissions by sector are energy and agriculture. For example, from Report on State of the Environment in the Republic of Croatia (2007) and data of the Croatian Environment Agency, agriculture sector contributed with 12.1% of the greenhouse gas emissions in 2004, which is not negligible. Due to the lack of research and our own national data related to the topics of soil respiration (CO_2 or flux) in the real agroclimatic conditions of Western Pannonian agricultural subregion, on the edge of the Nature Park Lonjsko polje, field experiment was conducted. At 2012 the effect of mineral fertilizer (N + P + K) on CO_2 emissions from soil during the cultivation of winter wheat (sowing / harvesting = 05.11.11./11.07.12.) was determined. Experiment trial was conducted in 1996 with the aim of determining the effect of nitrogen fertilization on the yield of different agricultural crops, and on the quality of groundwater and surface water (primarily NO_3^-). At 2011 research was extended to the monitoring of fertilization impact on the atmosphere (CO_2 emissions). The experiment consists of 10 treatments (each in 4 replicates), which differ in the applied nitrogen doses (from 0 up to 300 kg N/ ha), total size of the experiment is nearly 4.5 ha, type of soil is drained lowland distric Stagnosols, with average altitude of 97.2 m. The area has typical temperate continental climate with an average temperature of 10.7° C and mean annual precipitation of 865 mm. From October 2011 to November 2012 ten measurements were conducted. Mean annual values of CO_2-C flux ranged from 9.8 kg / ha × day noted in the variant no. X (black fallow-tillage without sowing) up to 31.4 kg / ha × day recorded in the variant no. V with applied 200 kg N / ha.

[1] University of Zagreb Faculty of Agriculture, Svetosimunska street 25, 10000 Zagreb
[2] Student – Master study programme Agroecology

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Pašalić, G.[1]

EMISIJE U ZRAK IZ CENTRA ZA GOSPODARENJE OTPADOM

Ključne riječi: *emisije u zrak, centar za gospodarenje otpadom*

Strategijom gospodarenja otpadom RH (NN 130/05) kao i Planom gospodarenja otpadom u RH (NN 85/07, 126/10 i 31/11) u cilju racionalnog gospodarenja otpadom u RH predviđena je uspostava centara za gospodarenje otpadom (CGO) na županijskoj odnosno regionalnoj razini. CGO je sklop više međusobno funkcionalno i/ili tehnološki povezanih građevina i uređaja za oporabu i/ili zbrinjavanje otpada uključujući i pripremu otpada prije oporabe ili zbrinjavanja. Prilikom uspostave CGo, primjenom najboljih raspoloživih tehnika (NRT) postignute razine emisija svode se na minimum odnosno postiže se visoka opća razina zaštite okoliša.
U radu je opisan CGO "Lučino razdolje" u Dubrovačko-neretvanskoj županiji, tehnologija rada, mjesta emisija te tehnike smanjivanja emisija u zrak.

[1] IPZ Uniprojekt MCF d.o.o., Zagreb, Babonićeva 32

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Pašalić, G.[1]

AIR EMISSIONS FROM WASTE MANAGEMENT CENTER

Keywords: *air emissions, waste management center*

The Republic of Croatia in order of rational waste management predicted on the basis of National Waste Management Strategy (OG 130/05) and the Waste Management Plan of the Republic of Croatia (OG 85/07, 126/10 and 31/11) the establishment of waste management centers (WMC) on county or regional level. WMC is a composite of several functionally and / or technology-related facilities and devices for recycling and / or disposal of waste, including the preparation of waste prior to recovery or disposal. When establishing WMC, using best available techniques (BAT), achieved emission levels are reduced to a minimum and achieves high overall level of environmental protection.

The paper describes the WMC "Lucino razdolje" in the Dubrovačko-neretvanska county, working technology, places of emissions origin and techniques for reducing air emissions.

[1] IPZ Uniprojekt MCF d.o.o., Zagreb, Babonićeva 32

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Orlović-Leko, P.[1], Trkmić, M.[2] i Galić, I.[1]

CO_2 EMISIJSKI FAKTORI ZA UGLJENE

Ključne riječi: *CO_2 emisijski faktor, ugljen, IPCC metodologija.*

Za procjenu emisije ugljikovog dioksida uslijed izgaranja ugljena, CO_2 emisijski faktor (CEF), specificiran prema rangu ugljena, važan je ulazni parametar. Iako su vrijednosti CEF za izgaranje ugljena zadane prema Uputama Međuvladinog tijela za klimatske promjene iz 2006. godine (IPCC Upute), pri izradi nacionalnog inventara stakleničkih plinova preporučuje se primjena nacionalnih EF (IPCC, 2006). Sadržaj ugljika najvažniji je parametar ugljena i pokazatelj je stupnja ugljenifikacije (ranga ugljena). Međutim, mnoga svojstva ugljena vrlo su specifična (npr. sadržaj sumpora, pepela, vlage, macerala). Zbog toga, CEF za ugljen ne ovisi samo o rangu ugljena već i o zemljopisnom podrijetlu ugljena.

U ovom radu, izračunati su CEF za ugljene različitog zemljopisnog podrijetla: kamene ugljene (N = 10), smeđe ugljene (N = 3), lignit (N = 2) i treset (N = 2). Korišteni su podaci o sadržaju ugljika dobiveni ultimativnom analizom ugljena kao i rezultati aproksimativne analize ugljena. Kemijska analiza ugljena provedena je sukladno ASTM i ISO standardima za ispitivanje ugljena. Vrijednosti CEF su se kretale između 93,3 tCO2/TJ i 97,7 tCO2/TJ (razlika do 4,4%) za kamene ugljene; između 96,4 tCO2/TJ i 101,3 tCO2/TJ (razlika do 5%) za smeđe ugljena; oko 109.5 tCO2/TJ za lignit; 110.2 tCO2/TJ i 147,9 t CO2/TJ (razlika do 37,7% razlike) za treset. CEF za razmatrane uzorke razlikuju se od referentnih CEF (IPCC Upute). Najveća razlika između izračunatih i referentnih CEF uočena je kod treseta (do 39,7%), a zatim slijede: lignit (do 8,5%), smeđi ugljen (do 5,5%) i kameni ugljen (do 3,4 %).

Rezultati potvrđuju važnost primjene specifičnih, nacionalnih CEF za ugljen u svrhu što točnije procjene emisije stakleničkih plinova.

[1] Rudarsko-Geološko-Naftni fakultet, Sveučilište u Zagrebu, Hrvatska
[2] HEP-Proizvodnja d.o.o. Sektor za termoelektrane, Centralni kemijsko-tehnološki laboratorij, Zagreb, Hrvatska

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Orlović-Leko, P.[1], Trkmić, M.[2] and Galić, I.[1]

CO_2 EMISSION FACTORS FOR COALS

Keywords: *CO_2 emission factor, coal, Greenhouse IPCC methodology*

Carbon dioxide emission factor (CEF) specified according to the rank of the coal is an important input parameter for estimate emission of CO_2 from coal combustion. Although 2006 IPCC (Inter Governmental Panel on Climate Change) Guidelines provided default values, applying country-specific emission factors was recommended when estimating national greenhouse gas emissions (IPCC, 2006). The most important coal parameter is carbon content, which is the measure of the degree of coalification (coal rank). However, many coal properties are actually rather specific (e.g. content of sulphur, ash, moisture, macerals). Because of this fact, CO_2 emission factors (CEFs) for coal vary with both rank and geographic origin

In this study, CEFs values were calculated for coals from different countries: bituminous (N = 10), sub-bituminous coals (N = 3), lignite (N = 2) and peat (N = 2) utilizing the carbon content data from elemental analysis and the proximate analysis results. All of the analyses of coal samples were performed according to International Organization for Standardization (ISO) and American Society for Testing Materials (ASTM). The CEFs values were between 93.3 tCO_2/TJ and 97.7 tCO_2/TJ (4.4% difference) for bituminous coals; between 96.4 and 101.3 tCO_2/TJ (5% difference) for sub- bituminous coals; about 109.5 tCO_2/TJ for lignite; 110.2 tCO_2/TJ and 147.9 t CO_2/TJ (37.7% difference) for peat.

The differences between calculated CEFs and IPCC default values were analysed. The considerable difference was observed for peat (up to 39.7%). After that came lignite (up to 8.5% difference), sub – bituminous coal (up to 5.5% difference) and bituminous coal (up to 3.4% difference).

The results confirm the importance of the implementation of specific national CEFs for coals for the accurate assessment of greenhouse gas emissions.

[1] Mining, Geology and Petrology Engineering Faculty, Zagreb, University of Zagreb, Croatia
[2] HEP-Proizvodnja d.o.o. Thermal Power Plants Sector, Central chem. teh. laboratory Zagreb, Croatia

Tema 3
Onečišćenja vanjske atmosfere – imisije

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Vađić, V.[1], Žužul, S.[1], Rinkovec, J.[1] i Pehnec, G.[1]

SEZONSKE VARIJACIJE U KONCENTRACIJAMA KADMIJA U SITNIM ČESTICAMA U ZRAKU ZAGREBA

Ključne riječi: *PM_{10}, $PM_{2,5}$, PM_1 čestice, toksičnost čestica*

Internacionalna agencija za istraživanje raka (IARC) svrstala je kadmij i njegove spojeve u grupu 1 kancerogenosti za ljude. Kadmij i njegovi spojevi mogu uzrokovati rak pluća kod ljudi i životinja pri ekspoziciji inhalacijom.

U ovom radu prikazani su prvi rezultati određivanja sezonskih varijacija u masenim koncentracijama kadmija sakupljenih u uzorcima lebdećih čestica čiji je aerodinamički promjer manji od 10 μm, 2,5 μm i 1 μm (PM_{10}, $PM_{2,5}$ i PM_1). Njihove razine koncentracija određivane su na jednoj mjernoj postaji u sjevernom dijelu Zagreba tijekom 2011. godine.

Uzorci kadmija sakupljani su na kvarcne filtre tijekom 24 sata prosisavanjem oko 50 m^3 zraka. Sakupljeni uzorci lebdećih čestica razoreni su uz dušičnu kiselinu i mikrovalove, a sadržaj kadmija određen je spektroskopijom masa uz induktivno spregnutu plazmu (ICP-MS). Za analizu odabran je izotop mase 111 za kadmij uz dodatak rodija kao unutarnjeg standarda. Donja granica određivanja bila je 0,022 ng m^{-3}.

Za vrijeme mjernog razdoblja sakupljeno je po 334 uzorka svake frakcije lebdećih čestica. Najviše koncentracije kadmija izmjerene su u zimi, a maksimalne dnevne vrijednosti bile su 1,79 ng m^{-3} za PM_{10}, 1,42 ng m^{-3} za $PM_{2,5}$ i 0,81 ng m^{-3} za PM_1 frakciju lebdećih čestica.

U usporedbi s kadmijem u frakciji lebdećih čestica PM_{10}, 85,0% je izmjereno u frakciji lebdećih čestica $PM_{2,5}$, a 49,3% u frakciji lebdećih čestica PM_1, u zimskom razdoblju mjerenja. U proljeće, koncentracije kadmija bile su u odnosu na one u frakciji lebdećih čestica PM_{10} 86,2% u frakciji lebdećih čestica $PM_{2,5}$ te 66,4% u frakciji lebdećih čestica PM_1. U usporedbi s kadmijem u frakciji lebdećih čestica PM_{10} 72,4% nađeno je u frakciji lebdećih čestica $PM_{2,5}$, a 55,1% u frakciji lebdećih čestica PM_1 za vrijeme ljetnog razdoblja mjerenja. U jesen, u usporedbi s koncentracijama kadmija u frakciji lebdećih čestica PM_{10} 92,3% nađeno je u frakciji lebdećih čestica $PM_{2,5}$ te 63,4% u frakciji lebdećih čestica PM_1.

Epidemiološke studije pokazale su da veličina čestica i kemijski sastav igraju najveću ulogu u relativnoj toksičnosti čestica. Kadmij i njegovi spojevi su kancerogeni.

Dobiveni rezultati ovih istraživanja pokazuju veliki postotak kadmija u sitnim česticama u svim sezonama. Najveći postotak kadmija u frakciji lebdećih čestica $PM_{2,5}$ u usporedbi s koncentracijama u frakciji lebdećih čestica PM_{10}, nađen je u jesen, a kod frakcije lebdećih čestica PM_1 u proljeće.

[1] Institut za medicinska istraživanja i medicinu rada, Ksaverska c. 2, Zagreb, Hrvatska

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Vađić, V.[1], Žužul, S.[1], Rinkovec, J.[1] and Pehnec, G.[1]

SEASONAL DIFFERENCES OF CADMIUM CONCENTRATIONS IN FINE PARTICLES IN ZAGREB AIR

Keywords: *PM_{10}, $PM_{2.5}$, PM_1 particles, toxicity of particles*

The International Agency for Research on Cancer (IARC) has classified cadmium and cadmium compounds as Group 1 human carcinogens, having concluded that there was sufficient evidence that cadmium can produce lung cancer in humans and animals exposed by inhalation.
This paper presents the first results and seasonal differences of cadmium monitoring in fine particulate matter with aerodynamic diameter of less than 10 μm, 2.5 μm or 1 μm (PM_{10}, $PM_{2.5}$ or PM_1). Its levels were monitored at one measuring site in the northern part of Zagreb during 2011.
Particulate matter was collected from approximately 50 m^3 of ambient air on quartz filters every 24 hours. Samples were digested with nitric acid and microwaves while cadmium content was determined with inductively coupled plasma mass spectrometry (ICP-MS).
Selected isotope for the ICP-MS analysis was 111 for cadmium. Samples were analysed with addition of rhodium as internal standard. Limit of detection was 0.022 ng m^{-3}.
During the monitoring period, 334 samples of each particle size were collected. The highest cadmium concentrations were measured in the winter and maximum daily values were 1.79 ng m^{-3} for PM_{10}, 1.42 ng m^{-3} for $PM_{2.5}$ and 0.81 ng m^{-3} for PM_1 particles.
Compared to cadmium in PM_{10} particles 85.0% was found in $PM_{2.5}$ and 49.3% in PM_1 particles, during winter period. In spring, compared to cadmium in PM_{10} particles 86.2% was found in $PM_{2.5}$ and 66.4% in PM_1 particles. Compared to cadmium in PM_{10} particles 72.4% was found in $PM_{2.5}$ and 55.1% in PM_1 particles, during summer period. In autumn, compared to cadmium in PM_{10} particles 92.3% was found in $PM_{2.5}$ and 63.4% in PM_1 particles.
Epidemiological studies have shown that particle size and chemical composition play a major role in the relative toxicity of particles. Cadmium and cadmium compounds are human carcinogens. The obtained data have shown a high percentage of cadmium in small particles in all seasons. The highest percentage of cadmium in $PM_{2.5}$ compared to cadmium in PM_{10} particles was found in autumn while for PM_1 particles was found in spring.

[1] Institute for Medical Research and Occupational Health, Ksaverska c. 2, 10000 Zagreb, Croatia. vvadjic@imi.hr

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Pehnec, G.[1], Bešlić, I.[1] i Vađić, V.[1]

KONCENTRACIJE OZONA U ZRAKU ZAGREBA U RAZDOBLJU 2003. – 2012.

Ključne riječi: *trend, urbano područje, uredba*

Ozon (O_3) je onečišćenje koje u nižim slojevima atmosfere nastaje djelovanjem sunčeva zračenja na dušikov dioksid te uz lebdeće čestice najviše utječe na ljudsko zdravlje. Prema podacima Europske agencije za zaštitu okoliša više od 50 % stanovništva europskih gradova izloženo je povišenim razinama ozona. U proteklih petnaestak godina u Hrvatskoj su se tri puta mijenjali zakonski propisi vezani uz kvalitetu zraka. Do 2005. godine rezultati mjerenja ozona interpretirali su se prema Uredbi o preporučenim i graničnim vrijednostima kakvoće zraka (NN 101/1996) uzimajući u obzir vrijednost 98. percentila za vrijeme usrednjavanja 1 sat i 24 sata. Nakon što je 2005. godine donesena Uredba o ozonu u zraku (NN 133/2005) kategorizacija se provodila na temelju 24-satnih prosjeka i najviših dnevnih osmosatnih prosjeka. Prema novoj Uredbi o razinama onečišćujućih tvari u zraku (NN 117/2012), a uslijed usklađivanja s propisima Europske Unije, za ozon je propisana ciljna vrijednost za najviši dnevni osmosatni prosjek (120 μg/m^3) koja ne smije biti prekoračena više od 25 puta tijekom kalendarske godine te dugoročni cilj od 120 μg/m^3 za najviši dnevni osmosatni prosjek. Koncentracije ozona mjere se u Zagrebu kontinuirano od 1999. godine u sklopu lokalne mreže za praćenje kakvoće zraka. U ovom radu prikazani su rezultati mjerenja ozona u posljednjih deset godina (2003.-2012.) na mjernom mjestu smještenom u sjevernom dijelu grada. Mjerenja su provedena automatskim uređajem na temelju UV apsorpcije pri 254 nm te su izračunati satni, 8-satni i 24-satni prosjeci koncentracija. Proučavan je trend koncentracija ozona u proteklih deset godina uzimajući u obzir sve navedene pokazatelje iz sadašnje kao i iz prethodnih uredbi. U navedenom razdoblju srednje godišnje koncentracije ozona kretale su se između 29,6 μg/m^3 (2003.) i 43,3 μg/m^3 (2006. i 2012.). Najviši 24-satni prosjek izmjeren je 2005. godine, te je iznosio 190,2 μg/m^3. U istoj godini izmjeren je i najviši 8-satni prosjek (258,7 μg/m^3) te najviša satna vrijednost (296,3 μg/m^3). Ciljna vrijednost od 120 μg/m^3 bila je najčešće prekoračena tijekom 2005. (34 dana) i 2012. godine (19 dana), a do prekoračenja je najčešće dolazilo tijekom mjeseca srpnja. Premda postoje značajne razlike u razinama ozona izmjerenih tijekom pojedinih godina bilježi se slab rastući trend kako srednjih godišnjih vrijednosti tako i broja dana s povišenim koncentracijama ozona.

[1] Institut za medicinska istraživanja i medicinu rada, Ksaverska cesta 2, Zagreb

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Pehnec, G.[1], Bešlić, I.[1] and Vađić, V.[1]

OZONE CONCENTRATIONS IN THE AIR OF ZAGREB IN THE PERIOD 2003 – 2012

Keywords: *regulation, trend, urban area*

In the lower levels of the atmosphere, ozone (O_3) is formed through the impact of solar radiation on nitrogen dioxide. Particulate matter and ozone are pollutants that significantly affect human health. According to the European Environmental Agency, up to 50 % of the European urban population is exposed to elevated levels of ozone. Over the last fifteen years, the Croatian legislation regarding air pollution has changed three times. Before 2005, the results of ozone measurements were interpreted according to the Ordinance on Recommended and Limit Values of Air Pollutants (OG 101/1996) taking into account 98th percentile values for averaging times of 1 hour and 24 hours. In 2005, the Regulation of Ozone in the Air (OG 133/2005) was adopted and categorization was carried out with regard to 24-hour averages and maximum daily eight-hour averages. According to the new Regulation on Levels of Pollutants in the Air (OG 177/2012), and due to the harmonization with EU legislation, a target value has been established for the maximum ozone daily eight-hour average (120 μg/m^3), which must not be exceeded for more than 25 times annually. Long-term objective for maximum eight-hour average is 120 μg/m^3. Ozone concentrations have continuously been measured in Zagreb since 1999 within the local network for air quality monitoring. This paper presents the results of ozone measurements at a measuring site located in the northern part of the city during the last ten years (2003-2012). Measurements were carried out by an automatic device based on UV absorption at 254 nm. One-hour, eight-hour and 24-hour averages of ozone concentrations were calculated. The trend of ozone concentrations over the period was analysed taking into account all of the indicators from present and previous regulations. In the mentioned period, annual ozone concentrations were between 29.6 μg/m^3 (2003) and 43.3 μg/m^3 (2006 and 2012). The maximum 24-hour average was measured in 2005 and amounted to 190.2 μg/m^3. In that same year, maximum 8-hour and maximum hourly values were also recorded (258.7 μg/m^3 and 296.3 μg/m^3, respectively). The target value of 120 μg/m^3 was exceeded most often during 2005 (over 34 days) and during 2012 (over 19 days), whereas most of the exceeding occurred during July. Although there are significant differences among annual ozone levels, there is a weak increasing trend of both annual averages and number of days with elevated ozone concentrations.

[1] Institute for Medical Research and Occupational Health, Ksaverska c. 2, Zagreb

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Jakovljević, I.[1], Pehnec, G.[1], Vađić, V.[1] i Bešlić, I.[1]

MASENE KONCENTRACIJE I KARCINOGENA AKTIVNOST POLICIKLIČKIH AROMATSKIH UGLJIKOVODIKA U ZRAKU

Ključne riječi*: Benzo(a)piren, BaP_{eq}, karcinogen, HPLC*

Policiklički aromatski ugljikovodici (PAU) u velikoj su mjeri rasprostranjeni u atmosferi i jedni su od prvih onečišćujućih tvari koji su definirani kao karcinogeni. Produkt su nepotpunog izgaranja organskih materijala. Istraživanja štetnosti PAU na zdravlje ljudi započela su još u 18. stoljeću kada se uvidjelo da dimnjačari i radnici zaposleni u preradi parafina i katrana kamenog ugljena češće obolijevaju od raka kože. Zbog svojih karcinogenih i mutagenih svojstava predstavljaju velik rizik na ljudsko zdravlje, a mnogi od njih svrstani su u 2A i 2B grupu karcinogenosti po IARC (Međunarodna agencija za istraživanje raka). Karcinogenost PAU raste s porastom molarne mase. U atmosferi uglavnom su vezani na lebdeće čestice. U organizam čovjeka dospijevaju putem prehrambenih navika i respiratornim putem.

U ovom radu mjerene su masene koncentracije benzo(a)pirena (BaP), dibenzo(ah)antracena (DahA), benzo(a)antracena (BaA), benzo(b)fluorantena (BbF), benzo(k)fluorantena (BkF), indeno(1,2,3-cd) pirena (IP), fluorantena (Flu), pirena (Pyr), benzo(ghi)perilena (BghiP), krizena (Chry) u PM_{10} frakciji lebdećih čestica, na dvije različite lokacije, u urbanom području opterećeno industrijom (A) te u urbanom području opterećeno prometom (B). Uzorci su sakupljani na filtar papire od kvarcnih vlakana tijekom 24 h u razdoblju od siječnja do prosinca 2012 godine. Masene koncentracije PAU određene su kromatografijom visoke djelotvornosti (HPLC) s fluorescentnim detektorom uz promjenjive valne duljine ekscitacije i emisije.

Cilj istraživanja je na temelju izmjerenih masenih koncentracija PAU u zraku te pomoću ekvivalentnih faktora toksičnosti odrediti moguću karcinogenu aktivnost mjerenih PAU.

Rezultati pokazuju da su izmjerene masene koncentracije PAU na lokaciji A i B slijede niz: BghiP >Chry> BbF> IP> BaP> BaA> Flu> BkF> Pyr> DahA.

Sumarne koncentracije izmjerenih PAU izražene kao ekvivalentni BaP (BaP_{eq}) na lokaciji A iznosi 2,191 ng/m^3, a na lokaciji B 1,476 ng/m^3.

Relativni karcinogeni potencijal izmjerenih policikličkih aromatskih ugljikovodika na obje lokacije je približno isti i iznosi 1,43 za urbano područje opterećeno industrijom, i 1,45 za urbano područje opterećeno prometom.

[1] Institut za medicinska istraživanja i medicinu rada, Ksaverska cesta 2, Zagreb, HRVATSKA

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Jakovljević, I.[1], Pehnec, G.[1], Vađić, V.[1] and Bešlić, I.[1]

MASS CONCENTRATIONS AND CARCINOGENIC ACTIVITY OF POLYCYCLIC AROMATIC HYDROCARBONS IN THE AIR

Keywords: *Benzo(a)pyrene, carcinogen, HPLC, BaP_{eq}*

PAHs are widely distributed in the atmosphere and were among the first pollutants identified as potential carcinogens. They are produced mainly by incomplete organic material combustion reactions. Research on the harmful effects of PAHs on human health began in the 18th century, when road sweepers and paraffin and coal tar factory workers began suffering from an increased number of skin cancer cases. Their carcinogenic and mutagenic properties represent a high risk to human health. Many PAHs have been classified as 2A or 2B group carcinogens by the International Agency for Research on Cancer (IARC). Any PAH with a larger molecular weight is carcinogenic. They are mostly bound in the atmosphere to particulate matter and they enter the human body through food and the respiratory route.

In this study, we measured the mass concentrations of Benzo(a)pyrene (BaP), dibenzo(ah)anthracene (DahA), benzo(a)anthracene (BaA), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), indeno(1,2,3-cd)pyren (IP), fluoranthene (Flu), pyrene (Pyr), benzo(ghi)perylene (BghiP), and chrysene (Chry) in PM_{10} particulate fraction, at two different locations, at an urban area whit industry (Location A), and at an urban area near an important traffic way (Location B).

Particulate fraction PM_{10} samples were collected on quartz filters during 24 h from January to December 2012. Mass PAH concentrations were determined by high performance liquid chromatography (HPLC) using fluorescence detection with changeable excitation and emission wavelength.

The aim of this study was to determine the potential carcinogenic activity of measured PAHs using toxicity equivalence factors and measured mass PAH concentrations in the air. The results showed that the measured mass PAH concentration at location A and B demonstrated the following sequence: BghiP> Chry> BBF> IP> BaP> BAA> Flu> bkf> Pyr> DahA.

The sum of PAH concentrations expressed as equivalent BaP (BaP_{eq}) at location A was 2.191 ng/m^3 and 1.476 ng/m^3 at location B.

The relative carcinogenic potential of polycyclic aromatic hydrocarbons measured at both locations was approximately the same; 1.43 for urban areas with industry and 1.45 for urban areas near important traffic ways.

[1] Institute for Medical Research and Occupational Health, Ksaverska cesta 2, Zagreb, CROATIA

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Čačković, M.[1], Vađić, V.[1], Šega, K.[1] i Bešlić, I.[1]

TREND MASENIH KONCENTRACIJA KISELIH KOMPONENTI U PM_{10} FRAKCIJI LEBDEĆIH ČESTICA U ZRAKU ZAGREBA

Ključne riječi: *onečišćenje zraka, lebdeće čestice, kloridi, nitrati, sulfati*

Mjerenje frakcija čestica PM_{10} kao i njihovog sastava uobičajeno je u većini razvijenih zemalja svijeta. Rezultati mnogih istraživanja pokazuju da su dominantni sastojci lebdećih čestica upravo sulfati, nitrati, kloridi, u vodi topljivi organski ugljik i dr.

Početkom 1999. godine u nas započelo se s kontinuiranim mjerenjima razina masenih koncentracija lebdećih čestica frakcije PM_{10}, a time i sadržaja kiselih komponenti (klorida, nitrata i sulfata) u njima. U radu su prikazani rezultati mjerenja sadržaja u vodi topljivih klorida, nitrata i sulfata u frakciji čestica PM_{10} u zraku Zagreba za razdoblje 1999 – 2012. godine.

Istraživanja su provedena u Jedinici za higijenu okoline Instituta za medicinska istraživanja i medicinu rada koja je akreditirana i ustrojena prema zahtjevima norme HRN EN ISO/IEC 17025:2007. Uzorci čestica sakupljani su na mjernoj postaji smještenoj u sjevernom dijelu Zagreba tijekom 24-satnih razdoblja sukladno normi HRN EN 12341:2006 (EN 12341:1998).

Masena koncentracija čestica određena je gravimetrijski. Sadržaj u vodi topljivih klorida, nitrata i sulfata određen je ionskom kromatografijom na uređaju DIONEX-DX 120 nakon ultrazvučne ekstrakcije aniona iz čestica i odvajanja netopljivog dijela centrifugiranjem.

Iz rezultata mjerenja masenih koncentracija klorida, nitrata i sulfata u PM_{10} frakciji čestica za razdoblje mjerenja od 1999. do 2012. je vidljivo da su tijekom promatranog razdoblja mjerenja srednje godišnje vrijednosti masenih koncentracija klorida, nitrata i sulfata u PM_{10} frakciji čestica bile u rasponu od 0,12 $\mu g\ m^{-3}$ do 1,00 $\mu g\ m^{-3}$ za kloride, od 1,99 $\mu g\ m^{-3}$ do 9,28 $\mu g\ m^{-3}$ za nitrate i od 3,15 $\mu g\ m^{-3}$ do 11,28 $\mu g\ m^{-3}$ za sulfate. Najviša srednja godišnja vrijednost za sva tri aniona bila je 2003. godine. Razine masenih koncentracija klorida, nitrata i sulfata u PM_{10} frakciji čestica tijekom promatranog razdoblja mjerenja pokazuju padajući trend, ali trend nije statistički značajan.

Primjenom nove zakonske regulative, Uredbe o razinama onečišćujućih tvari u zraku (N.N. 117/12), ocjenu kvalitete zraka s obzirom na mjerena onečišćenja (kisele komponente) nije moguće dati, jer Uredba ne propisuje granične vrijednosti za mjerena onečišćenja.

[1] Institut za medicinska istraživanja i medicinu rada, Zagreb, Ksaverska c. 2, HRVATSKA

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Čačković, M.,[1] Vađić, V., Šega, K. and Bešlić, I.

TREND OF MASS CONCENTRATIONS OF MAJOR ACIDIC SPECIES IN PM_{10} PARTICLE FRACTION IN ZAGREB AIR

Keywords: *air pollution, airborne particle, chlorides, nitrates, sulphates*

Many investigations have shown that, sulphates, nitrates, chlorides and water-soluble organic carbon are the dominant chemical species of water-soluble matter in aerosol particles.
This paper presents the results of continuously measurements of major acidic anions chlorides, nitrates, and sulphates in PM_{10} particle fractions in Zagreb air for the period 1999 – 2012.
Investigations were performed at Institute for Medical Research and Occupational Health, Environmental Hygiene Unit, which is competent according to HRN EN ISO/IEC 17025:2007 standard.
Daily samples of PM_{10} particle fraction were collected in the northern residential part of Zagreb, according to standard HRN EN 12341:2006 (EN 12341:1998). Mass concentrations of PM_{10} particle fraction were determined by gravimetry. Acidic anions chloride, nitrate and sulphate were analysed using ion chromatography.
Results show that the annual average mass concentrations of measured pollutants varied from 0.12 $\mu g\ m^{-3}$ to 1.00 $\mu g\ m^{-3}$ for chlorides, from 1.99 $\mu g\ m^{-3}$ to 9.28 $\mu g\ m^{-3}$ for nitrates, and from 3.15 $\mu g\ m^{-3}$ to 11.28 $\mu g\ m^{-3}$ for sulphates, respectively. The highest values were obtained in 2003 for all components. The mass concentration of measured pollutants show decreasing trend for the investigated period, but the trend was not significant.
*The air quality in Zagreb with respect to acidic components in PM_{10} particle fraction in the period 1999 – 2012, could not be given with regard to the new **Regulation on levels of pollutants in ambient air** (OG No. 117/12), where the limit values were not adopted.*

[1] Institute for Medical Research and Occupational Health, Zagreb, Ksaverska c. 2, Croatia,

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Avirović, G.[1], Živković, N.[1], Horak, R.[1] i Puškarić, I.[1]

PROMJENE U PRAĆENJU KVALITETE ZRAKA KUTINSKOG PODRUČJA TEMELJEM NOVIH PROPISA

Ključne riječi: *granična vrijednost, mjere nadzora emisije, mjerenja posebne namjene, plinoviti fluoridi*

Proizvodna postrojenja pri proizvodnji mineralnih gnojiva u Petrokemiji d.d. u Kutini su, točkasti izvori emisije specifičnih plinovitih i krutih onečišćujućih tvari u zraka i to: amonijaka (NH_3), dušikovih oksida (NO_x), sumporova dioksida (SO_2), plinovitih fluorida (kao HF), ugljikova monoksida (CO), čestica sirovina i gotovih proizvoda. Sukladno važećim propisima u okviru procesa dobivanja uporabne dozvole Petrokemija je još 1976.g. uspostavila mjerenja kvalitete zraka posebne namjene koja su postala sastavni dio lokalne mreže za praćenje kvalitete zraka. Prihvaćeni program mjerenja provodi akreditirani Laboratorij za zaštitu okoliša, Petrokemije d.d., a obuhvaća mjerenja navedenih onečišćujućih tvari. Temeljem rezultata mjerenja provodila se kategorizacija zraka i utvrđivane mjere zaštite i poboljšanja kvalitete zraka. Ostvareni su višegodišnji padajući trendovi koncentracija onečišćujućih tvari i poboljšanja u kategorizaciji kvalitete zraka kutinskog područja primjenom tada važećih propisa. Novi propisi u području praćenja onečišćujućih tvari u zraku koji su na snazi od 1. siječnja 2013.g. otvaraju mogućnost odnosno potrebu promjene uspostavljenog programa praćenja kvalitete zraka kako u pogledu broja mjernih postaja tako i u pogledu onečišćujućih tvari koje treba pratiti. Prikazan je prijedlog mjerenja koji je sastavni dio zahtjeva u postupku utvrđivanja objedinjenih uvjeta zaštite okoliša ("okolišna dozvola") Petrokemije d.d. Sukladno novim propisima Petrokemija planira izostaviti mjerenje razine plinovitih fluorida u zraku, iako se radi o specifičnoj onečišćujućoj tvari iz njenih proizvodnih procesa, jer za isto ne postoji granična vrijednost (GV) prema kojoj bi se utvrdila kategorizacija kvalitete zraka. U radu je prikazan pregled graničnih vrijednosti za plinovite fluoride drugih država prema dostupnoj literaturi. Razmotrena je primjena propisane odredbe da se za tvari za koje nisu propisane GV u upravljanju kvalitetom zraka koriste mjere nadzora emisije tih tvari iz nepokretnih izvora.

[1] Petrokemija d.d. tvornica gnojiva, Aleja Vukovar 4, 4430 Kutina, HRVATSKA

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CHANGES IN AIR QUALITY MONITORING IN THE KUTINA AREA UNDER NEW REGULATIONS

Keywords: *limit value, measures of emissions control, measurements for special purposes, gaseous fluorides*

In the production of mineral fertilizers in Petrokemija, Plc. in Kutina, production plants are point sources of emissions of specific gaseous and particulate pollutants into the air, such as: ammonia (NH_3), nitrogen oxide (NOx), sulphur dioxide (SO_2), gaseous fluoride (as HF), carbon monoxide (CO), particulate matter of raw materials and finished products. In accordance with the regulations in force in the process of obtaining the operating permit, as early as 1976 Petrokemija introduced a special purpose air quality measurements, became an integral part of the local network of monitoring air quality. The accepted measurement program, conducted by an accredited Laboratory for Environmental Protection of Petrokemija, Plc., includes measurements of these pollutants. Based on the results of the measurements, the categorization of air was carried out and measures to protect and improve air quality were established. Long-term downward trends were achieved in concentrations of pollutants and improvement of the air quality category of the Kutina area using the then current regulations. New regulations in the monitoring of air pollutants that are effective as of January 1, 2013, have opened the possibility and the need to change the established air quality monitoring program both in terms of number of stations and in terms of pollutants to be monitored. This paper shows the proposed measurement that is an integral part of the application in the process of determining integrated environmental protection requirements ("environmental permit") of the Company. In accordance with the new regulations, Petrokemija is planning to leave out the measurement of gaseous fluoride levels in the air, although it is a specific pollutant from the Company manufacturing processes, because for gaseous fluorides there is no limit value (LV) by which to determine the air quality category. This paper presents a review of the limit values for gaseous fluorides of other countries according to the available sources. The paper also considers the application of the laid down provision that in the air quality management, monitoring of the substances for which no GV is prescribed is done by monitoring these emissions from stationary sources.

[1] Petrokemija, Plc. Fertilizer Company, Aleja Vukovar 4, 44320 Kutina, CROATIA

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SADRŽAJ GLAVNIH IONA U OBORINI I LEBDEĆIM ČESTICAMA U ZRAKU U SJEVERNOJ HRVATSKOJ

Ključne riječi*: glavni ioni, oborina, $PM_{2,5}$*

Kvaliteta zraka na nekom području može se pratiti preko različitih medija i komponenti. Sadržaj glavnih iona u oborini pokazuje opterećenje okoliša mokrim taloženjem onečišćenja iz zraka i odraz je prvenstveno utjecaja udaljenih izvora. Lebdeće čestice u zraku dio su suhog taloženja i pokazuju pretežit utjecaj lokalnih izvora onečišćenja zraka.

Cilj ovog rada je usporedba kemijskog sastava oborine i lebdećih čestica u zraku.

Na promatranoj pozadinskoj postaji u sjevernoj Hrvatskoj tijekom 2012. godine sakupljani su bulk dnevni uzorci oborine i tjedni uzorci $PM_{2,5}$ frakcije lebdećih čestica u zraku. Čestice su sakupljane LVS uzorkivačem na teflonske filtre veličine pora 1 μm, količina oborine mjerena je ombrografom, masena koncentracija čestica određena je gravimetrijski, a sadržaj u vodi topljivih iona (klorida, sulfata, nitrata, amonija, natrija, kalija, kalcija i magnezija) određen je metodom ionske kromatografije.

U 2012. godini analizirano je 99 % ukupne količine oborine i 87 % uzoraka lebdećih čestica u zraku. Kod 14 uzoraka protok je bio premalen. To se dešavalo u hladnom dijelu godine (I–III i X–XII mjesec), uz temperaturu zraka nižu od 5 °C i relativnu vlažnost zraka iznad 70 %. Masena koncentracija $PM_{2,5}$ bila je velika (18–50 μg/m ^{3}). Odnos masene koncentracije čestica i uzorkovanog volumena zraka pokazuje da u slučajevima masene koncentracije veće od 20-tak μgm^{-3} dolazi do prezasićenosti filtra, pa bi u zimskom periodu trebalo vrijeme uzorkovanja skratiti na dva do tri dana.

Paralelni uzorci oborine i čestica za usporedbu kemijskog sastava odabrani su tako da je za svaki dan s oborinom promatran uzorak $PM_{2,5}$ čije su koncentracije komponenata za taj dan izračunate iz odgovarajućeg tjednog uzorka čestica.

Odnos glavnih iona u oborini je $K^+ > Ca^{2+} > Cl^- > NH_4^+ = SO_4^{2-} > NO_3^- > Na^+ > Mg^{2+}$, a u $PM_{2,5}$ $NH_4^+ > SO_4^{2-} > K^+ > NO_3^- > Na^+ > Ca^{2+} > Cl^- > Mg^{2+}$. U dostupnoj literaturi navedeno je da se u $PM_{2,5}$ frakciji lebdećih čestica u zraku nalazi najviše nitrata i sulfata, dok na ovoj lokaciji prevladavaju amonij ioni, kojih u prosjeku ima 20 % više od sulfata. Glavni ioni čine svega 10–24 % ukupne mase čestica $PM_{2,5}$ a ostalo su vjerojatno organski i drugi spojevi. Omjer amonij iona i sulfata u $PM_{2,5}$ je veći u hladnom dijelu godine, dok je omjer amonij iona i nitrata, te sulfata i nitrata veći u toplom dijelu godine. U oborini je najveća korelacija između iona natrija i klorida, te nitrata i amonij iona, a u česticama između amonij iona i sulfata, te kalcija i magnezija.

U oborini niti jedna promatrana komponenta nema izražen godišnji hod, ali se pojedinačne veće koncentracije svih glavnih iona, osim kalija, javljaju u proljeće i jesen, a kalija ljeti. U $PM_{2,5}$ koncentracije amonij iona, sulfata, nitrata pa i kalija su veće u hladnom dijelu godine (naročito izraženo kod nitrata), a povećane koncentracije kalcija i magnezija javljaju se češće u toplom dijelu godine.

Rezultati istraživanja glavnih iona u oborini i $PM_{2,5}$ frakciji lebdećih čestica u zraku pokazuju da je pozadinska postaja u sjevernoj Hrvatskoj u relativno čistom području, pod utjecajem lokalnog poljoprivrednog okruženja.

[1] Državni hidrometeorološki zavod, Grič 3, 10000 Zagreb, Hrvatska

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Đuričić, V.[1], Škevin-Sović, J.[1], Igrec, I.[1] i Kosanović, C.[1]

MAJOR IONS CONTENT IN PRECIPITATION AND AIRBORNE PARTICLES IN NORTHERN CROATIA

Keywords: *major ions, precipitation, $PM_{2,5}$*

Air quality of certain area can be monitored by different media and compounds. Major ions in precipitation show loading of environment by wet deposition, mainly from distant pollution sources. Airborne particles represent dry deposition and show prevailing influence of local pollution sources. The aim of this paper is to compare chemical composition of precipitation and airborne particles.
At one background station in northern Croatia bulk daily precipitation samples and weekly $PM_{2,5}$ samples were collected during year 2012. For airborne particles LVS sampler with teflon filters (1 μm pores) was used, while precipitation was sampled by bulk sampler. Precipitation amount was measured by ombrograph, $PM_{2,5}$ mass concentration was determined by gravimetry and water soluble ions (chloride, sulphate, nitrate, ammonia, potassium, sodium, calcium, magnesium) were analysed using ion chromatography.
In 2012 99 % of total precipitation amount and 87 % of airborne particle samples were analysed. For 14 airborne particle samples the air flow was too low. This happened in the cold part of the year (Jan-March and Oct-Dec) with the air temperature bellow 5 °C and relative humidity over 70 %. $PM_{2,5}$ mass concentration was high (18–50 μgm^{-3}). It seems that mass concentration over 20 μgm^{-3} causes filter overloading, and in wintertime sampling period should be reduced from seven to two or three days.
Parallel precipitation and airborne particle samples were picked up in a way that for every day with precipitation major ions concentrations in airborne particles were calculated from related weekly particle sample.
The order of major ions concentrations in precipitation is $K^+ > Ca^{2+} > Cl^- > NH_4^+ = SO_4^{2-} > NO_3^- > Na^+ > Mg^{2+}$, while in $PM_{2,5}$ is $NH_4^+ > SO_4^{2-} > K^+ > NO_3^- > Na^+ > Ca^{2+} > Cl^- > Mg^{2+}$. As can be found in the literature, $PM_{2,5}$ particles consist mainly from nitrates and sulphates. At considered location in northern Croatia ammonia prevails, with 20 % higher concentration that those of sulphate. Major ions contribute with only 10–24 % to total $PM_{2,5}$ mass, and the rest are probably organic and other compounds. Ammonia to sulphate ratio in $PM_{2,5}$ is higher in the cold part of the year, while ammonia to nitrate and sulphate to nitrate ratios are higher in the warm part of the year. Correlation is the highest for sodium – chloride and nitrate – ammonia in precipitation, but in airborne particles for ammonia – sulphate and calcium – magnesium.
Annual course is not visible for any of compounds in precipitation, but higher individual concentrations of all major ions except potassium occur during spring and autumn, while of potassium in summer. In $PM_{2,5}$ ammonia, sulphate, nitrate and potassium concentrations are higher in wintertime (especially visible for nitrates), and higher concentrations of calcium and magnesium occur in the warm part of the year.
Results show that background station in northern Croatia considered in this paper is situated in relatively clean area, influenced mainly by sources from local agricultural surrounding.

[1] Meteorological and Hydrological Service, Grič 3, 10000 Zagreb, Croatia

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Rinkovec, J.[1], Žužul, S.[1], Pehnec, G.[1] i Vađić, V.[1]

ODREĐIVANJE NISKIH KONCENTRACIJA PLATINE, PALADIJA I RODIJA U ZRAKU

Ključne riječi: *ICP MS, nitratna kiselina, klorovodična kiselina, PM10*

Platina (Pt), paladij (Pd) i rodij (Rh) ubrajaju se u platinsku skupinu elemenata, uz osmij (Os), iridij (Ir) i rutenij (Ru), i prijelazni su metali periodnog sustava elemenata. Kemijski su vrlo inertni, a na zraku potpuno stabilni. Smatraju se strateškim metalima zbog svoje specijalizirane primjene u automobilskoj, poljoprivrednoj, kemijskoj, naftnoj, stomatološkoj, medicinskoj i zrakoplovnoj industriji. Zbog sve veće primjene u industriji i važne uloge spomenutih metala u izradi automobilskih katalitičkih konvertera, tijekom godina se sve više provode kvantitativna mjerenja platine, paladija i rodija u istraživanjima onečišćenja okoliša, posebno onih vezanih uz promet. Nestabilnost razrijeđenih vodenih otopina platine, paladija i rodija predstavlja problem kod analize niskih koncentracija tih metala u okolišu.

U Republici Hrvatskoj nema podataka o mjerenju navedenih metala u okolišu ni njihovog eventualnog utjecaja na vegetaciju, tlo, vodu, zrak pa tako i na ljude. Cilj istraživanja je ispitati stabilnost standardnih otopina niskih koncentracija platine, paladija i rodija kako bi se omogućilo kvantitativno određivanje tih elemenata u uzorcima lebdećih čestica u zraku. Stabilnost razrijeđenih standardnih otopina platine, paladija i rodija mjerena je u otopinama koje su sadržavale različite omjere nitratne i klorovodične kiseline (1 – 10%). Analiza je provedena masenom spektrometrijom induktivno spregnute plazme (ICP MS). Istraživanja su pokazala da standardne otopine koje ne sadrže klorovodičnu kiselinu nakon deset dana pokazuju značajno više vrijednosti platine, paladija i rodija. Ista ispitivanja provedena su i na slijepim probama (neizloženi filter papir) na koje je dodana poznata koncentracija metala te je utvrđen analitički povrat tih elemenata. Prva mjerenja platine, paladija i rodija u uzorcima lebdećih čestica aerodinamičkog promjera manjeg od 10μm (PM10) pokazala su da je, iako se radi o niskim vrijednostima, moguće odrediti koncentracije (pg/m^3) tih elemenata u zraku.

[1] Institut za medicinska istraživanja i medicinu rada, Ksaverska cesta 2, 10000 Zagreb, Hrvatska

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Rinkovec, J.[1], Žužul, S.[1], Pehnec, G.[1] and Vađić, V.[1]

DETERMINATION OF LOW CONCENTRATIONS OF PLATINUM, PALLADIUM, AND RHODIUM IN THE AIR

Keywords: *ICP-MS, nitric acid, hydrochloric acid, PM10*

Platinum (Pt), palladium (Pd), and rhodium (Rh) are among the platinum group elements (PGE) that contain osmium (Os), iridium (Ir), and ruthenium (Ru). They belong to transition metals. They are chemically very inert and completely stable in the air. PGEs are regarded as strategic metals because of their specialized applications in the automotive, agriculture, chemical, oil, dental, medical, and aerospace industries.

Due to their increasing application in industry and important role in the development of automotive catalytic converters, quite a few quantitative measurements of platinum, palladium, and rhodium have been done over the years in environmental pollution studies, especially those related to traffic. The instability of the diluted aqueous platinum, palladium and rhodium solutions presents a problem in the analysis of low concentrations of these metals in the environment.

There is no measurement data regarding the concentrations of these metals in the environment or their possible impact on vegetation, soil, water, air, and people in Croatia. The aim of this study was to examine the stability of standard low concentration platinum, palladium, and rhodium solutions to provide a quantitative determination of these elements in samples of particulate matter in the air. The stability of diluted standard platinum, palladium, and rhodium solutions was measured in solutions containing different ratios of nitric and hydrochloric acid (1-10%). The analysis was carried out by inductively coupled plasma mass spectrometry (ICP-MS). Studies have shown that standard solutions that do not contain hydrochloric acid show significantly higher platinum, palladium, and rhodium values after ten days. The same test was carried out on a blank (unexposed) filter paper, to which a known concentration of metals was added to establish their analytical recovery. The first platinum, palladium, and rhodium measurements in samples of particulate matter with an aerodynamic diameter less than 10μm (PM10) have shown that, regardless of the low value, it is possible to determine the concentration (pg/m^3) of these elements in the air

[1] Institute for Medical Research and Occupational Health, Ksaverska cesta 2, 10000 Zagreb, Croatia

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Žero, S.[1], Huremović, J.[1] i Memić, M.[1]

KARAKTERIZACIJA PM_{10} FRAKCIJE ČESTICA ZRAKA U URBANOM I RURALNOM PODRUČJU KANTONA SARAJEVO

Ključne riječi: *PM_{10}, teški metali, Kanton Sarajevo*

Karakterizacija PM10 frakcije čestica zraka u urbanom i ruralnom području Kantona Sarajevo urađena je s ciljem procjene kakvoće zraka na području Kantona Sarajevo i usporedbe dobivenih vrijednosti s nacionalnim, EU pravilnicima i smjernicama Svjetske zdravstvene organizacije. Uzorkovanje je provedeno referentnim sakupljačem MVS6 tijekom proljeća i ljeta 2010. godine na dvjema lokacijama u Kantonu Sarajevo, Prirodno-matematičkom fakultetu u Sarajevu kao urbanoj i Vogošći kao ruralnoj lokaciji. Masene koncentracije PM10 frakcije čestica određene su gravimetrijskom metodom. Ukupni sadržaj metala u PM10 frakciji čestica određen je metodom atomske apsorpcijske spektrometrije (AAS), Cu, Cd, Ni, V, Cr, Co, Mo i Mn – grafitnom tehnikom a Fe, Zn i Pb – plamenom tehnikom i Hg – tehnikom hladnih para. Kontrola kakvoće rezultata provjerena je uporabom certificiranih referentnih materijala. Dnevne masene koncentracije PM10 frakcije čestica zraka odstupale su od granične vrijednosti propisane EU smjernicama za kakvoću zraka u tri slučaja tijekom proljetnog perioda uzorkovanja na urbanoj lokaciji i iznosile su 58,4 μg m^{-3}; 61,1 μg m^{-3} i 63 μg m^{-3}. Ukupni sadržaj metala u PM10 frakciji čestica zraka kretao se u većini slučajeva u dozvoljenim granicama za kakvoću zraka.

[1] Prirodno-matematički fakultet, Univerzitet u Sarajevu, Zmaja od Bosne 33-35, Sarajevo, Bosna i Hercegovina

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Žero, S.[1], Huremović, J.[1] and Memić, M.[1]

CHARACTERIZATION OF PM_{10} FRACTION IN URBAN AND RURAL AIR IN CANTON SARAJEVO

Keywords: *PM_{10}, heavy metals, Canton Sarajevo*

The characterization of PM10 fraction in urban and rural air in Canton Sarajevo was performed to estimate the air quality in Canton Sarajevo and to compare the obtained values with national, EU regulations and World Health Organization guidelines. The sampling was carried out by referent sampler MVS6 during the spring and summer in 2010 at two locations, the Faculty of Science Sarajevo as an urban and Vogošća as a rural location. Mass concentration of PM10 fraction was determined by using the gravimetric method. The total metal contents in PM10 were determined by atomic absorption spectrometry (AAS), Cu, Cd, Ni, V, Cr, Co, Mo and Mn by graphite furnace, Fe, Zn and Pb by flame technique and Hg by cold vapour technique. The accuracy of results was verified by the use of the certified reference materials. Daily mass PM10 concentrations exceeded the limit value prescribed by the EU air quality regulation in three cases (58,4 μg m^{-3}; 61,1 μg m^{-3} and 63 μg m^{-3}) during the spring sampling period at the urban location. The metal contents in PM10 in most of cases were below the limit values.

[1] Faculty of Science, University of Sarajevo, Zmaja od Bosne 33-35, Sarajevo, Bosnia and Herzegovina

Tema 4
Razvoj i provjera mjernih metoda

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Bešlić, I.[1], Šega, K.[1] i Davila, S.[1]

PROSTORNA OVISNOST KOREKCIJSKIH FUNKCIJA AUTOMATSKIH ANALIZATORA LEBDEĆIH ČESTICA

Ključne riječi: *PM10, ortogonalna regresija, prostorna ovisnost*

Referentna metoda za određivanje masenih koncentracija PM10 frakcije lebdećih čestica je gravimetrijska metoda HRN EN 14234. Zbog rasprostranjenosti automatskih analizatora za određivanje masenih koncentracija lebdećih čestica te u skladu s Europskom CAFE direktivom 2008/50/EC, nužno je provesti njihovu ekvivalenciju s referentnim sakupljačima lebdećih čestica. Dosadašnja provedena istraživanja ukazuju na značajnu sezonsku i prostornu ovisnost korekcijskih funkcija dobivenih postupkom ekvivalencije.

Cilj ovog rada je utvrditi godišnje i sezonske korekcijske funkcije za automatski analizator ESM Andersen FH-61 IR na dva mjerna mjesta Državne mreže u svrhu procjene prostorne ovisnosti korekcijskih funkcija.

Sakupljanje i određivanje dnevnih vrijednosti koncentracija PM10 frakcije lebdećih čestica provedeno je mjesec dana tijekom svake sezone na mjernim postajama Državne mreže Zagreb-1 i Sisak-1. Mjerna postaja Zagreb-1 definirana je kao urbana mjerna postaja opterećena prometom dok je mjerna postaja Sisak-1 definirana kao industrijska mjerna postaja. Uzorci su sakupljani na filtrima od kvarcnih vlakana Whatman-QMA. Kao referentni sakupljač korišten je sekvencijalni sakupljač LVS Sven Leckel SEQ. Vaganje i kondicioniranje filtara provedeni su u skladu sa zahtjevima HRN EN 14907.

Pri određivanju stupnja ekvivalencije i korekcijskih funkcija korištena je ortogonalna regresija.

Godišnje i sezonske korekcijske funkcije određene na mjernim mjestima Državne mreže međusobno su usporedive. Međutim, međusobni omjeri raspršenja rezultata i omjeri nagiba korekcijskih funkcija dobiveni na različitim mjernim postajama razlikuju se po sezonama.

Također, korištenje korekcijskih funkcija jedne mjerne postaje na izvorne podatke druge mjerne postaje pri određivanju parametara za ocjenu kvalitete nije primjenjivo.

Različiti dominantni izvori kao i kemijski sastav lebdećih čestica potencijalni su uzrok različitih rezultata ekvivalencije s obzirom na mjerno mjesto. Rezultati istraživanja ukazuju na nužnost provedbe ekvivalencije za svaku sezonu i svako mjerno mjesto.

[1] Institut za medicinska istraživanja i medicinu rada, Ksaverska cesta 2, 10000 Zagreb

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Bešlić, I.[1], Šega, K.[1] and Davila, S.[1]

SITE DEPENDANCE OF CORRECTION FUNCTIONS FOR AUTOMATIC PM ANALYSERS

Keywords: *PM10, orthogonal regression, spatial dependence*

Referent method for PM10 particle fraction mass determination is gravimetric method according to HRN EN 12341 standard. Automatic analysers for PM mass determination are widely used in European countries. Therefore, equivalence testing of automatic analysers with reference samplers is required according to European CAFE Directive 2008/50/EC. Former investigations pointed out significant seasonal and spatial dependence of correction functions obtained by equivalence testing. The aim of this article was to determine the annual and seasonal correction functions for the automatic analyser ESM Andersen FH-61 IR located at two measuring sites of national monitoring network in order to determine the spatial dependence of correction functions.

Sampling and daily values of PM10 concentrations determination were performed for a month in each season at national monitoring network measuring sites Zagreb-1 and Sisak-1. Monitoring site Zagreb-1 is defined as urban traffic, whereas Sisak-1 is defined as industrial site. Daily samples were collected on quartz Whatman-QMA filters, 45 mm in diameter. The referent sampler LVS Sven Leckel SEQ was used for equivalence testing. Weighing and filters conditioning were performed according to HRN EN 14907 standard. Orthogonal regression was used for equivalence and correction function assessment.

Yearly and seasonal correction functions obtained at different monitoring sites are comparable to each other. Meanwhile, dispersion of the results and correction function slopes obtained at different monitoring sites differ by season.

Moreover, correction functions obtained at one monitoring site are not applicable for the other site. Different dominant air pollution sources as well as chemical composition of PM are responsible for different equivalence test results.

The investigation results point out the necessity of seasonal and spatial correction of PM10 concentrations obtained by automatic analysers.

[1] Institute for medical research and occupational health, Ksaverska cesta 2, 10000 Zagreb

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Premec, K.[1]

OSIGURANJE SLJEDIVOSTI MJERENJA PRIZEMNOG OZONA – ZAKONSKA REGULATIVA, PREPORUKE I PRAKSA

Ključne riječi: *mjerna sljedivost, prizemni ozon, umjeravanje, akreditacija*

Za mjerenja kvalitete zraka koja se provode sukladno međunarodnim normama, direktivama i smjernicama, te nacionalnim zakonima i pravilnicima, nužan uvjet za osiguranje i kontrolu kvalitete, te harmonizaciju mjerenja je osiguranje mjerne sljedivosti. Državni hidrometeorološki zavod (DHMZ) osigurava sljedivost mjerenja prizemnog ozona umjeravanjem analizatora ozona u akreditiranom umjernom laboratoriju, čiji su etaloni umjereni u inozemnom akreditiranom umjernom laboratoriju, osiguravajući na taj način neprekinuti lanac usporedbi, koje imaju definirane mjerne nesigurnosti. Povjerenje u navedene mjerne nesigurnosti ostvaruje se kroz akreditirane umjerne i mjerne sposobnosti (CMC) koje akreditacijske službe prikazuje za akreditirane laboratorije na svojim internetskim stranicama. S obzirom na različita tumačenja osiguranja sljedivosti, namjera je ovim radom dati prikaz postojeće legislative, te smjernica i direktiva s naglaskom na najnoviju publikaciju Međunarodne organizacije za akreditaciju laboratorija (ILAC) P10:01/13. Kroz postojeća višegodišnja mjerenja prizemnog ozona u Gradištu i Makarskoj prikazat će se dobra laboratorijska praksa osiguranja sljedivosti u DHMZ-u, a kroz rezultate međulaboratorijskih usporedbenih mjerenja i akreditiranih umjernih sposobnosti ukazati na očekivane mjerne nesigurnosti koje se mogu dobiti različitim pristupima umjeravanju. Kroz analizu zakonodavno definiranih uloga referentnih laboratorija i nositelja državnih etalona ukazat će se na postojeće neusklađenosti, te iskazati potencijalna poboljšanja s obzirom na postojeću mjeriteljsku infrastrukturu u Hrvatskoj.

[1] Državni hidrometeorološki zavod, Zagreb, Grič 3

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Premec, K.[1]

TRACEABILITY ASSURANCE OF SURFACE OZONE MEASUREMENTS – LEGISLATION, RECOMMENDATIONS AND PRACTICE

Keywords: *measurement traceability, surface ozone, calibration, accreditation*

For the air quality measurements carried out in accordance with the international standards, directives and guidelines, and national laws and regulations, a necessary condition for the quality assurance and control, as well as harmonization of measurement, is to assure traceability. Meteorological and Hydrological Service of Croatia (MHSC) provides traceability of the surface ozone measurements by calibration of their ozone analysers in accredited calibration laboratory, whose standards are calibrated in foreign accredited calibration laboratory. In this way, an unbroken chain of comparisons which all have certified measurement uncertainties is assured. Reliability of the stated measurement uncertainties is assured through the accredited calibration and measurement capabilities (CMC), that are available for the accredited calibration laboratories at the web pages of the accreditation services. Due to different interpretations of a traceability assurance, the intention of this paper is to provide, concerning the traceability assurance, a review of existing legislation and the guidelines and directives, with emphasis on the latest publication of the International Laboratory Accreditation Cooperation (ILAC) P10:01/13. Through the existing multiannual measurements of surface ozone in Gradište and Makarska a good laboratory practice of traceability assurance at MHSC will be shown, and the results of interlaboratory comparisons and accredited calibration capabilities will be analysed with the aim to indicate the expected measurement uncertainties achievable through the different calibration methods. Additionally, an overview of the statutory defined roles of the reference laboratories and national standards will be used to indicate some inconsistencies and potential improvements with respect to the existing metrology infrastructure in Croatia.

[1] Meteorological and Hydrological Service of Croatia, Zagreb, Grič 3

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Bešlić, I.[1], Šega, K.[1] i Davila, S.[1]

REZULTATI EKVIVALENCIJE AUTOMATSKOG ANALIZATORA I NEREFERENTNOG SAKUPLJAČA S REFERENTNIM SAKUPLJAČEM NA MJERNOJ POSTAJI ZAGREB-1

Ključne riječi: *PM10, ortogonalna regresija, korekcijske funkcije, proširena mjerna nesigurnost*

Europskom CAFE direktivom 2008/50/EC propisana je nužnost provedbe ekvivalencije automatskih analizatora i ne-referentnih sakupljača s referentnim sakupljačem u svrhu validacije podataka.
Cilj ovog rada je utvrditi godišnje i sezonske korekcijske funkcije za automatski analizator ESM Andersen FH-61 IR i sakupljač lebdećih čestica HVS Digitel DH-80. Pri provedbi ekvivalencije korišten je sekvencijalni referentni sakupljač LVS Sven Leckel SEQ 47/50-CD.
Nadalje, cilj istraživanja je i odrediti utjecaj postupka ekvivalencije na parametre za ocjenu kvalitete zraka.
Sakupljanje i određivanje dnevnih vrijednosti koncentracija PM10 frakcije lebdećih čestica provođeno je mjesec dana tijekom svake sezone na mjernoj postaji Državne mreže Zagreb-1. Uzorci su sakupljani na filtrima od kvarcnih vlakana Whatman-QMA. Vaganje i kondicioniranje filtara provedeni su u skladu sa zahtjevima HRN EN 12341.
Pri određivanju stupnja ekvivalencije i korekcijskih funkcija korištena je ortogonalna regresija.
Ne-referentni uređaji na zadovoljavaju zahtjevu za proširenom mjernom nesigurnosti na razini dnevne granične vrijednosti nižom od 25 % ni za cjelogodišnje razdoblje niti po pojedinoj sezoni.
Korigirani rezultati zadovoljavaju zahtjevu za maksimalnom mjernom nesigurnošću, osim za jesensko razdoblje te korigirani rezultati dobiveni automatskim analizatorom za cjelogodišnje razdoblje.
Korekcijske funkcije za oba ne-referentna uređaja značajno se razlikuju po sezonama. Nadalje, korekcijske funkcije ne-referentnih uređaja međusobno se značajno razlikuju.
Statistički parametri za ocjenu kvalitete zraka određeni na osnovi rezultata ne-referentnog sakupljača značajno su niži od parametara određenih na osnovi korigiranih rezultata.
Rezultati istraživanja ukazuju na nužnost provedbe sezonske korekcije rezultata dobivenih ne-referentnim uređajima za sakupljanje PM10 frakcije lebdećih čestica.

[1] Institut za medicinska istraživanja i medicinu rada, Ksaverska cesta 2, 10000 Zagreb

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Bešlić, I.[1], Šega, K.[1] and Davila, S.[1]

EQUIVALENCE TESTING RESULTS OF AUTOMATIC DEVICES AND NON-REFERENT SAMPLER WITH REFERENT SAMPLER ON ZAGREB-1 MEASURING SITE

Keywords: *PM10, orthogonal regression, correction function, expanded measuring uncertainty*

The equivalence testing of automatic analyser and non-referent samplers for PM10 particle fractions with reference one is required according to European Directive 2008/50/EC.
The aim of this article was to determine the annual and seasonal correction functions for the automatic analyser ESM Andersen FH-61 IR and for the non-referent sampler HVS Digitel DH-80. The referent sampler LVS Sven Leckel SEQ was used for equivalence testing.
Furthermore, aim of this investigation was to determine the influence of equivalence testing on statistical parameters for air quality assessment.
Sampling and daily concentration values determination of PM10 particle fraction was performed monthly in each season during 2012 on Zagreb-1 measuring site. Whatman-QMA quartz filters with 45 mm in diameter were used for PM10 sampling. The weighing and filters conditioning were performed according HRN EN 140907 standard. Orthogonal regression was used for equivalence and correction function assessment.
The non-referent devices didn't satisfy the measuring uncertainty requirements (U < 25 %) for yearly and seasonally data set. Corrected results satisfied measuring uncertainty requirements, except for autumn season data set obtained by both non-reference devices, and for yearly data set obtained by automatic analyser.
The given correction functions were significantly seasonally dependant. Furthermore, the correction functions of non-referent devices significantly differed among each other. The statistical parameters for air quality assessment obtained by non-referent devices are significantly lower than parameters given by referent sampler.
The investigation results point to the necessity of seasonally correcting PM10 results obtained by non-referent devices.

[1] Institute for medical research and occupational health, Ksaverska cesta 2, 10000 Zagreb

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Petrinec, B.[1], Šoštarić, M.[1], Babić, D.[1] i Senčar, J.[1]

OSIGURANJE KVALITETE KOD GAMASPEKTROMETRIJSKIH MJERENJA UZORAKA ZRAKA

Ključne riječi: *Gamaspektrometrijska mjerenja, korekcijski faktori, promjena protoka, ^{7}Be, ^{131}I*

U Jedinici za zaštitu od zračenja Instituta za medicinska istraživanja i medicinu rada od 1962. godine provodi se program praćenja radioaktivnosti životne okoline. U sklopu toga programa provode se gamaspektrometrijska mjerenja uzoraka zraka uzorkovanih na uzorkivaču zraka velikog volumena (High Volume Sampler ASS-500). Određivanje radionuklida u zraku provodi se visokorezolucijskom gamaspektrometrijom, akreditiranom metodom prema zahtjevima norme HRN EN ISO/IEC 17025:2007. Određuju se fisijski (umjetni, antropogeni) radionuklidi kao i oni prirodni, terestrijalnog i kozmogenog porijekla. Kalibracija energije i efikasnosti gamaspektrometra učinjena je uz pomoć kalibracijskih izvora (standarda) Češkog metrološkog instituta koji pokrivaju energiju između 40 i 2500 keV. Doziranje standarda (kapanje) provodi se ravnomjerno po filteru za zrak koji se pakira u geometriju mjerenja korištenoj u kalibraciji efikasnosti gamaspektrometrijskih detektora. Na taj se način izbjegava dodatna korekcija na geometriju mjerenja kao i na atenuaciju. Uzorak zraka se sakuplja propumpavanjem zraka kroz celulozni filter. Kod radionuklida s vremenom poluraspada u danima (npr. ^{131}I, ^{7}Be) potrebno je izračunati korekcijske faktore za koncentracije aktivnosti. Korekcijski faktori radioaktivnog raspada (korekcija) se mogu podijeliti u tri glavne kategorije, a to su: korekcija tijekom uzorkovanja, korekcija između kraja uzorkovanja i početka mjerenja i korekcija tijekom mjerenja. U izračun koncentracije aktivnosti treba uračunati i utjecaj promjene protoka i to posebice kod radionuklida čije je vrijeme poluraspada usporedivo s vremenom uzorkovanja. Promjena protoka u našem sustavu linearno pada s vremenom. Za ^{131}I utjecaj promjene protoka na izračun koncentracije aktivnosti iznosi čak do 30%, dok je isti za ^{7}Be do 5%.

[1] Institut za medicinska istraživanja i medicinu rada, Ksaverska cesta 2, 10001 Zagreb

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Petrinec, B.[1], Šoštarić, M.[1], Babić, D.[1] and Senčar, J.[1]

QUALITY ASSURANCE IN GAMMA-RAY SPECTROMETRY ON AIR SAMPLES

Keywords: *Gammy-ray spectrometry, correction factors, flow-rate change, ^{7}Be, ^{131}I*

In the Radiation protection unit of the Institute for medical research and occupational health, monitoring of environmental radioactivity has been carried out since1962. Part of this programme relies on gamma-ray spectrometry on air samples that are sampled by a high volume air sampler (High Volume Sampler ASS-500). Determination of radionuclides in air is performed by means of high resolution gamma-ray spectrometry, using a method that is accredited according to the HRN EN ISO/IEC 17025:2007 standard. We determine fission (artificial, anthropogenic) radionuclides as well as those of natural (terrestrial and cosmogenic) origin. Energy and efficiency calibrations of the gamma spectrometer has been carried out using calibration sources (standards) by the Czech metrology institute, covering an energy range between 40 and 2500 keV. Droplets of the standard are patterned over an air filter uniformly, and the filter is subsequently prepared for measurements in the same geometry that was used in the efficiency calibration of the spectrometer. Sampling is performed by pumping the air through a cellulose filter. For radionuclides with the half-life of the order of days, it is necessary to calculate correction factors for activity concentration. These factors can be assorted into three main categories, which are: correction for sampling time, correction for time period between the end of a sampling and the beginning of a measurement, and correction for measurement time. When the half-life of a radionuclide is comparable with the sampling time, in calculating the activity concentration, one has to take into account changes in the pumping flow rate during the sampling. In our case, the flow rate decreases with time linearly. For ^{131}I, the flow-rate decrease affects the calculated activity concentration by as much as 30%, whereas this correction for ^{7}Be is 5%.

[1] Institute for Medical Research and Occupational Health, Ksaverska cesta 3, Zagreb, Croatia

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Doko Jelinić, J.[1], Filipović, B.[2], Bertović–Žunec, I.[3], Capak, K.[4] i Bilajac, L.[5]

NANOTEHNOLOGIJA I KVALITETA ZRAKA ZATVORENIH PROSTORA

Ključne riječi: *mikrobiološka kvaliteta zraka, nanotehnologija, titanijev dioksid*

Uvod: Mikrobiološka kvaliteta zraka zatvorenih prostora ovisi o koncentracijama bakterija, virusa, gljivica te ostalih štetnih organskih spojeva (VOC) u zraku. Mikroorganizmi izravno sudjeluju u patogenezi infektivnih bolesti, imunološkoj osjetljivosti i razvoju alergija. Primjenom postojeće tehnologije (HEPA filteri, itd.) djelomično se smanjuje broj mikroorganizama. Nanotehnologija, tehnologija budućnosti, temelji na preslagivanju pojedinih atoma u tvarima s ciljem dobivanja novih s potpuno promijenjenim svojstvima. Titanijev dioksid (TiO_2), kao produkt nanotehnologije, pod djelovanjem ultraljubičastog zračenja otpušta elektrone koji sudjeluju u velikom broju reakcija fotokatalize. Fotokatalitičke reakcije uništavaju sve mikroorganizme (uključujući i viruse) i organske spojeve u zraku, a konačni proizvodi niza reakcija su ugljični dioksid i vodena para.
Cilj: Procijeniti učinak primjene nanotehnologije na poboljšanje mikrobiološke kvalitete zraka zatvorenih prostora.
Metode: Učinkovitost nanotehnologije na mikrobiološku kvalitetu zraka ispitivana je u poslovnim prostorijama i bolničkom prostoru za pripremu citostatika. Prisutnost mikroorganizama tj. bakterija, kvasaca i plijesni određivana je standardiziranom metodom, prije (početno stanje) i nakon instalacije i uključenja uređaja (AiroCide) koji radi na bazi titanijeva dioksida. Djelovanje AiroCide uređaja na kvalitetu zraka određivano je u uzorcima nakon 24, 48 i 72 sata njegova rada. Za uzorkovanje zraka korišten je uređaj EMS E6® (Andersen sampler), a za kultivaciju mikroorganizama korištene su certificirane mikrobiološke podloge. Analiziran je ukupan broj kolonija (CFU) bakterija (AB), te plijesni i kvasaca (KiP) na pojedinim mjestima mjerenja, te kao srednja vrijednost istih.
Rezultati: Rezultati mjerenja pokazuju učinkovitost AiroCide uređaja na mikrobiološku kvalitetu zraka. Značajno smanjenje mikroorganizama prisutnih u zraku izmjereno je nakon uključenja uređaja i to nakon 24 sata za 59%-64%, 48 sata 85%-89% i nakon 72 sata 95%-100%.
Zaključak: Primjena uređaja baziranog na nanotehnologiji značajno smanjuje prisutnost bakterija, plijesni i kvasaca, te značajno pridonosi kvaliteti zraka zatvorenih prostora. Također, primjena nanotehnologije bazirane na titanijevom dioksidu omogućava uklanjanje virusa kao i drugih onečišćenja zraka (VOC).

[1] Sveučilište u Zagrebu, Medicinski fakultet, Škola narodnog zdravlja "Andrija Štampar"
[2] Klinička bolnica "Sveti duh", Zagreb
[3] IB-O2 d.o.o., Zagreb
[4] Hrvatski zavod za javno zdravstvo, Zagreb
[5] Sveučilište u Rijeci, Medicinski fakultet

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Doko Jelinić, J.[1], Filipović, B.[2], Bertović–Žunec, I.[3], Capak, K.[4] and Bilajac, L.[5]

NANOTECHNOLOGY AND INDOOR AIR QUALITY

Keywords: *microbiological air quality, nanotechnology, titanium dioxide*

Introduction: Microbial air quality depends on the concentrations of bacteria, viruses, fungi and other harmful organic compounds (VOCs) in indoor air. Those directly involved in the pathogenesis of infectious diseases, immunologic sensitization and development of allergy. The number of microorganisms in indoor air can be partly reducing by application of existing technologies (HEPA filters, etc.). Nanotechnology, technology of the future, is based on the rearrangement of individual atoms in compounds with the aim of obtaining new with completely new properties. Titanium dioxide (TiO_2), as a product of nanotechnology, under the action of ultraviolet radiation releases electrons to a higher level of energy are involved in a number of photo catalytic reaction. Photo catalytic reactions destroy all microorganisms (including viruses) and organic compounds in the air and the final products of the reactions are carbon dioxide and water vapour.

Aim: To investigate the effect of nanotechnology in improving the microbiological quality of air in indoor spaces.

Methods: The effectiveness of nanotechnology on the microbiological quality of air was investigated in offices and hospital space for the preparation of cytostatic. The presence of micro-organisms i.e. bacteria, yeasts and molds was determined by a standardized method, before (initial state) and after installation of the titanium dioxide technology (AiroCide). After installation of AiroCide, we took and analysed air samples after 24, 48 and 72 h. For air sampling procedures we used EMS E6® (Andersen sampler) and certificated microbiological plates.

Results: Present results are shown as number of colony forming units (CFU) of bacteria (AB), yeast and fungi (KiP) at specific points, and as a mean value. Study results show high efficiency in improving microbiological quality of air after 24, 48 and 72 h at all measurement points. Time course measurement showed reduction of air microbiological contamination after: 24 h 59%-64%, 48 h 85%-89% and 72 h 95%-100%. In all spaces is measured reduction of concentration of bacteria and mold up to 100%.

Conclusion Study shows that application of nanotechnology drastically improves indoor microbiological quality of air, measured as the total number of bacteria, molds and yeasts. Also, the same nanotechnology based on titanium dioxide is capable to remove other microorganism such as viruses and other air pollution (VOC).

[1] University of Zagreb, Medical School, Andrija Stampar School of Public Health
[2] University Hospital "Sveti duh", Zagreb
[3] IB-O2 d.o.o., Zagreb
[4] Croatian National Institute of Public Health, Zagreb
[5] University of Rijeka, Medical School

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Hercog, P.[1], Bilić, M.[1] i Peternel, R.[2]

AUTOMATSKA MJERENJA BENZENA I REDUCIRANIH SUMPORNIH SPOJEVA U HRVATSKOJ

Ključne riječi: *benzen, reducirani sumporni spojevi, QA/QC postupci, PID i FID detektori, donja granica detekcije za ultraljubičastu fluorescenciju*

Cilj rada bio je ukratko opisati razvoj automatskih mjerenja koncentracija benzena i reduciranih sumpornih spojeva u zraku u Republici Hrvatskoj s detaljnim opisom trenutnog stanja s obzirom na broj i lokacije mjernih mjesta kao i metoda koje se upotrebljavaju. U radu se poseban naglasak daje na QA/QC postupke koji se izvode kod mjerenja benzena te uspoređuju rezultati rutinskih QC postupaka plinskih kromatografa koji koriste PID i FID detektore. Korišteni su podatci sa automatskih postaja za praćenje kvalitete zraka u Republici Hrvatskoj u kojima se koriste plinski kromatografi sa detektorima plamene i foto ionizacije (za benzen), elektrokemijski senzori (za merkaptane i disulfide), te instrumenti za H_2S i totalni reducirani sumpor koji rade po metodi ultraljubičaste fluorescencije uz prethodno uklanjane SO_x spojeva i konverziju reduciranih sumpornih spojeva u SO_2. Obrađeni rezultati svakodnevnih provjera odgovora plinskih kromatografa za benzen na span plin pokazuju puno veću pouzdanost FID detektora u odnosu na PID detektore. Rezultati svakodnevnih provjera odgovora instrumenata za H_2S na zero plin pokazuju probleme s donjom granicom detekcije koja je relativno visoka u odnosu na izuzetno nisku graničnu vrijednost zadanu Uredbom o razinama onečišćujućih tvari u zraku (NN 117/12).

[1] EKONERG-Institut za energetiku i zaštitu okoliša, 10 000 Zagreb, Koranska 5, Hrvatska
[2] Veleučilište Velika Gorica, 10 410 Velika Gorica, Zagrebačka c. 5, Hrvatska

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Hercog, P.[1], Bilić, M.[1] and Peternel, R.[2]

AUTOMATIC MEASUREMENTS OF BENZENE AND REDUCED SULPHUR COMPOUNDS IN CROATIA

Keywords: *benzene, reduced sulphur compounds, QA/QC procedures, PID and FID detectors, lower detection limit for ultraviolet florescence*

In this paper the short history of automatic measurements of benzene and reduced sulphur compounds in Croatia is given. Present situation of the same issue is given in more detail with regards to number of measuring points, types of locations and methods in use. Special emphasis is given on QA/QC procedures in benzene measurements with comparison of results of routine QC span checks of different GC instruments with FID and PID detectors. Data from different automatic measuring stations in Croatia were used. Methods in use at those stations are GC-FID and GC-PID for benzene, GC-electrochemical detector for mercaptanes and disulphides and ultraviolet florescence with SO_x scrubbing and reduced sulphur compounds conversion to SO_2 for H_2S and TRS. QC results of routine span checks of benzene with GC-FID method showed much more reliable than those obtained with GC-PID. QC results of routine zero checks of instruments for H_2S measurements showed certain problems due to relatively high lower detection limit compared to very low limit value defined by Croatian legislative.

[1] EKONERG-Energy and Environmental Protection Institute, 10 000 Zagreb, Koranska 5, Croatia
[2] University of Applied Sciences Velika Gorica, 10 410 Velika Gorica, Zagrebačka c. 5, Croatia

Tema 5
Procjena izloženosti i učinci na zdravlje i okoliš

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Aliefendić, S.[1], Ranica, A.[1], Adžemović, S.[1], Huremović, J.[1] i Žero, S.[1]

BIOMONITORING ZAGAĐENOSTI ZRAKA U FEDERACIJI BOSNE I HERCEGOVINE

Ključne riječi: *lišaj, mahovina, bimonitoring, zagađenje, AAS*

Biološki monitoring može biti veoma efikasan sistem ranog otkrivanja promjena u okolišu. Ciljevi ovog istraživanja bili su (1) ispitati sadržaj Co, Cu, Cd, Cr, Fe, Mn, Zn, Bi, Ni, Hg i Pb u lišajima (Hypogymnia physodes) i mahovinama (Hypnum cupressiforme) sakupljenim sa tri kantona (Kanton Sarajevo, Zeničko-dobojski kanton i Tuzlanski kanton) u Federaciji Bosne i Hercegovine; (2) usporediti razinu akumulacije metala između pojedinih lokaliteta; (3) izvršiti procjenu eventualnog zagađenja. Uzorci su sakupljeni na 34 lokacije tijekom ožujka 2010. godine i veljače 2011. godine. Koncentracija metala određena je metodom atomske apsorpcijske spektrometrije, plamenom tehnikom i tehnikom hladnih para. Viši sadržaj svih analiziranih metala nađen je uglavnom u uzorcima mahovine u odnosu na uzorke lišaja. Uzorci mahovina su također pokazali značajnije variranje sadržaja teških metala na pojedinim lokalitetima u odnosu na uzorke lišaja.

[1] Prirodno-matematički fakultet, Univerzitet u Sarajevu, Zmaja od Bosne 33-35, Sarajevo, Bosna i Hercegovina

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Aliefendić, S.[1], Ranica, A.[1], Adžemović, S.[1], Huremović, J.[1] and Žero, S.[1]

BIOMONITORING OF AIR POLLUTION IN THE FEDERATION OF BOSNIA AND HERZEGOVINA

Keywords: *lichen, moss, biomonitoring, pollution, AAS*

Biological monitoring can be very effective as an early warning system to detect environmental changes. The aims of this investigation were (1) to examine the content of Co, Cu, Cd, Cr, Fe, Mn, Zn, Bi, Ni, Hg and Pb in lichen (Hypogymnia physodes) and moss (Hypnum cupressiforme) collected in three cantons (Canton Sarajevo, Zeničko-dobojski canton and Tuzla canton) in the Federation of Bosnia and Herzegovina; (2) to compare the accumulation level among different locations; (3) to estimate the possible pollution. Samples were collected at 34 locations during March and February in 2011. Metal concentrations were determined by atomic absorption spectrometry, flame and cold vapour techniques. The higher concentrations of all analysed metals were found mainly in moss samples in relation to lichen samples. Moss samples also showed significant variation in the heavy metal contents at some locations.

[1] Faculty of Science, University of Sarajevo, Zmaja od Bosne 33-35, Sarajevo, Bosnia and Herzegovina

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Peternel, R.[1] i Hercog, P.[2]

UTJECAJ SEZONSKIH FLUKTUACIJA I PROSTORNE RASPODJELE PELUDNOG SPEKTRA NA UČESTALOST PELUDNIH ALERGIJA U ZAGREBU I ZAGREBAČKOJ ŽUPANIJI

Ključne riječi: *alergijske bolesti, peludni spektar, skin-prick test, inhalatorni alergeni, senzibilizacija.*

Cilj istraživanja bio je utvrditi vremenske i prostorne varijacije peludnog spektra u Gradu Zagrebu i Zagrebačkoj županiji po prostornim mikrolokacijama, te učestalost inhalacijskih alergija u odrasloj populaciji s postavljanjem odnosa alergen/pacijent.
Istraživanje se sastojalo iz dva dijela: aerobiološko i epidemiološko, koje se provodilo standardiziranim metodama.
Rezultati su pokazali da mikroregionalno postoje statistički značajne razlike u prosječnim ukupnim godišnjim koncentracijama svih vrsta peluda. Za pojedine vrste peluda to se odnosilo na pelud taksona Betula spp. i Ambrosia spp. gdje su nađene statistički značajne razlike između sjeverne i zapadne mikrolokacije (prevladavao pelud breze) i južne i istočne (prevladavao pelud ambrozije), te na pelud johe, hrasta i pelina kao i na alergene grinja. Od ukupno 2192 pacijenta na pelud je bilo senzibilizirano 86,72%, na grinje 36,45%, spore gljiva i plijesni 2,46% i na ostale alergene u čiju skupinu spadaju alergeni žohara, perje i životinjske dlake 5,1% pacijenata. Najveći broj pacijenata alergičnih na peludne alergene bio je senzibiliziran na alergene iz peluda biljaka koje pripadaju botaničkoj porodici trava 46,91%, ambrozije 42,07%, breze 25,66%, lijeske 15,19%. Bez obzira na mjesto stanovanja, najviše je pacijenata bilo senzibilizirano na peludne alergene trava, ali bez statistički značajnih razlika u udjelima alergičnih pacijenata obzirom na mjesto stanovanja. U sjevernim i zapadnim dijelovima grada i županije najviše je pacijenata bilo senzibilizirano na peludne alergene breze dok je na južnim i istočnim lokacijama prevladavao udio senzibiliziranih na ambroziju. Između urbane i ruralne populacije nisu nađene statistički značajne razlike u udjelima pacijenata alergičnih na pojedine alergene. Pojačani simptomi bolesti kod pacijenata alergičnih na peludne alergene su se u cijelom razdoblju istraživanja podudarali sa razdobljima peludnih sezona.
Može se zaključiti da mikroregionalno postoje statistički značajne razlike u koncentracijama peluda u zraku i udjelu senzibiliziranih osoba samo na neke vrste inhalatornih alergena.

[1] Veleučilište Velika Gorica, 10 410 Velika Gorica, Zagrebačka c. 5, Hrvatska
[2] EKONERG-Institut za energetiku i zaštitu okoliša, 10 000 Zagreb, Koranska 5, Hrvatska

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Peternel, R.[1] and Hercog, P.[2]

EFFECT OF SEASONAL FLUCTUATIONS AND SPATIAL DISTRIBUTION OF POLLEN SPECTRUM ON THE FREQUENCY OF POLLEN ALLERGIES IN ZAGREB AND ZAGREB COUNTY

Keywords: *allergic diseases, pollen spectrum, skin-prick test, aeroallergens, sensitization.*

The aim of this study was to determine the temporal and spatial variations of pollen spectra in the City of Zagreb and Zagreb County according to spatial microlocations and frequency of inhalation allergy in the adult population by setting the allergen / patient relationship.
The research consisted of two parts: aerobiological and epidemiological, which was conducted with standardized methods.
The results showed microregional statistically significant differences in average total annual pollen concentrations of all kinds. For certain types of pollen to be related to pollen taxa Betula spp. and Ambrosia spp. where significant differences were found between the Northern and Western microlocations (dominated birch pollen) and Southern and Eastern (dominant ragweed pollen), and the pollen of alder, oak and wormwood and the mite allergens. From a total of 2192 patients to pollen were sensitized 86.72%, 36.45% of dust mites, fungi and mold spores 2.46% and other allergens in whose group includes cockroach's allergens, feathers and animal hair (5.1% of patients). Most patients (46.91%) allergic to pollen allergens were sensitized to the pollen allergens of plants that belong to the botanical family of grasses, 42.07% to ragweed pollen, 25.66% birch, hazel 15.19%. Regardless of where they live, most patients were sensitized to grass pollen allergens, but no statistically significant difference in the proportion of allergic patients given the place of residence. In Northern and Western parts of the city and county, most patients were sensitized to birch pollen allergens, while the Southern and Eastern locations predominant proportion sensitized to ragweed. Between urban and rural populations revealed no statistically significant differences in the proportion of patients allergic to certain allergens. Increased symptoms in patients allergic to pollen allergens are in the whole period of research coincided with the periods of pollen season.
Our results show statistically significant differences in concentrations of pollen in the air and the proportion of sensitized individuals to only some kinds of inhaled allergens according to microlocations.

[1] University of Applied Sciences Velika Gorica, 10 410 Velika Gorica, Zagrebačka c. 5, Croatia
[2] EKONERG-Energy and Environmental Protection Institute, 10 000 Zagreb, Koranska 5, Croatia

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Špirić, Z.[1], Stafilov, T.[2], Kušan, V.[3], Vučković I., Barišić, D.[3], Vekić, B.[3], Šmit, Z.[4], Glad, M.[5] i Frontasyeva, M.[6]

BIOMONITORING MAHOVINAMA U HRVATSKOJ U 2010.

Ključne riječi: *biomonitoring, mahovina, zrak, Hrvatska*

Po drugi puta zaredom, Hrvatska je tijekom 2010. sudjelovala u zajedničkim istraživanjima i provedbi biomonitoringa mahovinama u okviru Međunarodnog Programa suradnje na proučavanju učinaka onečišćenja zraka na prirodnu vegetaciju i usjeve (UNECE ICP Vegetation – http://icpvegetation.ceh.ac.uk)

Uzorci mahovina su prikupljeni tijekom ljeta / jeseni 2010. na 121 točki uzorkovanja koje su bile ravnomjerno raspoređene po cijeloj Hrvatskoj s dodatnim uzorcima u velikim urbanim / industrijskim područjima (ukupno 161 lokacija).

Koncentracija 21 elemenata određena je u mahovinama korištenjem NAA, ICP-AES i AAS. Iz rezultata mjerenja u 2010, može se zaključiti da su srednje vrijednosti i rasponi svih elemenata dobiveni u ovoj studiji vrlo slični srednjim vrijednostima dobivenim u prethodnoj studiji u 2006 (Špirić et al., 2012). Samo nekoliko elemenata (kadmij, bakar, magnezij, nikal i olovo) ima nešto veću srednju vrijednost. Za neke tipične antropogene elemente, kao što su krom, živa, vanadij i cink, zabilježene su niže srednje vrijednosti.

Osim laboratorijskih istraživanja i kemijske analize svih prikupljenih uzoraka mahovina (Špirić et al., 2013), 22 od 161 uzoraka podvrgnuti su gama spektrometriji radi procjene aktivnosti prirodnih radionuklida. Također, korištenjem Kjeldahlove analitičke metode utvrđena je koncentracija dušika u svim prikupljenim uzorcima, a nekoliko uzoraka analizirano je na PAH, PCB, PCDD i PCDF.

Prema ovom istraživanju i u usporedbi s rezultatima iz 2006, očito je da se antropogeno onečišćenje u posljednjih pet godina u Hrvatskoj nije značajnije promijenilo, iako je očito da se antropogeni utjecaj smanjuje.

Špiric Z, Frontasyeva M, Steinnes E, Stafilov T. (2012): Multi-element atmospheric deposition study in Croatia, International Journal of Environmental Analytical Chemistry, International Journal of environmental analithical chemistry, 92:10, 1200-1214

Špirić Z, Vučković I, Stafilov T, Kušan V, Frontasyeva M: Air pollution study in Croatia by using moss biomonitoring, ICP-AES AND AAS analytical technique; Archives of Environmental Contamination and Toxicology, (2013) in press

[1] OIKON – Institut za primijenjenu ekologiju, Trg senjskih uskoka 1-2, 10020 Zagreb, Croatia
[2] Institute of Chemistry, Faculty of Natural Sciences and Mathematics, Ss. Cyril and Methodius University, Skopje, Macedonia
[3] Institut Ruđer Bošković, Zagreb
[4] Zavod za javno zdravstvo "Dr. Andrija Štampar" Zagreb
[5] Nastavni zavod za javno zdravstvo Primorsko goranske županije, Rijeka, Croatia
[6] Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Moscow, Russia

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Špirić, Z.[1], Stafilov, T.[2], Kušan, V.[3], Vučković I., Barišić, D.[3], Vekić, B.[3], Šmit, Z.[4], Glad, M.[5] and Frontasyeva, M.[6]

MOSS BIOMONITORING 2010 IN CROATIA

Keywords: *biomonitoring, moss, air, Croatia*

For the second consecutive time, Croatia participated in moss 2010 survey in the framework of the International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops heavy metals in Europe. http://icpvegetation.ceh.ac.uk
Moss samples were collected during the summer/autumn of 2010, from 121 locations evenly distributed over the country with additional samples in/around urban/industrial areas (with a total of 161 locations).
The content of 21 elements was determined by NAA, ICP-AES and AAS. From data obtained in 2010, it can be concluded that the median values and ranges of all elements obtained in this study are very similar to the median values and ranges obtained in the previous study in 2006 (Špirić et al., 2012). Only a few elements (Cd, Cu, Mg, Ni and Pb) have a slightly higher median value. For some typical anthropogenic elements such as chromium, mercury, vanadium and zinc, lower median values were recorded.
In addition to the comprehensive qualitative and quantitative chemical analysis of all samples collected (Špirić et al., 2013), 22 out of 161 moss samples were subjected to gamma-spectrometric analyses for assessing activity of the naturally occurring radionuclides. Also, laboratory research by using the Kjeldahl analytical method was conducted in order to determine nitrogen concentration in all collected moss samples. Some selected samples were analysed for PAHs, PCBs, PCDDs and PCDFs.
According to this research and in comparison with results in 2006, it is obvious that the state of anthropogenic pollution in the last five years in Croatia has not changed significantly, although it is obvious that the anthropogenic influence in decreasing.
Špiric Z, Frontasyeva M, Steinnes E, Stafilov T. (2012): Multi-element atmospheric deposition study in Croatia; International Journal of environmental analithical chemistry, 92:10, 1200-1214
Špirić Z, Vučković I, Stafilov T, Kušan V, Frontasyeva M. (2013): Air pollution study in Croatia by using moss biomonitoring, ICP-AES AND AAS analytical technique; Archives of Environmental Contamination and Toxicology, in press

[1] OIKON Ltd. – Institute for Applied Ecology, Trg senjskih uskoka 1-2, 10020 Zagreb, Croatia
[2] Institute of Chemistry, Faculty of Natural Sciences and Mathematics, Ss. Cyril and Methodius University, Skopje, Macedonia
[3] Ruđer Bošković Institute, Zagreb
[4] Public Health Institute "Dr. Andrija Štampar" Zagreb
[5] Teaching Institute of Public Health, Primorsko-Goranska County, Rijeka, Croatia
[6] Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Moscow, Russia

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Bobić, V.[1]

MIKROBIOLOŠKO ISPITIVANJE ZRAKA KONDICIONIRANIH PROSTORA KEMIJSKOG LABORATORIJA

Ključne riječi: *mikroorganizmi, zrak zatvorenih prostora, taloženje na hranjive podloge, SEM*

Lebdeće čestice glavni su uzrok respiratornih bolesti . Bakterijske i gljivične stanice u zraku mogu biti važan izvor infekcija u bolnicama, ali niti uredskim zgradama ih ne treba zanemariti gdje mogu doprinijeti kao faktor u takozvanom "sindromu bolesnih zgrada". Mikroorganizmi su prisutni u kapljicama kao bioaerosoli – male pojedinačne čestice koje ostaju u zraku duže vrijeme ili kao veći agregati koje se talože na površinama. Anorganske lebdeće čestice mogu biti nositelji bakterijskih i gljivičnih stanica i spora.

U ispitivanim laboratorijskim prostorijama provode se različita kemijska i mikrobiološka ispitivanja. Sve sobe su povezan klimatizacijskom sustavom u kojem se 40% zraka izmjenjuje.

Kako je periodično čišćenje sustava ventilacije rijetko i nepotpuno u ovom radu obavljena su preliminarna ispitivanje živih bioloških stanica koje se talože iz zraka u određenom vremenskom period. Za određivanje vrste mikrobioloških stanica korištene su tri vrste selektivnih hranjivih podloga. Uzorkovan je zrak zatvorenog prostora prosisavanjem i filtriranjem kroz filtar od 0,8μ veličine pora i ispitan na SEM elektronskom mikroskopu kako bi se utvrdio kemijski sastav anorganskih lebdećih čestica.

U uzorcima sa hranjivim podlogama koji su bili izloženi 8 radnih sati zraku, više od 30 različitih vrsta mikroorganizama je utvrđeno.

Utvrđeno je da broj mikroorganizama ne ovisi o vrsti analiza koji se obavljaju u određenim prostorijama kao na primjer BPK_5, ICP ili analize otpadnih voda.

U sedimentu na filtru SEM analize pokazale su prisutnost različitih kemijskih elemenata koji bi mogli biti povezani s vrstom uzoraka i kemijskim ispitivanjima koje se provodi u pojedinom prostoru kao što je na primjer krom.

[1] INA d.d.,Centralni ispitni laboratorij, Lovinčićeva b.b.,Zagreb

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Bobić, V.[1]

MICROBIAL TESTING OF CHEMICAL LABORATORY AIR CONDITIONED SPACES

Keywords: *microorganisms, indoor air, SEM, settling plates*

Airborne particles are a major cause of respiratory diseases of humans. Air borne bacterial and fungal cells may be important source of infections in hospitals but in office buildings should be not neglected because they may be contributory factor of so-called "sick building syndrome". They are present in droplets as bio aerosols as small individual particles that stay suspended for long periods or as larger aggregates that settle onto surfaces. Inorganic particles may be carriers of bacterial and fungal cells and spores as well.

In the laboratory premises the various chemical and microbiological testing are performed. All rooms are connected thorough air conditioned system where 40% of fresh air is exchanged.

As the periodic cleaning of ventilation systems are rare and incomplete in this work the preliminary testing of viable biological particles that sediment out of the air and settle onto surfaces over the time was tested. In order to collect settling particles three different selective culture media was used and microorganism's species were determined.

The indoor air was also sampled by pumping thorough 0,8µ pore size filter and examined by SEM electron microscope in order to determine chemical composition of the inorganic air particles.

In the samples which were exposed thorough 8 working hours to the air, more than 30 different species of microorganisms were recorded.

Number of microorganisms was not dependent on the type of tests that are carried in the certain areas e.g.BPK_5, ICP or waste water.

In the sediment on filter by SEM analyses different chemical elements were found which could be connected with the type of samples and chemical testing performed in the laboratory such as chromium.

[1] INA d.d.,Central Testing Laboratory, Lovinčićeva b.b.,Zagreb

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Bilajac, L.[1,2], Vukić Lušić, D.[1,2], Tomić Linšak, D.[2], Bilajac, M.[2], Furlan, N.[2], Mišurac, Š.[2], Linšak, Ž.[1,2] i Doko Jelinić, J.[3]

KVALITETA ZRAKA U VRTIĆIMA

Ključne riječi: *dječji vrtić, zdravlje djece, mikrobiološka kvaliteta zraka, respiratorne infekcije*

Djeca u vrtićima provode većinu dnevnog vremena, što u većini slučajeva podrazumijeva boravak u zatvorenom prostoru. Kakvoća zraka zatvorenih prostora značajno utječe na opće zdravstveno stanje te je stoga vrlo važno u vrtićkoj dobi djetetu osigurati dobru kvalitetu zraka kako bi se prevenirao nastanak respiratornih bolesti kojima je zrak osnovni put prijenosa. Prema statističkim podacima respiratorne bolesti su vodeći razlog posjete liječniku pedijatru (preko 50% djece), a astma je postala najčešća kronična bolest među djecom. Kao uzrok navode se loša kvaliteta unutarnjeg zraka, boravak djece u prostoru s povećanom vlagom, plijesnima i slično. Cilj ovog pilot istraživanja je usporediti količinu mikroorganizama u zraku u prostorijama gdje borave djeca s količinom mikroorganizama u vanjskom zraku te utvrditi učinak prirodnog provjetravanja prostorija u trajanju od 10 minuta do pola sata, kao i korištenje klima uređaja na kvalitetu zraka. Korištene metode u istraživanju su uzorkovanje zraka s uređajem MAS 100 (Merck Air Sampler), pri čemu se na TSA (Tryptic Soy Agar) podlogama procjenjivao ukupan broj bakterija, a korištenjem podloge SA (Sabouraud agar) broj poraslih kvasaca i plijesni. Obzirom da plijesni i bakterije mogu biti uzročnici mnogih infekcija, ali i alergijskih reakcija, posljednjih se godina sve veća pažnja posvećuje kvaliteti zraka u zatvorenim prostorima te su prioriteti znanstvenih istraživanja sve više usmjereni na istraživanja utjecaja na zdravlje ljudi, u ovom slučaju djece.

[1] Medicinski fakultet Sveučilište u Rijeci, Braće Branchetta 20, Rijeka, HRVATSKA
[2] Nastavni zavod za javno zdravstvo Primorsko- goranske županije, Krešimirova 52a, Rijeka, HRVATSKA
[3] Medicinski fakultet Sveučilište u Zagrebu, Škola narodnog zdravlja "Andrija Štampar", Rockfelerova 4, Zagreb, HRVATSKA

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Bilajac, L.[1,2], Vukić Lušić, D.[1,2], Tomić Linšak, D.[2], Bilajac, M.[2], Furlan, N.[2], Mišurac, Š.[2], Linšak, Ž.[1,2] and Doko Jelinić, J.[3]

INDOOR AIR QUALITY IN KINDERGARDENS

Keywords: *kindergarten, children's health, microbiological air quality, respiratory infections*

Children spend most of daily time in kindergarten, which implies staying indoors. The quality of indoor air has a significant impact on the general health condition. Thus, it is very important to ensure good indoor air quality in kindergarten in order to prevent respiratory outbreaks. According to statistical data, respiratory diseases are the leading reason for visiting paediatrician (over 50% of children), and asthma has become the most common chronic disease among children. As the cause is given poor indoor air quality, staying in the area with increased humidity, mold etc. The aim of this study is to present quantity of microorganisms in the indoor air in compares with outdoor air and to determine the effect of natural ventilation in the room for 10 minutes to half an hour, as well as the use of air conditioners. The methods used in the study were sampling air conditioning MAS 100 (Merck Air Sampler), with the TSA (Tryptic Soy Agar) media estimated the total number of bacteria, and of medium SA (Sabouraud agar) for increased number of yeasts and molds. Mold and bacteria may cause many infections and allergic reactions, and that is why increasing attention is given to the quality of indoor air. The priorities of scientific research in recent years are increasingly focused on the research on the impact on human health, and in this case impact on children health.

[1] University of Rijeka, School of Medicine, Brace Branchetta 20, Rijeka, Croatia
[2] Teaching Institute for Public Health Primorsko- goranska county, Krešimirova 52a, Rijeka, Croatia
[3] University of Zagreb, School of Medicine, School of Public Health "Andrija Štampar", Rockfelerova 4, Zagreb, Croatia

Tema 6
Azbest u zraku

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Pavičić, I.[1] i Trošić, I.[1]

KONCENTRACIJA AZBESTNIH VLAKANA U ZRAKU NA PODRUČJU GRADA PLOČA – POLARIZACIJSKA SVJETLOSNA I SKENIRAJUĆA ELEKTRONSKA MIKROSKOPIJA

Ključne riječi: *SEM, PLM, azbest u zraku, mikroskopija*

Radi određivanja koncentracije azbestnih vlakana uzorkovan je zrak na šest mjernih mjesta na području grada Ploče i delte Neretve i to u okruženju tvornice Novi Plobest d.o.o., u neposrednoj blizini zgrade policijske i željezničke postaje, u naseljenom mjestu Stablina, pri Pučkom učilištu, na lokaciji Lovornik gdje je smješteno odlagalište komunalnog otpada i kazeta za odlaganje azbestnog otpada te u luci uz hotel. Uzorkovanje je provedeno u mjesecu studenom 2011. Uzorci su analizirani polarizacijskom svjetlosnom (PLM) i elektronskom skenirajućom (SEM) mikroskopijom. Komparativna analiza je pokazala da se rezultati koncentracije azbestnih vlakana dobiveni PLM i SEM metodologijom znatno ne razlikuju. Na lokacijama okruženje tvornice Novi Plobest, naseljeno mjesto Stablina i pri Pučkom učilištu niti jednom od korištenih mikroskopskih metodologija nije pronađen azbest respirabilne veličine u zraku. Azbestna vlakna respirabilne veličine otkrivena su u zraku mjernih mjesta uz zgradu policijske postaje i u luci. Na mjernom mjestu u neposrednoj blizini zgrade policijske i željezničke postaje SEM metodologijom je izmjereno 0.0001 vlakna/cm^3, a PLM-om 0.002 vlakna u cm^3 zraka. Na mjernom mjestu u luci uz hotel nađeno je 0.0001 vlakna/cm^3 zraka SEM odnosno 0.003 vlakna/cm^3 PLM mikroskopijom. Na mjernom mjestu na lokaciji Lovornik gdje je odlagalište komunalnog otpada i kazeta za odlaganje azbestnog otpada nađeno je 0.001 vlakna/cm^3 PLM-om, dok je SEM metodologijom koncentracija azbesta na toj lokaciji bila 0.0000 vlakna/cm^3 zraka. Dobivene pozitivne vrijednosti respirabilne veličine azbestnih vlakana PLM i SEM metodologijom u općem okolišu na području grada Ploče i delte Neretve su ispod one koja je određena Pravilnikom o zaštiti radnika od rizika zbog izlaganja azbestu NN 40/07, Zakona o zaštiti na radu (NN 59/96; 94/96, 114/03 i 100/04) Republike Hrvatske, gdje je Člankom 9 propisano da u osmosatnom vremenski prilagođenom prosjeku nijedan radnik nije izložen koncentraciji azbesta u zraku većoj od 0,1 vlakno na cm^3.

[1] Institut za medicinska istraživanja i medicinu rada, Ksaverska cesta 2, Zagreb, HRVATSKA

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Pavičić, I.[1] and Trošić, I.[1]

THE CONCENTRATION OF ASBESTOS FIBERS IN THE AIR IN THE TOWN OF PLOČE – POLARIZED LIGHT AND SCANNING ELECTRON MICROSCOPY

Keywords: *PLM, SEM, asbestos in air, microscopy*

In order to determine the concentration of asbestos fibres in air from six locations at the town of Ploče and the Neretva River Delta were sampled. Positions were at the surrounding factory Novi Plobest Ltd, near the police building and the train station, in a populated place Stablina, the Open University, at the location Lovornik where is situated municipal waste landfill and cassette disposal of asbestos waste, and in the port next to the hotel. Sampling was conducted in November of 2011. Samples were analysed by means of polarized light (PLM) and scanning electron (SEM) microscopy. Comparative analysis showed that there is not significantly difference between the results of asbestos fibre concentrations obtained PLM and SEM methodology. At locations surrounding the factory Novi Plobest, settlement Stablina and the Open University respirable size asbestos in air was not found. Asbestos fibres of respirable size were detected in the air at the police station and the harbour. At the location near the police building and the train station SEM methodology was measured concentration of 0.0001 fibres/cm^3 and PLM 0,002 fibres/cm^3. At the location in the harbour near the hotel, concentration of asbestos fibres in air was 0.0001 fibres/cm^3 by SEM, and 0.003 fibres/cm^3 by PLM microscopy. At the measuring location Lovornik municipal waste landfill and cassette disposal of asbestos waste, concentration of asbestos fibres in air was found to be by PLM 0.001 fibres/cm^3, while the SEM methodology determined concentration of asbestos at the site to be 0.0001 fibres/cm^3. Obtained positive values of respirable asbestos fibres by PLM and SEM methodology in the general environment in the city of Ploče and Neretva delta are below that specified by the Croatian Occupational Safety and Health Law (NN 59/96, 94/96, 114/03 and 100/04), and the Risks related to exposure of workers to asbestos bylaw (NN 40/07), where the Article 9. instruct that the eight-hour time-adjusted average single worker is allowed to be exposed to a concentration of asbestos in the air no more than 0.1 fibres per cm^3.

[1] Institute for Medical Research and Occupational Health, Ksaverska c 2, Zagreb, CROATIA

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Ivašković, R.[1], Emling, M.[1], Trbojević, V.[1], Šmitran, Ž.[1] i Glažar, B.[1]

GOSPODARENJE MATERIJALIMA KOJI SADRŽE AZBEST

Ključne riječi: *azbest, opasnost, gospodarenje materijalima koji sadrže azbest*

Azbest je prirodni vlaknasti mineral iz skupine silikata. U prirodi ga nalazimo u stijenama i u tlu. Ima nisku toplinsku i električnu vodljivost, iznimnu čvrstoću te je otporan na visoke temperature i na djelovanje kemikalija. Materijali koji sadrže azbest zbog svojih su iznimno dobrih svojstava našli široku primjenu u različitim granama gospodarstva i proširili su se relativno brzo po cijelom svijetu. Primjenjivali su se u najvećem udjelu u građevinskoj industriji, zatim u automobilskoj industriji, za proizvodnju materijala otpornih na visoke temperature i na mnogim drugim poljima. Smatrali su ga "čudom od materijala", sve dok se nije otkrilo pogubno djelovanje azbestnih vlakana na ljudsko zdravlje. Azbest spada u skupinu deset supstanci koje imaju najveći karcinogeni potencijal za zloćudne tumore. Kada se nađu slobodni u zraku, azbestna vlakna i prašina imaju vrlo nepovoljan utjecaj na zdravlje ljudi i životinja, jer pri udisanju dospijevaju na dišne organe i ostavljaju dugoročne posljedice na živa bića.

U nerazvijenim zemljama azbest se još uvijek naveliko koristi, pošto zakonodavstvo vezano za materijale koji sadrže azbest u takvim zemljama ili uopće ne postoji ili se ne provodi. U razvijenim zemljama, kao i kod nas, azbest je zabranjen, ali još je uvijek sveprisutan u našem okruženju i radi se na njegovom sustavnom uklanjanju. Republika Hrvatska donijela je niz propisa kojima se regulira postupanje s materijalima koji sadrže azbest i propisane su stroge mjere zaštite pri radu s materijalima koji sadrže azbest. IND-EKO d.o.o. ima višegodišnje iskustvo u radu s posebnim kategorijama otpada, među koje spadaju i materijali koji sadrže azbest. Tvrtka posjeduje najsuvremeniju opremu za siguran rad s azbestom, ima educirano i specijalizirano osoblje, kao i sve potrebne dozvole od nadležnih institucija za gospodarenje ovom vrstom otpada te značajne reference u sanacijama azbestom kontaminiranih prostora i područja.

[1] IND-EKO d.o.o., Korzo 40/II, Rijeka

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Ivašković, R.[1], Emling, M.[1], Trbojević, V.[1], Šmitran, Ž.[1] and Glažar, B.[1]

MANAGEMENT OF MATERIALS CONTAINING ASBESTOS

Key words*: asbestos, danger, management of materials containing asbestos*

Asbestos is a natural mineral fibre from the group of silicates. In nature it can be found in rocks and soil. Asbestos has a low thermal and electrical conductivity, extreme strength, and it is resistant to high temperature and effects of chemicals. Due to their extremely good characteristics, asbestos materials are widely used in different fields of economics and have spread relatively quickly throughout the world. They have been used largely in the construction industry, automotive industry, for production of materials resistant to high temperatures and in many others fields. It was considered as "the wonder material" until discovery of pernicious effects of asbestos fibres on human health. Asbestos belongs to a group of ten substances that have the greatest carcinogenic potential for malignant tumours. Floating freely in the air, asbestos fibres and dust have a very adverse effect on human and animal health, because during inhalation they enter into respiratory system and have long term effects on living beings.

In undeveloped countries, asbestos is still widely used, as the legislation on asbestos-containing materials in these countries does not exist or is not implemented. In developed countries, as in the Republic of Croatia, asbestos is prohibited, however it is still present in our surroundings and his systematic elimination is in process. The Republic of Croatia adopted a series of regulations governing the handling of materials containing asbestos and prescribing strict safety measures how to work with asbestos materials. IND-EKO d.o.o. has many years of experience working with special categories of waste, among which are materials containing asbestos. The company possesses the latest equipment for safe handling of asbestos, has trained and specialized staff and it has the necessary permits from the authorized institutions for the management of this type of waste and significant references in the recovery of asbestos-contaminated area and areas.

[1] IND-EKO d.o.o., Korzo 40/II, Rijeka

Tema 7
EFCA sekcija "Carbon in particles"

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Murlis, J.[1]

REDUCING IMPACTS OF PARTICULATE POLLUTION: OPPORTUNITIES FOR ACHIEVING COST EFFECTIVE AIR QUALITY AND CLIMATE CHANGE BENEFITS

Keywords: *particulate pollution, climate change, EFCA, BC*

Until recently, policies on air quality and climate change were considered to be quite separate matters, with different drivers and impacts, requiring different solutions. Although at an institutional level policy development in these two topic areas continues to be largely separate, there is a growing interest in, and political recognition of, the interactions between them and in the potential for cost effective ways of achieving combined benefits.

Benefits from air pollution control tend to act over short time scales of a few years, as human health responds to the reduction of the pollution burden. The benefits from the current approach to climate change, based on the reduction of emissions of long-lived greenhouse gases (CO2, F-gases, N2O), however, will appear only over time scales of many decades. This difference is one reason for separate approaches. In addition, significant institutional and practical barriers favour the separate approach.

Motivated by the potential for cost effective linked policies, EFCA (the European Federation of Clean Air and Environmental Protection Associations) has adopted, as a priority, an initiative under the title "One Atmosphere" to understand these barriers and to see how they can be overcome. EFCA observed that, while the EU's Climate and Energy package of 2008 also produced considerable co-benefits for air quality, existing legislation on air quality had completely ignored its impact on climate change, and so missed opportunities for more cost-effective measures. In support of this view it has championed the case for control of a specific short-term climate forcing agent, black carbon.

This fitted perfectly in a further initiative on the effective regulation of pollution from air-borne particles. This has emphasised the growing body of evidence of impacts of particulate pollution on human health. It has highlighted the importance of using the most appropriate measures of particulate pollution in assessing the effectiveness of different measures in reducing harm to human health. These two initiatives are complementary; by making the case for action on short-term climate forcers, the One Atmosphere initiative has highlighted the role of particulate pollution, and, within the Policy Initiative on Black Carbon Particles, the use of effective metrics for particulate pollution, including its impacts on health and climate, have been explored.

This presentation describes the case for linking air pollution policy to policies designed to reduce impacts of climate change. It outlines the EFCA initiative to promote this linkage, and the requirements for evidence to develop and guide cost effective implementation. The development of effective metrics for representing the different harms of particulate pollution will be considered.

[1] EFCA, President Environment Protection UK

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Mücke, H. G.[1]

HEALTH AND AIR QUALITY MANAGEMENT ASPECTS OF BLACK CARBON

Keywords: *WHO, BC, PM2.5, health impacts*

The Task Force on Health working under the Convention on Long-range Transboundary Air Pollution, lead by its secretariat at the WHO European Centre for Environment and Health, Bonn/Germany, World Health Organization, Regional Office for Europe, conducted in 2010/2011 and published in 2012 an assessment of the health impacts of black carbon (BC) as a component of fine particulate matter (PM2,5) (http://www.euro.who.int/en/what-we-do/health-topics/environment-and-health/air-quality/publications/2012/health-effects-of-black-carbon). BC is an indicator of combustion-related air pollution and was recently recognized as one of the short-lived climate-forcers. The assessment is based on a systematic review of evidence of health effects of BC in ambient air. The respective WHO report concludes that epidemiological studies provide sufficient evidence of the association of cardiopulmonary morbidity and mortality with BC exposure. The review of toxicological studies suggested that BC may not be a major directly toxic component of fine particulate matter (PM2,5), but it may operate as a universal carrier of a wide variety of chemicals of varying toxicity to human health.

There is evidence that decreased PM levels following a sustained intervention result in public health benefits. A high amount of PM air pollution can be reduced using current available abatement technologies. Successful air quality management and policy in general requires concerted action by public authorities, industry and individuals at national, regional and international levels. Air pollution interventions to protect public health range from regulatory measures (e.g. stricter air quality standards; limits for emission from various sources), structural changes (such as reducing energy consumption, particularly from combustion process; changing modes of transport; establishing alternative energy sources), as well as behavioural changes by individuals (e.g. using cleaner transport modes and/or household energy sources).

Thus, a reduction of BC emissions and in human exposure to PM2,5 containing BC, and other combustion-related particulate material for which BC is an indirect indicator, should lead to a reduction in the health effects associated with PM in ambient air and simultaneously contribute as a co-benefit to the mitigation of climate change.

[1] WHO Collaborating Centre for Air Quality Management and Air Pollution Control at the Federal Environment Agency, Berlin, Germany

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Šega, K.[1], Godec, R.[1] i Bešlić, I.[1]

PROCJENA KONCENTRACIJA BC MODELIRANJEM REZULTATA MJERENJA REFLEKSIJA UZORAKA $PM_{2,5}$

Ključne riječi: *PM10, PM2.5, PM1, reflektivnost uzorka, koeficijent apsorpcije svjetlosti, crni ugljik, elementni ugljik*

U svrhu procjene koncentracija elementnog ugljika u frakcijama po veličini lebdećih čestica uporabom izmjerenih koeficijenata apsorpcije svjetlosti uzoraka učinjene su dvije pretpostavke: a) koncentracija elementnog ugljika jednaka je koncentraciji crnog ugljika izmjerenoj transmisijom svjetlosti kroz uzorak i b) koeficijent apsorpcije svjetlosti izmjeren refleksijom na uzorku jednak je koeficijentu apsorpcije izmjerenom metodom transmisije svjetlosti kroz uzorak. Tako dobiveni rezultati korelirani su s rezultatima analiza EC TOT metodom prema NIOSH-like protokolu nazvanom Quartz. Ispitivanje je provedeno na uzorcima frakcija lebdećih čestica PM10, PM2.5 i PM1 sakupljenih tijekom dvogodišnjeg razdoblja (2009.-2010.) na dva mjerna mjesta u gradu Zagrebu. Rezultati pokazuju vrlo dobro slaganje modeliranih i izmjerenih srednjih godišnjih koncentracija EC što omogućava brze i jeftine procjene bez dodatnih vremenski zahtjevnih i skupih analiza uzoraka.

[1] Institut za medicinska istraživanja i medicinu rada, Ksaverska cesta 2, Zagreb, Hrvatska

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Šega, K.[1], Godec, R.[1] i Bešlić, I.[1]

ASSESMENT OF BC CONCENTRATIONS BY MODELLING REFLECTION OF $PM_{2.5}$ SAMPLES

Keywords: *PM10, PM2.5, PM1, sample reflectivity, light absorption coefficient, black carbon, elemental carbon*

Two assumptions were adopted in order to assess elemental carbon concentrations in airborne particle samples using the results of light absorption coefficients: a) elemental carbon concentration is equal to the black carbon concentration measured by light transmission through the sample and b) light absorption coefficient measured by the reflection of the sample is equal to the light absorption coefficient measured by light transmission through the sample. Values of elemental carbon assessed by this procedure were correlated to the measured values obtained by EC TOT NIOSH-like method called Quartz. In this assessment samples of airborne particle fractions PM10, PM2.5 i PM1 collected during the two year period (2009-2010) at two monitoring sites in Zagreb were used. The results show good correlation between modelled and measured elemental carbon yearly average concentrations thus enabling quick and low-cost predictions of elemental carbon concentrations eliminating in that way tedious, time consuming and costly analyses.

[1] Institute for Medical Research and Occupational Health, Ksaverska cesta 2, Zagreb, Croatia

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Godec, R.[1], Šega, K. and Bešlić, I.

MASENE KONCENTRACIJE UGLJIKA U PM_{10} FRAKCIJI LEBDEĆIH ČESTICA U ATMOSFERI ZAGREBA (2009.-2012.)

Ključne riječi: *EC, OC, omjer OC/EC, PM_{10}, TC*

Cilj rada bio je ustanoviti vremensku raspodjelu masenih koncentracija ugljika u frakciji lebdećih čestica PM_{10} u zraku grada Zagreba tijekom dužeg razdoblja. Sakupljanje uzoraka provedeno je tijekom četiri godine (od 2009. do 2012.) na mjernoj postaji smještenoj u sjevernom dijelu grada, na području Instituta za medicinska istraživanja i medicinu rada. Uzorci frakcije lebdećih čestica PM_{10} sakupljani su iz približno 50 m^3 zraka na filtre od kvarcnih vlakana (Pallflex Tissuequartz 2500QAT-UP, Pall Life Science), prethodno žarenih na 900 ºC tijekom tri sata. Masene koncentracije lebdećih čestica određene su gravimetrijski sukladno normi HRN EN 12341. Sadržaj organskog (OC), elementnog (EC) i ukupnog (TC=EC+OC) ugljika u frakciji lebdećih čestica PM_{10} u zraku određen je metodom termičko-optičke transmisije (TOT) uporabom uređaja Carbon aerosol analyser (Sunset Laboratory inc.) uz korištenje protokola NIOSH-like. Statistička obrada podataka provedena je korištenjem statističkog programskog paketa STATISTICA 12.0.

Ustanovljeno je postojanje statistički značajnih sezonskih varijacija masenih koncentracija ugljika u PM_{10} frakciji lebdećih čestica. Najviše masene koncentracije lebdećih čestica i ugljika u njima zamijećene su tijekom hladnijeg razdoblja mjerenja (zime i jeseni), dok su najniže bile tijekom ljeta. Analizom varijance ustanovljeno je da su masene koncentracije lebdećih čestica PM_{10} u zraku kao i sadržaj EC, OC i TC u PM_{10} statistički značajno različiti na razini $p=0,05$ između mjerenih godina, dok je t-testom ustanovljeno da se samo OC u PM_{10} između 2009. i 2010. te PM_{10} između 2010. i 2011. statistički nisu razlikovali. Srednje godišnje masene koncentracije mjerenih onečišćenja naznačuju silazni trend. Srednje vrijednosti masenih koncentracija EC, OC i TC tijekom cijelog perioda mjerenja iznose redom 1,1 $\mu g\ m^{-3}$, 6,9 $\mu g\ m^{-3}$ i 8,0 $\mu g\ m^{-3}$ i usporedive su s drugim europskim gradovima (Barcelona, Beč, Helsinki i Prag). Određeni su maseni udjeli ugljika u lebdećim česticama u zraku. Maseni udjeli EC u lebdećim česticama slijedili su sljedeći niz: 2009.(5,9 %) > 2012. (3,0 %) > 2010. (4,2 %) > 2011. (2,7 %). Za razliku od njih izmjereni maseni udjeli OC i TC u PM_{10} bili su najviši u 2010. godini, nešto niži 2009. godine, te su najniži zabilježeni udjeli tijekom 2011. i 2012. godine. Omjeri masenih koncentracija OC/EC slijede niz: 2011. > 2010. > 2012. > 2009. s napomenom da se omjeri masenih koncentracija OC/EC za 2010., 2011. i 2012. nisu značajno statistički razlikovali. Srednja vrijednost OC/EC omjera za mjereni period iznosi 7,3 te je usporediv s omjerom nađenim u literaturi za Prag, dok je viši od omjera određenih u Barceloni, Beči i Helsinkiju. Takav visoki iznos omjera upućuje na postojanje sekundarnog OC u atmosferi Zagreba.

[1] Institut za medicinska istraživanja i medicinu rada, Zagreb, HRVATSKA

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Godec, R.[1], Šega, K. and Bešlić, I.

CARBON MASS CONCENTRATIONS IN AIRBORNE PARTICULATES PM_{10} IN ZAGREB (2009-2012)

Keywords: *EC, OC, OC/EC ratio, PM_{10}, TC*

The aim of this study was to determine the temporal distribution of carbon in particulate matter PM_{10} in the air of Zagreb, Croatia over a longer period of monitoring. The samples were collected at a monitoring site in the northern residential part of Zagreb between 2009 and 2012. Small-volume air samples (50 m^3) of airborne particles were collected on quartz fibre filters (Pallflex Tissuequartz 2500QAT-UP, Pall Life Science) pre-fired at 900 ºC for three hours. PM mass concentrations were determined gravimetrically according to the HRN EN 12341 standard. Organic carbon (OC), elemental carbon (EC), and total carbon (TC, a sum of EC and OC) in fraction PM_{10} were determined by the thermal-optical transmittance method (TOT), using a Carbon Aerosol Analyzer (Sunset Laboratory Inc.) according to a NIOSH-like protocol. Statistical analysis was performed using the STATISTICA 12.0 statistical software.

Statistically significant seasonal variations of the carbon mass concentration in PM_{10} particulate matter were found. The highest levels of the mass concentration of particulate matter and the carbon contained within were observed during the winter measurement period (winter and fall), while the lowest were recorded during the summer. Analysis of variance revealed that the mass concentration of particulate matter PM_{10} in the air as well as EC, OC, and TC in PM_{10} were statistically significantly different at $p = 0.05$ between the measured years, while a t-test revealed that only OC in PM_{10} between 2009 and 2010 and PM_{10} between 2010 and 2011 were not statistically different. Mean annual mass concentrations of the measured pollutions indicate a downward trend. Mean values of EC, OC and TC mass concentrations during the entire measurement period were 1.1 $\mu g\ m^{-3}$, 6.9 $\mu g\ m^{-3}$, and 8.0 $\mu g\ m^{-3}$, respectively, and are comparable to other European cities (Barcelona, Vienna, Helsinki, and Prague). Mass contributions of particulate carbon in the air to total PM mass were determined. Mass contributions of particulate EC followed the following sequence: 2009 (5.9%) > 2012 (3.0%) > 2010 (4.2%) > 2011 (2.7%). Unlike these, the mass contributions of OC and TC to the total PM_{10} mass were highest in 2010, slightly lower in 2009, and lowest in 2011 and 2012. Ratios of OC / EC mass concentrations followed the sequence: 2011 > 2010 > 2012 > 2009. The OC/EC ratios in 2010, 2011, and 2012 were not statistically significantly different. The mean OC/EC ratio for the measured period was 7.3 and is comparable to the ratios found in the literature for Prague, but higher than those for Barcelona, Vienna, and Helsinki. Such a high ratio also indicates the existence of secondary OC.

[1] Institute for Medical Research and Occupational Health, Zagreb, CROATIA

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Eleftheriadis, K.[1]

PARAMETERS AFFECTING THE OPTICAL MEASUREMENTS OF BLACK CARBON AEROSOLS

The measurement of the aerosol mass concentration of light absorbing carbon in the atmosphere or commonly referred as Black carbon (BC) is especially important and has been the focus of many recent investigations pertaining to the changing Arctic climate or health studies in the urban environment. Although black carbon (BC) as a generic term, is often used, separate terms such as Equivalent Black Carbon, (EBC), Refractory Black Carbon (rBC) and Elemental Carbon (EC) are also introduced in order to distinguish amongst different methodologies employed for the measurement of the BC mass concentrations and are explicitly described. These definitions are in line with the latest state-of-science terminology summarized by Petzold et al. (2013). Hence, light absorption-derived black carbon concentrations obtained by Aethalometers or the Particle Soot Absorption Photometer (PSAP) should be referred to as equivalent black carbon (EBC), and vertical profiles of BC derived using the Single Particle Soot Photometer (SP2) during recent aircraft campaigns should be referred to as refractory black carbon (rBC). Determination of a specific instrumental mass absorption coefficient is necessary in order to convert light absorption to black carbon mass and applies to all optical filter based techniques. The parameter is site dependent, as the composition and state of mixing of aerosol particles may change due to ageing and atmospheric chemistry. Instrumental specific features such as the filter matrix, humidity and air flow have an additional effect to this coefficient. Taking into account other studies where the evaluation of aethalometer performance is tested against other instruments such as the MAAP (Collaud Coen et al., 2010), a mean uncertainty of maximum 100% is expected for filter based transmittance techniques. While there are uncertainties associated with each method, particularly the use of Aethalometers can allow uninterrupted long term measurements to be recorded with minimum maintenance and, data are comparable and useful for climate assessments as will be discussed below.

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[1] Institute of Nuclear & Radiological Sciences & Technology, Energy & Safety, National Centre of Scientific Research "Demokritos", 15310 Ag. Paraskevi, Attiki, Greece

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Diapouli, E.[1]

ADVANTAGES AND ARTIFACTS OF EC/OC THERMO-OPTICAL METHOD AND PROTOCOLS

Carbonaceous aerosol has received growing attention during the last years, as it has been acknowledged as a key air pollutant, with significant effects both in climate and human health. Carbonaceous material accounts for a large fraction of airborne particulate matter (PM) and has a strong influence on the physicochemical, biological, climate- and health-related properties and effects of atmospheric aerosol. Carbonaceous species are usually classified into two categories, organic carbon (OC) and elemental carbon (EC), while a third component, carbonate carbon (CC) is often not considered due to its very small contribution. It should be noted that the most recent EU Directive 2008/50/EC includes a requirement to monitor EC and OC at selected rural background sites. Nevertheless, due to the complex and highly variable molecular structures of carbon species, as well as the lack of reference material for methods calibration and validation, there is still no standard methodology for the quantification of elemental and organic carbon.

The most common methodology for EC-OC determination is thermo-optical analysis (TOA). The main concept is to separate elemental and organic carbon based on their chemical refractiveness. Initially organic carbon is quantified as the fraction of carbonaceous material that evolves in inert (Helium) atmosphere, while elemental carbon is oxidized at a next stage in Helium-Oxygen atmosphere. During the evolution of OC, part of the organic material may char, forming pyrolytic carbon (PC) which desorbs usually in oxidizing atmosphere like native EC. In order to correct for organic material charring, the optical properties (light transmission or reflectance) of the sample are monitored continuously during the analysis by a laser beam. The point at which the transmission and reflectance reaches the pre-pyrolysis value is used to discriminate between OC and EC. A number of thermal protocols have been developed, in an effort to find the optimum temperatures and duration of temperature steps that will allow all OC to evolve, while decreasing charring and avoiding premature oxidation of EC.

Even though TOA is widely used worldwide, there are still several open issues regarding the reliable quantification of elemental and organic carbon. The method is based on the collection of particles onto quartz filter samples. A pre-treatment of filters is needed in order to decrease their organic content, while there are sampling artifacts associated with the collected OC mass. Regarding the analysis, inter-comparison results of different thermal protocols and instruments indicate good agreement in total carbon (TC) values but demonstrate that both the temperature protocol and the optical detection technique (transmission versus reflection) may have a significant effect on the measured OC and EC concentrations. On the other hand, optical correction is based on a number of assumptions that are not strictly valid, rendering thus the distinction between EC and OC somewhat arbitrary. Finally there may be interference in the evolution of OC and EC by the presence in the sample of inorganic matter, such as mineral oxides and salts, as well as carbonate carbon. All these factors increase uncertainties and limitations in EC-OC quantification and highlight the need for the development of standard methodologies and appropriate reference material, specifically in view of a future carbonaceous aerosol air quality standard.

[1] Institute of Nuclear & Radiological Sciences & Technology, Energy & Safety, National Centre of Scientific Research "Demokritos", 15310 Ag. Paraskevi, Attiki, Greece

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Miljevic, B.[1], Stevanovic, S.[1,2], Surawski, N.C.[3], Ristovski, Z.D.[1,4], Bottle, S.[2] and Brown, R.[4]

LOOKING BEYOND SOOT: THE ROLE OF ORGANIC FRACTION IN THE TOXICITY OF COMBUSTION-GENERATED PARTICULATE MATTER

Keywords: *combustion particles, health effects, oxidative stress, reactive oxygen species (ROS)*

While epidemiological studies have established a link between exposure to ambient particulate matter (PM) and respiratory morbidity and mortality, studies of this design are not able to identify the PM constituents responsible for driving adverse health effects. There is strong evidence that organic compounds play an important role in the toxicity of airborne particles. Many toxicological studies associate Reactive Oxygen Species (ROS) and oxidated stress they engender with the observed adverse health effects. Taking this into account we have explored the correlation between particulate organic material and the potential of combustion-generated PM to cause oxidative stress (oxidative potential). We have assessed the oxidative potential of combustion related particles using a novel profluorescent nitroxide probe BPEAnit (developed at Queensland University of Technology). The probe is weakly fluorescent, but yields strong fluorescent emission upon radical trapping or redox activity. The organic content of PM was measured by an Aerosol Mass Spectrometer (AMS) and Volatility – Differential Mobility Analyser (V-DMA). We found that there was a strong correlation between the organic fraction of particles and the oxidative potential measured by the PFN assay, which clearly highlights the importance of organic species in particle-induced toxicity. This was observed for both wood combustion and diesel exhaust.

Our recent research was focused on investigating the role of ethanol supplementation, as well as the use of biodiesel on the oxidative potential of particles emitted by a modern diesel engine. We found that the oxidative potential of PM although proportional to the total organic content in certain cases shows a much better correlation with the oxygenated organic fraction (measured by the Aerosol Mass Spectrometer). This highlights the importance of knowing the surface chemistry of particles for assessing their health impacts. It also sheds a light onto new aspects of combustion PM emissions that should be taken into account when establishing relevant metrics for health implications of emissions from various future fuels.

[1] ILAQH, Queensland University of Technology, 2 George St, Brisbane, 4001 QLD, Australia
[2] ARC Centre of Excellence for Free Radical Chemistry and Biotechnology, QUT, 2 George St, Brisbane, 4001 QLD, Australia
[3] CSIRO Ecosystem Sciences, Clunies Ross St, Acton ACT 2601, Australia
[4] Biofuel Engine Research Facility, QUT, 2 George St, Brisbane, 4001 QLD, Australia

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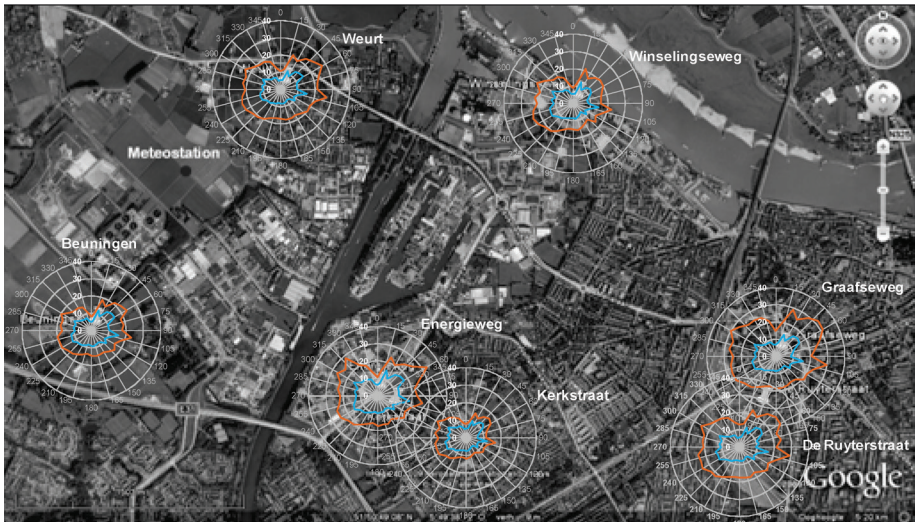
Valk, K.[1] and Groen, R.[1]

MONITORING AMBIENT $PM_{2.5}$ AND PM_{10} IN THE CITY OF NIJMEGEN, THE NETHERLANDS

Keywords: *ambient air quality, particulate matter, automated monitoring stations, air quality modelling*

Since January 2012 Witteveen+Bos is maintaining the continues PM2.5-PM10 measurement network of the city of Nijmegen. The PM network contains 7 automated monitoring stations. The data is measured every 10 minutes and presented on the internet (www.westenweurt.nl). The Osiris dust monitor (Turnkey Instruments Ltd) is used to measure the de PM2.5-PM10 concentrations. The Osiris is a relatively simple instrument, operating on the principal of light diffraction. For this is not the officially approved method in the Netherlands, the network is calibrated on officially validated data from the National Institute for Public Health and the Environment (RIVM). Therefore the networks gives accurate information and is very useful for policy makers and the public. The daily results show similar patterns for all different locations. For example the overall results of location De Ruyterstraat, a quiet city road, shows lower concentrations than the busy Graafseweg, but the pattern is very much the same. This confirms that ambient PM10 concentrations are influenced by background fluctuations to a large extend (especially peaks), although local sources, like traffic add a significant portion. Sometimes background concentrations can be traced to incidents. Our conclusion is the network gives accurate concentrations and real time health information for the public. Furthermore prevailing meteorological conditions and large-scale emissions determine ambient concentrations significantly. Additional to monitoring of the air quality, modelling is used to give a complete view of air quality situation in the city of Nijmegen. Emissions and immissions are calculated from traffic flows from cars, trains and ships, and from industrial sources.



[1] Witteveen+Bos Consulting Engineers, The Netherlands, P.O. Box 233, 7400 AE, Deventer. www.witteveenbos.com

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Deniz, A.[1], Sezen, I.[2,3], Efe, B.[1], Özdemir, T.[2,3], Ünal, A.[2], Çapraz, Ö.[2,4], Korur, Y.[2,4] and Aydinöz, E.[2]

SAHARAN DUST CONTRIBUTION TO THE PM10 PROFILE: A CASE STUDY ON AIR POLLUTION EPISODE IN KAĞITHANE, ISTANBUL, TURKEY

Keywords: *PM_{10}, Episode, Dust, WRF, HYSPLIT, Kagithane*

Air pollution is one of the most important problems in the world which affects human life. Besides local air pollution, long range transport of pollutants like PM_{10} seriously deteriorates local air quality. Air pollution in Istanbul, the largest urban settlement in Turkey with more than 13 million inhabitants, contains many components that originate from a wide range of anthropogenic and natural emissions sources. One of the natural emission sources, the long range Saharan dust transport significantly affects Istanbul's air quality. The aim of this study is to investigate the contribution of the Saharan dust transport to high PM_{10} levels in Kağıthane, Istanbul for the period from 11 March 2011 to 17 March 2011. During the episode days, daily average PM_{10} concentrations were ranged between 121 μg/m^3 and 275 μg/m^3 at Kağıthane monitoring station. In order to evaluate the episode days, the corresponding synoptic maps, precipitation and relative humidity observations are compared with WRF and HYSPLIT model outputs. As a result, one of the most important contributions to high PM_{10} concentrations is Saharan dust transport.

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[1] Istanbul Technical University, Faculty of Aeronautics and Astronautics, Department of Meteorology, 34469, Maslak, Istanbul, Turkey.
denizali@itu.edu.tr, efeba@itu.edu.tr
[2] Graduate School of Science Engineering and Technology, Atmospheric Sciences Programme, Istanbul, Turkey.
unalay@itu.edu.tr, aydinoze@itu.edu.tr
[3] General Directorate of Meteorology, Atatürk Airport Meteorogy Office, Yeşilköy, İstanbul, Turkey.
sezenismail@gmail.com, etozdemir@gmail.com
[4] Marmara Clean Air Center, Ministry of Environment and Urbanization, Nisantası, 34365, Istanbul, Turkey.
yenerkorur@hotmail.com, ozzqa@hotmail.com

Posteri

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Alebić-Juretić, A.[1], Shaaref, A.[2] i Liaquat, H.[2]

PRVI REZULTATI MJERENJA CRNOG (ELEMENTARNOG) UGLJIKA U RIJECI

Ključne riječi: *kvaliteta zraka, crni ugljik, ukupne lebdeće čestice*

Crni (elementarni) ugljik (CB- carbon black) važan je sastojak onečišćenja zraka kako zbog njegove uloge u fenomenu globalnog zagrijavanja (apsorpcijom sunčevog zračenja), tako i u pogledu štetnog djelovanja na ljudsko zdravlje. Nastaje nepotpunim izgaranjem fosilnog goriva te je sastavni dio lebdećih čestica. S ciljem da se odredi razina u atmosferi grada Rijeke, filtri sa uzorcima ukupnih lebdećih čestica sakupljeni 1983 (25 uzoraka) i 2006 godine (21 uzorak) analizirani su na sadržaj CB. Pri tom su korištene dvije metode: 1. uzorci ULČ sakupljeni na filtrima sa staklenim vlaknima obrađeni su s HF, NH_4Cl, te HNO_3 i HCl, otopina je profiltrirana kroz kvarcni filtre (Φ= 47 mm) te je količina CB određena UV i IR spektroskopijom sa površine; 2. Direktnim mjerenjem sa GF(Φ= 25 mm) filtra pomoću UV i IR spektroskopijom. Najbolji rezultati dobiveni su obradom GF filtra smjesom kemikalija te kvantificiranjem sa kvarcnog filtra UV spektroskopijom. Dobiveni rezultati ukazuju da se prosječne koncentracije CB bitno ne razlikuju (2,91±1,26 μg m^{-3} u 1983 prema 2,9±0,86 μg m^{-3} u 2006). Isto tako, ne postoji statistički značajna razlika između prosječne vrijednosti CB dobivene zimi (3,10±0,92 μg m^{-3}) i ljeti (2,59±0,71 μg m^{-3}) 2006. godine, što govori u prilog konstantnim emisijama tijekom godine i njihovom inertnosti u atmosferi, za razliku od policikličkih aromatskih ugljikovodika koji podliježu, u prvom redu fotorazgradnji. Udio CB u ULČ iznosi oko 5%, kako po sezonama, tako i kroz cijelu godinu.

[1] Nastavni Zavod za javno zdravstvo/Medicinski fakultet Sveučilišta u Rijeci, Krešimirova 52a, 51000 Rijeka
[2] Department of Environmental Health Sciences, SUNY Albany, Albany, New York Area, USA

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Alebić-Juretić, A.[1], Shaaref, A.[2] and Liaquat, H.[2]

FIRST RESULTS OF CARBON BLACK MONITORING IN RIJEKA, CROATIA

Key-words: *air quality, carbon black, TSP*

Carbon black (CB) is an air pollutant crucial either for global warming (due to absorption of sunlight) or having harmful impact on human health. CB is the result of the incomplete combustion of organic fuel and is constituent part of suspended particulates. In order to estimate their level in the urban atmosphere of Rijeka, 46 samples of total suspended particulates (TSP) collected in Rijeka in 1983 (25 samples) and 2006 (21 samples) were analysed on CB content.

The analyses were carried on with two methods: the first included treatment of glass fibre (GF) Exposed filters were treated with HF, HH_4Cl, HNO_3 and HCl, the obtained suspension was filtered through quartz filter (Φ= 47 mm) and concentrations of CB were quantified with IR and UV spectroscopy from the surface. The second method employed direct UV and IR spectroscopy on a piece of originally loaded glass fibre filters (Φ= 25 mm). The best results were obtained with UV spectroscopy of the deposit on the quartz filters. The obtained results indicate that the levels of CB were similar at both periods: (2, 91±1,26 μg m^{-3} in1983 vs.2,90±0,86 μg m^{-3} in 2006). Furthermore, there is no statistical difference between summer (2,59±0,71 μg m^{-3}) and winter (3,10±0,92 μg m^{-3}) mean values indicating constant emissions throughout the year and resistance to atmospheric reaction (contrary to polynuclear aromatic hydrocarbons that are susceptible to photodegradatin). The contribution of CB to TSP is approx, 5% during winter and summer seasons, and all over the year.

[1] Teaching Institute of Public Health/ School of Medicine, University of Rijeka, Krešimirova 52a 51000 Rijeka
[2] Department of Environmental Health Sciences, SUNY Albany, Albany, New York Area, USA

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Alebić-Juretić, A.[1]

EU-HR RAZLIKOVNI POJMOVNIK U MJERENJU KVALITETE ZRAKA

Ključne riječi: *kvaliteta zraka, EU direktiva, nacionalni propisi*

Približavanjem Hrvatske Europskoj uniji pristupilo se harmonizaciji i zakonodavstva na području zaštite okoliša, odnosno zaštite zraka. U radu će se usporediti odrednice našeg Zakona o zaštiti zraka (NN 133/11) s europskom Direktivom 2008/50 te Aquilom (2009) u pogledu umjeravanja i održavanja opreme te validacije rezultata mjerenja. Iz teško dokučivih razloga, ova je harmonizacija rezultirala nacionalnom regulativom koja je u mnogim segmentima upravo suprotna izvornim propisima i važećoj europskoj praksi.

[1] Nastavni Zavod za javno zdravstvo/Medicinski fakultet Sveučilišta u Rijeci, Krešimirova 52a , 51000 Rijeka

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Alebić-Juretić, A.[1]

EU-HR DIFFERENTIAL DICTIONARY IN AIR POLLUTION MONITORING

Keywords: *air quality, legislation, harmonization*

The process of approaching the European Union comprised also the harmonization of legislation regarding environmental issues, i.e. clean air acts. In this work the provisions of Croatian Clean Air Act (NN 133/11) will be compared with the corresponding items in European Directive 2008/50 and Aquila (2009) regarding the role of national and local networks for air quality monitoring, the needs for accreditation, equipment calibration and maintenance and validation of raw data. For the unknown reasons, this harmonization resulted with national regulations being opposite to the original European legislation and practice.

[1] Teaching Institute of Public Health/ School of Medicine, University of Rijeka, Krešimirova 52a, 51000 Rijeka

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Alebić-Juretić, A.[1]

POLICIKLIČKI AROMATSKI UGLJIKOVODICI U LEBDEĆIM ČESTICAMA GRADA RIJEKE

Ključne riječi: *lebdeće čestice, policiklički aromatski ugljikovodici (PAU), izvori PAU*

Iako je određivanje pojedinačnih policikličkih aromatskih ugljikovodika (PAU) započelo u Rijeci već početkom osamdesetih, ova su se mjerenja povremeno provodila tijekom devedesetih godina, dok je sustavno praćenje započelo tek 2001. godine. Dnevne koncentracije pojedinačnih PAU određivale su se u ukupnim lebdećim česticama (ULČ) do 2006. godine, kad se prešlo na uzorkovanje PM_{10}. U radu su prikazani rezultati desetgodišnjih mjerenja ovih spojeva. Rezultati za 2010 godinu uspoređeni su s onima dobivenim za prometnu stanicu, gdje se ovi spojevi određuju od srpnja 2008. godine. Uzorci lebdećih čestica (ULČ i PM_{10}) sakupljeni su na filtrima pomoću uzorkivača velikih volumena zraka s odgovarajućim ulazima zraka, postavljenom na krovu zgrade Zavoda (20 m n.m.- Postaja 1). Prometna postaja za praćenje kvalitete zraka smještena je u prometnoj ulici u širem centru grada, na 1.6 km udaljenosti od zgrade Zavoda (Postaja 2). Za kvantitativno određivanje pojedinih PAU korišten je HPLC sistem uz UV/VIS-fluorescentni detektor. Koncentracije pojedinačnih PAU pokazuju trend pada tijekom desetgodišnjeg razdoblja. To je posljedica smanjenja emisija, korištenja čišćeg goriva te vozila s katalizatorom. Iako se radi o različitom tipu međusobno udaljenih postaja na različitim visinama uzorkovanja, koncentracije pojedinih PAU u PM_{10} vrlo su slične i pokazuju dobru korelaciju među stanicama. Za objašnjenje ove pojave potrebna su daljnja ispitivanja, s posebnim osvrtom na meteorologiju. Profili pojedinih PAU ukazuju da je glavni izvor PAU diesel gorivo na obje postaje, čemu je vjerojatni uzrok transport u/iz luke.

[1] Nastavni Zavod za javno zdravstvo/Medicinski fakultet Sveučilišta u Rijeci, Krešimirova 52a , 51000 Rijeka

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Alebić-Juretić, A.[1]

POLYCYCLIC AROMATIC HYDROCARBONS IN SUSPENDED PARTICULATES FROM THE URBAN ATMOSPHERE OF RIJEKA

Keywords: *suspended particulates, polycyclic aromatic hydrocarbons (PAH), PAH sources*

Though determination of individual PAHs in the urban atmosphere of Rijeka started already in early eighties, these measurements were performed occasionally during the nineties, while the systematic measurements of these pollutants in total suspended particulates (TSP) started only in 2001. Since mid-2006 PAHs are determined in PM_{10} fraction. The results of 10-years survey of airborne PAHs are presented. The results for 2010 are compared with those obtained at traffic monitoring site in the same wider city centre, running the PAHs analyses since June 2008. Samples of suspended particulates (TSP and PM_{10}) were collected on filters on the roof of the Institute building (20 m a.s.l.) with high-volume sampler, supplied with adequate inlet (Site 1). Traffic monitoring station (as a part of national network) is located approx. 1.6 km east from the Institute building in the busy street (Site 2). The individual PAHs were determined by HPLC with UV/VIS-fluorescence detector. The results of PAHs measurements in TSP/PM_{10} at Site 1 show a constant decline of total PAHs over the last decade. This is the result of reduced industrial emissions, improved quality of fuel and use of catalytic converters in vehicles. Although sampled at two distant locations, at different height, the PAHs concentrations in PM_{10} are very similar, showing good correlations between both sites. Further work is required to clarify this observation. According to the PAHs profiles, diesel vehicles are the principal sources of airborne PAHs at both sites, presumably due to the intense transport to/from the nearby harbour.

[1] Teaching Institute of Public Health/ School of Medicine, University of Rijeka, Krešimirova 52a , 51000 Rijeka

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Bošnjak, D.[1], Dolšak, L.[1] i Tarnik, T.[2]

GOSPODARENJE KONTROLIRANOM TVARI FREON-22 NA PRIMJERU SERVISA KLIMATIZACIJSKIH UREĐAJA

Ključne riječi: *ozonski sloj, Freon-22, klimatizacijski uređaj, ovlašteni serviser*

Ministarstvo zaštite okoliša i prirode (MZOIP) nadležno je za provedbu Montrealskog protokola u Republici Hrvatskoj. Prihvaćanjem Montrealskog protokola ostvareni su preduvjeti za postupno ukidanja potrošnje tvari koje oštećuju ozonski sloj. Zakonski propisi u RH kojima se uređuje područje gospodarenja tvarima koje oštećuju ozonski sloj su Zakon o zaštiti zraka (NN 130/11) i Uredba o tvarima koje oštećuju ozonski sloj i fluoriranim stakleničkim plinovima (NN 92/2012).
U ovom radu analiziran je postojeći sustav gospodarenja kontroliranom tvari kemijskog naziva klorodifluorometan-22 (Freon-22) u RH sa stajališta tvrtke ovlaštenog servisera klimatizacijskih uređajima. Pod sustavom gospodarenja Freonom-22 u RH autorice podrazumijevaju edukaciju zaposlenika tvrtki ovlaštenih servisera klimatizacijskih uređaja o načinu gospodarenja Freonom-22, pristup informacijama vezano uz mogućnosti korištenja Freona-22 nakon ulaska RH u EU, zamjenskim tvarima koje ne oštećuju ozonski sloj, a mogu se koristiti umjesto Freona-22. U radu su na temelju ankete u kojoj su sudjelovale tvrtke serviseri klimatizacijskih uređaja predložene aktivnosti za unaprjeđenje sustava gospodarenja kontroliranom tvari Freon-22.

[1] Visoka škola za sigurnost s pravom javnost, Ivana Lučića 5, 10000 Zagreb
[2] Hrvatska elektroprivreda d.d., Sektor za održivi razvoj i unaprjeđenje kvalitete, Ulica grada Vukovara 37 Zagreb

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Bošnjak, D.[1], Dolšak, L.[1] and Tarnik, T.[2]

FREON 22 CONTROLLED SUBSTANCE MANAGEMENT IN THE EXAMPLE OF AIR CONDITIONER MAINTENANCE

Keywords: *air conditioner, authorized maintenance, Freon 22, ozone layer*

The Ministry of Environmental and Nature Protection is in charge of the implementation of the Montreal Protocol in the Republic of Croatia. By accepting the Montreal Protocol, conditions were met for the progressive elimination of consumption of ozone layer-damaging substances. The legal requirements in the Republic of Croatia regulating ozone layer-damaging substance management are the Air protection act (NN 130/11) and the Regulation on ozone layer-damaging substances and fluorinated glasshouse gases (NN 92/2012). This paper presents an analysis of the existing system of controlled substance management for chlorodifluoromethane r-22 (Freon 22) in the Republic of Croatia, from the point of view of an authorized air conditioner maintenance company. By addressing Freon 22 management system in the Republic of Croatia, the authors understand the education of authorized air conditioner maintenance company employees on the ways of Freon 22 management, access to information concerning to the possibilities of Freon 22 use after the accession of the Republic of Croatia to the European Union, as well as substitute substances, which are not harmful to the ozone layer and can be used instead of Freon 22. Based on a survey of air conditioner maintenance companies, the paper proposes activities for improving the Freon 22 controlled substance management system.

[1] College of Applied Sciences in Safety, Accredited, Ul. Ivana Lučića 5, Zagreb, Croatia
[2] Hrvatska elektroprivreda d.d., Sustainable development and quality improvement sector, Ulica grada Vukovara 37, Zagreb, Croatia

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Peroš-Pucar, D.[1], Ivandić, A.[1], Pucar, B.[1], Ivić, I.[1] i Mitić, B.[2]

MEĐUDJELOVANJE DINAIKE PELUDNIH ALERGENA I ONEČIŠĆIVAČA ZRAKA GRADA ZADRA (SJEVERNA DALMACIJA, HRVATSKA)

Ključne riječi: *aerobiologija, peludni alergeni, onečišćivači zraka, korelacije, Zadar (Hrvatska)*

Onečišćenje zraka i prisutnost peludnih zrnaca u zraku, kao vrlo značajnih vanjskih alergena, te njihova interakcija povećavaju rizik od osjetljivosti i uzrokuju pojavu simptoma alergijske reakcije. S obzirom na sve veći broj osoba koje pate od polinoza, cilj ovog istraživanja bio je prikazati spektar peludnih zrnaca i kvalitetu zraka grada Zadra (Hrvatska, Sjeverna Dalmacija) te utvrditi povezanost između onečišćivača zraka i najzastupljenijih peludnih zrnaca. Aerobiološko istraživanje provedeno je u razdoblju od 2006. do 2009. godine pomoću volumetrijskog sedmodnevnog uzorkivača tipa Hirst. Kvalitativna i kvantitativna analiza mikroskopskih preparata provedena je standardnim postupkom prema EAN/REA. Zabilježena su peludna zrnca 62 svojte, s ukupnom koncentracijom od 179 928 peludnih zrnaca /m^3 zraka. Najzastupljenije svojte s udjelom većim od 1% su: Cupressaceae/Taxaceae, Urticaceae, Olea sp., Pinus sp., Betula sp., Platanus sp., Poaceae, Ambrosia sp., Quercus sp., Salix sp. i Fraxinus sp. U zraku dominiraju peludna zrnca drveća (72,28%) od kojih su peludna zrnca porodice Cupressaceae/Taxaceae zastupljena s udjelom od 45,53%. Peludna zrnca porodice Urticaceae (22,03%) su najzastupljenija peludna zrnca korova. Praćenje kakvoće zraka na području grada Zadra provedeno je u razdoblju od 2006. do 2008. godine. Mjereni onečišćivači zraka su SO_2 i crni dim. Koncentracija SO_2 ($\mu g/m^3$) određena je acidimetrijskom metodom standardiziranim britanskim postupkom za rutinsko određivanje SO_2 u zraku. Koncentracija crnog dima ($\mu g/m3$) određena je metodom fotometrijskog mjerenja. Za vrijeme istraživanog razdoblja koncentracija SO_2 iznosila je 39,7 $\mu g/m^3$ i crnog dima 9,8 $\mu g/m^3$. Prema prosječnim vrijednostima koncentracija promatranih onečišćivača kvaliteta zraka grada Zadra pripada prvoj kategoriji. Korelacija onečišćivača zraka i koncentracije peludnih alergena je statistički značajna, pozitivna između onečišćivača zraka i peludnih alergena porodica Cupressaceae /Taxaceae te svojti Pinus sp. i Platanus sp., dok je utjecaj onečišćivača na peludne alergene porodice Poaceae negativan.

[1] Zavod za javno zdravstvo Zadar, Kolovare 2, Zadar, Hrvatska
[2] Sveučilište u Zagrebu, PMF, Biološki odsjek, Botanički Zavod s Botaničkim vrtom, Marulićev trg 9a, 10000 Zagreb, Hrvatska

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Peroš-Pucar, D.[1], Ivandić, A.[1], Pucar, B.[1], Ivić, I.[1] and Mitić, B.[2]

INTERACTION BETWEEN ALLERGENIC POLLEN DYNAMICS AND AIR POLLUTANT IN THE CITY OF ZADAR (NORTH DALMATIA, CROATIA)

Keywords: *aerobiology, allergenic pollen, air pollution, correlations, Zadar (Croatia)*

Growing air pollution and the presence of pollen grains in the air, as the very important outdoor allergen and their interaction increase the risk of sensibility and cause the appearance of symptoms of allergic reactions. Considering of that and increasing number of people who suffers of polinosis, the aim of this study was to present the pollen spectrum and air quality in city of Zadar (Croatia, North Dalmatia) and to determine the correlations between air pollutant and the most abundant pollen grains. The aerobiological study was carried out during 2006-2009 period by a Hirst-type, seven day volumetric sampler. Quantity and quality examination of microscopically slides were maintained by the standard methodology recommended by Spanish Aerobiological Network-EAN/REA. Pollen grains of 62 different taxa were identified with total concentration of 179 928 pollen grains in m^3 of air. The most abundant taxa with portion of pollen grains higher than 1% were: Cupressaceae/Taxaceae, Urticaceae, Olea sp., Pinus sp., Betula sp., Platanus sp., Poaceae, Ambrosia sp., Quercus sp., Salix sp. and Fraxinus sp. In the air dominate pollen grains of tree (72, 28%) represented by Cupressaceae/Taxaceae family with the portion of 45, 53%. Pollen grains of Urticaceae family (22, 03%) are the most abundant pollen grains of weeds. The monitoring of air quality was carried out during 2006-2008. Air pollutant such as SO_2 and black smoke were determinate. Acidimetric method, standard British method for routine determination of SO_2 ($\mu g/m^3$) was used. Concentration of black smoke ($\mu g/m^3$) was measured by photometric method. During the studied period an average concentration of SO_2 was 39,7 $\mu g/m^3$ and of black smoke was 9,8 $\mu g/m^3$ .According the average concentration of studied air pollutant air quality belongs to I category. Correlation between air pollutant and pollen concentration were statistically significant: influence on pollen grains of Cupressaceae/Taxaceae, Pinus sp. and Platanus sp. was positive, while on pollen grains of Poaceae family was negative.

[1] Public Health Institute Health Ecology Service, Zadar, Kolovare 2, Zadar
[2] University of Zagreb, Faculty of Science, Department of Biology, Marulićev trg 9a, Zagreb

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Marović, G.[1], Senčar, J.[1], Petrinec, B.[1], Babić, D.[1] i Šoštarić, M.[1]

IZLOŽENOST PROSJEČNOG STANOVNIKA HRVATSKE ^{7}BE U ZRAKU

Ključne riječi: *radioaktivne tvari u zraku, berilij, efektivna doza udisanjem*

Prisutnost radioaktivnih tvari u zraku na pojedinim mjestima Hrvatske prati se od 1962. godine do danas u sklopu programa praćenja stanja radioaktivnosti životne sredine u Republici Hrvatskoj. Neprekidno se prosisava zrak kroz plavi Schneider-Poelman i glass-fiber filter na visini jedan metar iznad tla, a od 2008. godine i kroz celulozne filtre. Određivanje radionuklida u zraku provodi se visokorezolucijskom gamaspektrometrijom, akreditiranom metodom prema zahtjevima norme HRN EN ISO/IEC 17025:2007. Određuju se fisijski (umjetni, antropogeni) radionuklidi i oni prirodni, terestrijalnog i kosmogenog porijekla. Berilij, ^{7}Be, γ emiter, prirodni je radionuklid koji nastaje u visokim slojevima atmosfere pod utjecajem kozmičkoga zračenja. Vrijeme poluraspada ^{7}Be je pedeset i tri dana, pripada III. skupini radionuklida srednje radiotoksičnosti. Vrijednosti koncentracija aktivnosti ^{7}Be u zraku jedne su od najvećih iznosom, i do dva, tri reda veličine veće su od onih npr. ^{40}K odnosno ^{137}Cs. U posljednjih dvadeset godina u zraku Zagreba koncentracije aktivnosti ^{7}Be kretale su se uz povremene skokove i padove oko srednje vrijednosti od 4,4 ± 2,1 mBqm^{-3}, dok su one u zraku Zadra iznosile 3,1 ± 1,2 mBqm^{-3}. Testiranjem značajnosti razlike prosječnih vrijednosti ustanovljeno je da se vrijednosti koncentracija aktivnosti ^{7}Be u Zagrebu i Zadru ne razlikuju statistički značajno. Izmjerene vrijednosti koncentracija aktivnosti ^{7}Be poslužile su za procjenu efektivne doze koju bi udisanjem primio odrasli stanovnik Hrvatske, odnosno Zagreba i Zadra. Zbog relativno niske radiotoksičnosti, doprinos efektivnoj dozi udisanjem u zraku prisutnog ^{7}Be je mali; procijenjene efektivne doze primljene udisanjem ^{7}Be kreću se od 1,4 do 2 nSv godišnje.

[1] Institut za medicinska istraživanja i medicinu rada, Zagreb, Ksaverska cesta 2

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Marović, G.[1], Senčar, J.[1], Petrinec, B.[1], Babić, D.[1] and Šoštarić, M.[1]

EXPOSURE OF AVERAGE INHABITANT OF CROATIA TO ^{7}BE IN AIR

Keywords: *radioactive substances in air, beryllium, effective dose by inhalation*

The presence of radioactive substances in air has been monitored at particular places in Croatia ever since 1962, which has been part of the programme of monitoring the state of environmental radioactivity in the Republic of Croatia. Air is continuously filtered through a blue Schneider-Poelman filter and a glass-fiber filter positioned 1m above the ground, and since 2008 this has been performed using cellulose filters as well. Determination of radionuclides in air is carried out by means of high-resolution gamma-ray spectrometry, accredited according to the HRN EN ISO/IEC 17025:2007 standard. We determine fission (artificial, anthropogenic) radionuclides together with those of terrestrial and cosmogenic origin. Beryllium, ^{7}Be, which is a gamma emitter, is a naturally-produced radionuclide the nucleosynthesis of which occurs in higher atmosphere under the influence of cosmic rays. The half-life of ^{7}Be is fifty-three days, it belongs to group III of radionuclides of medium radiotoxicity. Activity concentration of ^{7}Be in air is among the highest of all radionuclides, exceeding that of, e.g., ^{40}K or ^{137}Cs, by two to three orders of magnitude. In the last twenty years, activity concentration of ^{7}Be in Zagreb air has been about 4,4 ± 2,1 mBqm^{-3}, with occasional departures, whereas that in Zadar has been 3,1 ± 1,2 mBqm^{-3}. By testing the significance of the difference between the above mean values, we conclude that there is no statistically significant difference between the activity concentrations in Zagreb and Zadar. Measured values of the activity concentrations of ^{7}Be have been utilised in an assessment of the effective dose absorbed through inhalation by an adult inhabitant of Croatia, i.e., Zagreb and Zadar. Due to the relatively low toxicity of ^{7}Be, its contribution to the effective dose originating in inhalation is small; we estimate it at 1.4 to 2 nSv per year.

[1] Institute for medical research and occupational health, Zagreb, Ksaverska cesta 2

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Majić, I.[1] i Krivohlavek, A.[1]

USPOREDBA KONCENTRACIJA SO_2 U GRADSKOJ ZONI I ODLAGALIŠTU OTPADA GRADA ZAGREBA

Ključne riječi: *SO_2, kisele kiše,polutant zraka, urbana sredina,odlagalište otpada*

Jedan od najčešćih polutanata zraka je sumporni dioksid. Nastaje kao posljedica sagorijevanja fosilnih goriva bogatih sadržajem sumpora. Više od 90 % sumpora iz goriva emitira se u obliku sumpornog dioksida (SO_2). Glavni je uzročnik nastajanja tzv. kiselih kiša i relativno se kratko vrijeme zadržava u atmosferi (nekoliko dana).U određenim vremenskim razdobljima (zimi, zbog zagrijavanja) stalno je prisutan u zraku naseljenih mjesta. Štetno djeluje na organizam čovjeka, naročito na disajni trakt.

Svrha ovog rada bila je analiza dnevnih varijacija koncentracija SO_2 u gradskoj zoni urbane sredine i na odlagalištu otpada Jakuševec te usporedba koncentracija navedenog polutanta na navedenim područjima.

Koncentracije sumpornog dioksida (SO_2) bile su mjerene metodom ultra-violetne fluoroscencije, mjernim instrumentima smještenim u automatskim postajama na lokaciji Mirogojska c. 16, na udaljenosti 5 m od prometnice i naselju Jakuševec u neposrednoj blizini odlagališta otpada.

Prosječne 24 satne koncentracije sumpornog dioksida (SO_2) bile su najviše u zimskom razdoblju i to na Jakuševcu (11-51 $\mu g/m^3$ zraka) dok su u Mirogojskoj izmjerene znatno niže vrijednosti i kretale su se (1-37 $\mu g/m^3$ zraka). Srednja vrijednost iznosila je 11 $\mu g/m^3$ za Mirogoj, odnosna 19 $\mu g/m^3$ za Jakuševec. U ljetnom periodu koncentracije su se kretale između (1-12 $\mu g/m^3$ zraka) na Mirogoju odnosno (1 -25 $\mu g/m^3$ zraka) na Jakuševcu, dok je srednja dnevna koncentracija iznosila 4 $\mu g/m^3$ za Mirogojsku, odnosno 17 $\mu g/m^3$ na Jakuševcu.

Rezultati ovoga rada pokazuju da su za sjeverni urbani dio grada Mirogoj koncentracije sumpornog dioksida (SO_2) značajno niže i u zimskom i u ljetnom razdoblju u odnosu na Jakuševec. Važno je napomenuti da su na obje lokacije koncentracije znatno niže od granične vrijednosti (GV) za navedeni polutant.

[1] Zavod za javno zdravstvo"Dr.Andrija Štampar",Mirogojska 16,Zagreb

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Majić, I.[1] and Krivohlavek, A.[1]

COMPARISON OF SO_2 CONCENTRATIONS IN URBAN AREA AND LANDFILL IN THE ZAGREB CITY

Keywords: *SO_2, acid rain, air pollutant, urban environment, landfill*

One of the most common air pollutants is sulphur dioxide. It occurs as a result of burning fossil fuels rich in sulphur. More than 90% of sulphur in the fuel is emitted in the form of SO_2. It is the main cause of the formation of the so-called acid rain and remaining relatively short time in the atmosphere (a few days). At certain time periods (in winter, due to heating) is constantly present in the air of towns. It has adversely effect on the human body, especially the respiratory tract.

The purpose of this study was to analyse the diurnal variations of concentrations of SO_2 in the residential area of urban environment and the landfill Jakuševec and compare the concentrations of this pollutant in these areas.

SO_2 concentrations were measured using ultra-violet fluorescence, measuring instruments placed in the automatic stations on location Mirogojska str. 16, at a distance of 5 m from the road and the housewarming Jakuševec near landfills.

Average 24-hour SO_2 concentrations were highest in winter and in the Jakuševac (11-51 $\mu g/m^3$ air) while in Mirogojska measured significantly lower values ranged (1-37 $\mu g/m^3$ air). Average value was 11 $\mu g/m^3$ for Mirogoj, and 19 $\mu g/m^3$ for Jakuševec. In summer concentrations were ranged between (1-12 $\mu g/m^3$ air) at Mirogoj and (1-25 $\mu g/m^3$ air) on Jakuševac, while the average daily concentration reached 4 $\mu g/m^3$ for MIROGOJSKA or 17 $\mu g/m^3$ in the Jakuševac.

Results of this study shows that in the northern residential part of the city, Mirogoj, average concentrations of SO_2 were significantly lower in the winter and in the summer season compared to Jakuševec. It should be pointed that in both locations concentrations were much lower than the limit value for the specified pollutant.

[1] Institute of Public Health "Dr.Andrija Štampar"

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Sikora , M.[1], Šušić, Z.[1], Santo, V.[1] i Valek, M.[1]

KRETANJE KONCENTRACIJE AMBROZIJE U OSJEČKO-BARANJSKOJ ŽUPANIJI OD 2010.-2012. GODINE

Ključne riječi*: Osječko-baranjska županija***,** *ambrozija, pelud, monitoring*

Ambrozija (Ambrosia artemisiifolia L.) tijekom perioda polinacije stvara velike količine peludi koja kod osjetljivih osoba može izazvati simptome alergije – polinoze.
Zbog sve većeg broja ljudi osjetljivih na pelud ambrozije, tijekom 2001 godine se započelo sa mjerenjem koncentracije peludi na području grada Osijeka, koje traje već dvanaest godina. 2009. godine monitoring alergene peludi u zraku je proširen na još tri postaje u Osječko-baranjskoj županiji: Našice, Đakovo i Beli Manastir.
Cilj ovoga rada bio je utvrditi oscilacije u koncentracijama peludnih zrnaca biljke ambrozije u vremenskom periodu od 2010-2012 godine na području Osječko-baranjske županije.
Mjerenje se obavlja Burkard-ovim volumetrijskim aparatom, a izražava se brojem peludnih zrnaca/ m^3 zraka.
Tijekom 3 godine mjerenja koncentracija peludi ambrozije u zraku je varirala, a svoju maksimalnu vrijednost je imala u 2011 godini na mjernoj postaji Našice, koja je iznosila 17492 peludnih zrnaca /m^3 zraka, a najniža koncentracija peludnih zrnaca zabilježena je 2010 godine na mjernoj postaji u Belom Manastiru i iznosila je 2309 peludnih zrnaca ambrozije (Burkard-ov volumetrijski aparat na mjernoj postaji Beli Manastir je bio u kvaru u razdoblju od 14.07.2010. do 08.09.2010.).
Najviše dnevne koncentracije peludi ambrozije su bile tijekom prijepodnevnih sati. Mjerenja pokazuju da je pelud ambrozije prisutna u zraku oko tri mjeseca.
Na rezultate mjerenja koncentracije peludi utječu meteorološke prilike, ruža vjetrova i mjere koje se provode u cilju smanjenja površina zakorovljenih ambrozijom.
Od samog početka praćenja peludi u zraku, razvijena je vrlo dobra suradnja s Udrugom za borbu protiv alergijskih bolesti Osijek, lokalnom samoupravom i tvrtkama koja vrše košnju ambrozije. Obavljena je edukacija inkasatora i komunalnih redara o prepoznavanju biljke, tiskani leci sa fotografijom ambrozije, kliničkim znacima alergije i uputama za pravilno suzbijanje korova, uspostavljen je ambrozijski telefon, održano je niz sastanaka sa tvrtkama koja su zadužena za održavanje cesta, nasipa HŽ u cilju da se košnje nasipa usklade sa vremenom cvjetanja ambrozije, izrađen projekt za raspoznavanje parcela, te identifikacija vlasnika pomoću GPS aparata, uspostavljena je suradnja s laboratorijima u Mađarskoj, Sloveniji, Srbiji i Hrvatskoj.
Rezultati mjerenja se koriste za izradu regionalnih peludnih kalendara, planiranje preventivnih akcija suzbijanja, pravodobno liječenje oboljelih, sve u svrhu sveobuhvatnog rješavanja ovog javnozdravstvenog i socioekonomskog problema.
Podaci o početku pojavljivanja peludi u zraku pomažu pacijentima i liječnicima primijeniti preventivne mjere i odgovarajuću terapiju.

[1] Zavod za javno zdravstvo Osječko baranjske županije, Osijek, F. Krežme 1

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Sikora , M.[1], Šušić, Z.[1], Santo, V.[1] and Valek, M.[1]

VARIATION OF RAGWEED POLLEN CONCENTRATION IN OSIJEK-BARANYA COUNTY DURING 2010-2012

Keywords: *Osijek-Baranya County, ragweed, pollen, monitoring*

Ragweed (Ambrosia artemisiifolia L.) during the pollen seasons produce large amounts of pollen, who eliciting symptoms of pollen allergy in tetchy persons. Number of patients sensitive to ragweed pollen each year is increasing. 2001 year starts measurement the concentration of pollen in the city of Osijek, which continued through 12 years. In 2009. Osijek-Baranya County got three more stations for monitoring pollen allergens in the air: Našice, Đakovo, Beli Manastir.

The aim of this study was to determine variations in the concentrations of pollen grains of ragweed plants in the period of three years in the Osijek-Baranya County.

Pollen was collected with Burkards volumetric spore trap, and expressed by the number of pollen grains / m^3 air.

During 3 years measuring the concentration of ragweed pollen in the air varied, and maximum value was in 2011 at the measuring station Našice, with the concentration of 17492 pollen grains, the lowest concentration of pollen grains was recorded in 2010 at the measuring station Beli Manastir with the concentration of 2309 pollen grains (Burkards volumetric spore trap at Beli Manastir station was broken in the period 14.07.2010 to 08.09.2010.).

The highest daily concentration of ragweed pollen have been during the morning hours. Measurements have shown that ragweed pollen is present in the air during three months.

To the results of measurements concentration of pollen affect weather conditions, wind rose, and the activities that reduce surface that are overgrown with ragweed.

Since the start of monitoring airborne pollen in the air, it was developed very good cooperation with the Association for the fight against allergic diseases Osijek, local governments and companies that perform cutting ragweed.

Together they organized round tables with the theme "Living without ragweed", made the education fee collectors and the communal monitors that they can identify plant. Printed flyer with photograph of ragweed, the clinical symptoms of allergy and instructions for proper weed control, was established ragweed phone, held a series of meeting with companies who are responsible for maintenance of roads, embankments HŽ in order to be move weed before flowering, created a project for recognizing pitches and identify the owner by using GPS devices, made the collaboration with laboratories in Hungary, Slovenia, Serbia and other cities in Croatia.

The measurement results are used to create regional pollen calendar, planning of preventive action control, well-timed treatment of patients, all with purpose of a complete solution of this public health and socioeconomic problem.

Information on pollen concentration helps allergic patients and allergologists develop preventive measures and therapy.

[1] Public Health Institute of Osijek – Baranya County, Osijek, Hrvatska

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Žužul, S.[1], Rinkovec, J.[1], Pehnec, G.[1] i Vađić, V.[1]

UKUPNA TALOŽNA TVAR I TEŠKI METALI NA PODRUČJU NACIONALNOG PARKA PLITVIČKA JEZERA

Ključne riječi*: atmosfersko taloženje, ICP-MS*

Plitvička jezera najstariji su nacionalni park u Hrvatskoj, a obuhvaćaju površinu od 296 km^2. Zahvaljujući svojoj prirodnoj jedinstvenosti 1979. godine uvršteni su na UNESCO-ov Popis svjetske kulturne i prirodne baštine. U cilju očuvanja biološke raznolikosti nacionalnog parka i određivanja specifičnih izvora onečišćenja uzrokovanih ljudskom aktivnošću, 2011. godine započet je projekt "Monitoring organskih i anorganskih onečišćenja u okolišu NP Plitvička jezera". U sklopu navedenog projekta, razina onečišćujućih tvari u zraku praćena je sakupljanjem i analizom uzoraka ukupne taložne tvari (UTT).

Cilj ovog rada bio je odrediti razine UTT i metala u UTT te ispitati postoje li razlike obzirom na moguće antropogene utjecaje (naseljenost, poljoprivredu, utjecaj vojnog poligona Slunj) te obzirom na različite zone nacionalnog parka (zona naselja, zone aktivne zaštite staništa – travnjaka i šumskih ekoloških sustava, zone najstrože zaštite). Uzorci UTT sakupljani su uređajem po Bergerhoffu na četiri lokacije unutar nacionalnog parka u razdoblju od travnja 2011. godine do prosinca 2012. godine. Sakupljani su mjesečni uzorci UTT (30 ± 2 dana). Ukupna taložna tvar određena je gravimetrijski, a sadržaj olova, kadmija, nikla, arsena, talija, mangana, bakra i cinka određen je spektrometrijom masa uz induktivno spregnutu plazmu (ICP-MS).

Rezultati pokazuju da je ukupna masa onečišćujućih tvari koja se prenosi iz zraka na površinu (vode, tlo, vegetaciju i drugo) u promatranom vremenskom razdoblju bila niska i iznosila je od 63,28 mg / m^2 d do 100,04 mg / m^2 d. Srednja vrijednost mase metala u UTT iznosila je 57,44 µg / m^2 d za Zn, 14,43 µg / m^2 d za Mn, 5,80 µg / m^2 d za Cu, 2,70 µg / m^2 d za Ni, 2,20 µg / m^2 d za Pb, 0,55 µg / m^2 d za As, 0,27 za Cd i 0,02 µg / m^2 d za Tl. Nije pronađena statistički značajna razlika mjerenih onečišćenja između različitih lokacija uzorkovanja, osim za olovo. Dobiveni rezultati usporedivi su s kontrolnom mjernom postajom smještenom izvan granica nacionalnog parka.

[1] Institut za medicinska istraživanja i medicinu rada, Ksaverska cesta 2, 10000 Zagreb

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Žužul, S.[1], Rinkovec, J.[1], Pehnec, G.[1] and Vađić, V.[1]

TOTAL DEPOSITED MATTER AND HEAVY METAL CONTENT AT PLITVICE LAKES NATIONAL PARK

Keywords: *atmospheric deposition, ICP-MS*

Plitvice Lakes National Park is the oldest national park in Croatia, with an area of 296 km^2. The exceptional natural uniqueness of this national park was recognized by UNESCO, which added it to the list of World Heritage in 1979. The scientific project "Monitoring of organic and inorganic pollutants at Plitvice Lakes National Park" started in 2011 with the aim to preserve the biodiversity of this national park and determine the specific sources of anthropogenic pollution. Air pollution was monitored by collecting and analysing total deposited matter (TDM).

The aim of this paper was to determine the TDM levels and its heavy metal content, as well as to investigate sources of pollution (human activity, agriculture, the impact of the Slunj military polygon) and the differences between concentrations present within individual zones of the national park (settlement zone, the zone of active protection of habitats – grasslands and forest ecosystems, the most stringent protection zone). Monthly samples of deposited matter were collected at four sampling sites within the national park from April 2011 to December 2012. Bergerhoff type samplers were used to collect the bulk deposition. The total deposited matter was determined gravimetrically, while metallic content (Pb, Cd, Ni, As, Tl, Mn, Cu, and Zn) was determined using inductively coupled plasma mass spectrometry (ICP-MS).

The results show that the total mass of pollutants transferred from the atmosphere to the surface (water, soil, vegetation, etc.) was low throughout the entire period of measurement and ranged from 63.28 mg / m^2 d to 100.04 mg / m^2 d. Mean concentrations of heavy metals in the TDM were 57.44 μg / m^2 d for Zn, 14.43 μg / m^2 d for Mn, 5.80 μg / m^2 d for Cu, 2.70 μg / m^2 d for Ni, 2.20 μg / m^2 d for Pb, 0.55 μg / m^2 d for As, 0.27 for Cd, and 0.02 μg / m^2 d for Tl. There was no statistically significant difference in the measured concentrations between the different sampling sites, except for Pb. The results are comparable with those from the control sampling site located outside the national park.

[1] Institute for Medical Research and Occupational Health, Ksaverska cesta 2, 10000 Zagreb

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Herceg Romanić, S.[1] i Klinčić, D.[1]

ORGANOKLOROVI SPOJEVI U IGLICAMA CRNOGORICE SKUPLJENIM U NP PLITVIČKA JEZERA

Ključne riječi: *onečišćenje atmosfere, PCB, organoklorovi pesticidi, crnogorica*

Organoklorovi pesticidi (OCP) i poliklorbifenili (PCB) postojana su organska zagađivala. Njihova proizvodnja i upotreba u većini zemalja je ograničena ili potpuno zabranjena. Svojstvo koncentriranja lipofilnih zagađivala iz atmosfere omogućava korištenje bilja kao pasivnog sakupljača koji pokazuje prosječnu zagađenost zraka na određenom mjestu.

Nacionalni park Plitvička jezera najstariji je i najpoznatiji nacionalni park u Hrvatskoj i uvršten je na UNESCO-ov Popis svjetske kulturne i prirodne baštine. Svrha istraživanja bila je istražiti raspodjelu OCP-a i PCB-a u uzorcima iglica crnogorice sakupljenih u NP Plitvička jezera na četiri različite lokacije u NP PJ i znanstveno istraživačkom poligonu Šumbar. Uzorci crnogoričnih iglica (Picea abies) skupljeni su u travnju 2011.

Od ukupno 209 kongenera PCB-a određivano je šest tzv. indikatorskih kongenera PCB-a (PCB-28, PCB-52, PCB-101, PCB-138, PCB-153, PCB-180), toksikološki značajni (PCB-77, PCB-126, PCB-169, PCB-105, PCB-114, PCB-118, PCB-123, PCB-156, PCB-157, PCB-167, PCB-189, PCB-170) te kongeneri PCB-60 i PCB-74. Od OCP-a istraživani su HCB, α-, β- i γ-HCH, p,p'-DDE, p,p'-DDD i p,p'-DDT. Svježe, narezane iglice (10 g) ekstrahirane su sa 20 mL smjese ψ (n-heksan, aceton)=50:50 mikrovalnom ekstrakcijom. Radni uvjeti: snaga – 1200 W, zagrijavanje 10 min do 115 °C, održavanje te temperature 20 min te zatim hlađenje 1 sat. Ekstrakti su pročišćeni postupkom opisanim u radu Herceg Romanić i Krauthacker (2004) i analizirani plinskom kromatografijom visokog razlučivanja prema uvjetima navedenim u istom radu.

Raspon masenih udjela OCP-a u jednogodišnjim iglicama iz NP PJ bio je od 0,04 do 0,93 ng g^{-1}, a PCB-a od 0 (ispod granice određivanja) do 0,11 ng g^{-1} svježih iglica. U dvogodišnjim iglicama, raspon OCP-a bio je od 0,07 do 1,58 ng g^{-1}, a PCB-a od 0 (ispod granice određivanja) do 0,1 ng g^{-1} svježih iglica.

Raspon masenih udjela OCP-a u jednogodišnjim iglicama sa znanstveno istraživačkog poligona Šumbar bio je od 0,04 do 0,63 ng g^{-1}, a PCB-a od 0 (ispod granice određivanja) do 0,07 ng g^{-1} svježih iglica. U dvogodišnjim iglicama, raspon OCP-a bio je od 0,06 do 0,67 ng g^{-1}, a PCB-a od 0 (ispod granice određivanj) do 0,1 ng g^{-1} svježih iglica.

Rezultati podupiru tezu da se danas razine organoklorovih spojeva vrlo sporo snižavaju ili se uopće ne mijenjaju usprkos zabrani i/ili ograničenju njihove uporabe. Do promjena razina organoklorovih spojeva dolazi zbog novog unosa u okoliš i/ili prijenosa na velike udaljenosti. Može se zaključiti da su razine organoklorovih spojeva niske.

Referenca: S. Herceg Romanić, B.Krauthacker, Bulletin of Environmental Contamination and Toxicology 72 (2004) 1203-1210.

Rezultati su proizašli iz projekta "Monitoring organskih i anorganskih onečišćenja u okolišu NP Plitvička jezera", potpora Javne ustanove Nacionalnog parka Plitvička jezera.

[1] Institut za medicinska istraživanja i medicinu rada, Ksaverska cesta 2, 10 000 Zagreb

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Herceg Romanić, S.[1] and Klinčić, D.[1]

ORGANOCHLORINE COMPOUNDS IN CONIFER NEEDLES COLLECTED IN PLITVICE LAKES NATIONAL PARK

Keywords: *PCBs, Organochlorine pesticides, Conifer, Atmospheric pollution*

Polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) are persistent organic pollutants. Their use was banned or restricted worldwide. Pine needles are considered to be among the best passive indicators of environmental pollution with organochlorine compounds because of their waxy surface which accumulate lipophilic compounds from the surrounding air.
Plitvice Lakes National Park is the oldest and the most famous national park in Croatia and belongs to the UNESCO World Heritage register. The aim of this study was to investigate the distribution of OCPs and PCBs in pine needles collected at four locations in Plitvice Lakes National Park and the research polygon and hunting preserve "Šumbar". Needle samples (Picea abies) were collected in April 2011 (Table 1).
Out of 209 PCB congeners, six indicator PCBs (PCB-28, PCB-52, PCB-101, PCB-138, PCB-153, PCB-180), toxicologically relevant PCB (PCB-77, PCB-126, PCB-169, PCB-105, PCB-114, PCB-118, PCB-123, PCB-156, PCB-157, PCB-167, PCB-189, PCB-170) and PCB-60, PCB-74 were analyzed. Following OCPs were analyzed: HCB, α-, β- and γ-HCH, p,p'-DDE, p,p'-DDD and p,p'-DDT.
Fresh, cutted needles (10 g) was extracted with n-hexane:acetone=50:50 (20 mL) using the Microwave Accelerated Reaction System for Extraction at 1200 W and temperature programme: heating 10 min until 115 °C, 20 min isothermally, cooling 60 min. Clean-up procedure and high resolution gas chromatography determination was described in paper of Herceg Romanić and Krauthacker (2004).
At Plitvice Lakes National Park, the concentration of OCPs ranged between 0.04 and 0.93 ng g^{-1} in one-year-old needles and between 0.07 and 1.58 ng $g^{-1}_{fresh\ needles}$ in two-year-old needles. The concentration of PCBs in one-year-old needles ranged between 0 (below determination limit) and 0.11 ng g^{-1} and between 0 (below determination limit) and 0.1 ng $g^{-1}_{fresh\ needles}$ in two-year-old needles.
At research polygon and hunting preserve "Šumbar, the concentration of OCPs ranged between 0.04 and 0.63 ng g^{-1} in one-year-old needles and between 0.06 and 0.67 ng $g^{-1}_{fresh\ needles}$ in two-year-old needles. The concentration of PCBs in one-year-old needles ranged between 0 (below determination limit) and 0.07 ng g^{-1} and between 0 (below determination limit) and 0.1 ng $g^{-1}_{fresh\ needles}$ in two-year-old needles.
Results suggest that the levels are decreasing very slowly or not at all. Random increase in PCB and OCPs levels might have been caused by a fresh input and/or long range transport. Overall, levels could be considered as low.
Reference: S. Herceg Romanić, B.Krauthacker, Bulletin of Environmental Contamination and Toxicology 72 (2004) 1203-1210.

This work was supported by Plitvice Lakes National Park (Project "Monitoring of Organic and Inorganic Pollutants in the Environment of Plitvice Lakes National Park")

[1] Institute for Medical Research and Occupational Health, Ksaverska c. 2, 10001 Zagreb, Croatia

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Špirić, Z.[1], Kušan, V.[1], Kremer, D.[2], Posarić, Z.[3], Ribarić, N.[4] i Nikolić, S.[5]

ISTRAŽIVANJE UTJECAJA OZONA NA RAST I UROD GRAHA (*PHASEOLUS VULGARIS*)

Ključne riječi: *ozon, grah, biomonitoring, ICP Vegetation, Hrvatska*

U radu će biti prikazani rezultati istraživanja utjecaja ozona na rast i urod graha (Phaseolus vulgaris) koja se provode u većem broju europskih država (i u Hrvatskoj) u okviru Međunarodnog Programa suradnje na proučavanju učinaka onečišćenja zraka na prirodnu vegetaciju i usjeve UNECE ICP Vegetation http://icpvegetation.ceh.ac.uk/research/Ozone.html
Koordinator istraživanja je Centar za ekologiju i hidrologiju (CEH) u Bangoru, Velika Britanija, a Oikon je hrvatski partner u Projektu.

Cilj istraživanja je:

- *identificirati opseg i intenzitet pojave vidljivog oštećenja graha (Phaseolus vulgaris) uzrokovanog ozonom diljem Europe uključivo pokusna polja u Hrvatskoj*
- *istražiti i kvantificirati smanjenje prinosa/uroda graha (Phaseolus vulgaris) u testnim lončanicama na ispitnim plohama u Hrvatskoj*
- *procijeniti ekonomske gubitke uzrokovane onečišćenjem ozonom*
- *uspostaviti bazu podataka i kreirati kartografski prikaz prostorne i vremenske raspodjele oštećenja graha (Phaseolus vulgaris) u Europi*

Rezultati istraživanja koje će biti provedeno tijekom 2013. na pokusnim poljima u Zagrebu, M. Lošinju, Jastrebarskom i Križevcima pomoći će u boljem razumijevanju brojnih i složenih problema koji su posljedica štetnog djelovanja ozona na vegetaciju na lokalnoj, regionalnoj i globalnoj skali.

[1] Oikon d.o.o. – Institut za primijenjenu ekologiju, Zagreb
[2] Farmaceutsko-biokemijski fakultet, botanički vrt "Fran Kušan", Zagreb
[3] Abies d.o.o., Rasadnik Lještaki, Bukovje Križevačko
[4] Osnovna škola "Ljubo Babić", Jastrebarsko
[5] Miomirisni otočki vrt, Mali Lošinj

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EFFECTS OF OZONE ON BEAN (*PHASEOLUS VULGARIS*)

Keywords: *ozone, bean, biomonitoring,* ICP Vegetation, Croatia

The paper presents research results of the impact of ozone on growth and yield of bean (Phaseolus vulgaris), which are implemented in a number of European countries (and in Croatia) under the International Cooperative Programme on studying the effects of air pollution on natural vegetation and crops (the UNECE ICP Vegetation http://icpvegetation.ceh.ac.uk/research/Ozone.html Research is coordinated by the Centre for Ecology and Hydrology (CEH) at Bangor, UK with Oikon Ltd. as Croatian partner.

The research aims to:

- *identify the scope and intensity of occurrence of visible damage to the bean (Phaseolus vulgaris) caused by ozone across Europe including field trials in Croatia*
- *facilitate the production of European maps showing where critical levels for ozone are exceeded;*
- *investigate and quantify the reduction in yield / yield of beans (Phaseolus vulgaris) in the test pots on the examined surfaces in Croatia*
- *estimate the economic losses caused by ozone pollution*
- *establish a database and create a cartographic representation of spatial and temporal distribution of damage to bean (Phaseolus vulgaris) in Europe*

The research results achieved during 2013 in field trials in Zagreb, Križevci, M. Lošinj and Jastrebarsko will help provide a better understanding and resolve numerous and complex problems that result from the harmful effects of ozone on vegetation at local, regional and global scale.

[1] Oikon d.o.o. – Institute for Applied Ecology, Zagreb
[2] Farmaceutsko-biokemijski fakultet, botanički vrt "Fran Kušan", Zagreb
[3] Abies d.o.o., Rasadnik Lještaki, Bukovje Križevačko
[4] Osnovna škola "Ljubo Babić", Jastrebarsko
[5] Miomirisni otočki vrt, Mali Lošinj