HRVATSKO UDRUŽENJE ZA ZAŠTITU ZRAKA
CROATIAN AIR POLLUTION PREVENTION ASSOCIATION

**INTERNATIONAL CONFERENCE AND 13TH CROATIAN SCIENTIFIC AND PROFESSIONAL MEETING**

# AIR PROTECTION 2023

**MEĐUNARODNA KONFERENCIJA I TRINAESTI HRVATSKI ZNANSTVENO-STRUČNI SKUP**

# ZAŠTITA ZRAKA 2023

Dubrovnik, Croatia
20th - 23rd September 2023

## PROCEEDINGS
## ZBORNIK RADOVA

# INTERNATIONAL CONFERENCE AND
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# AIR PROTECTION 2023

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## ZBORNIK RADOVA

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Institute for Medical Research and Occupational Health
Croatian Meteorological and Hydrological Service
European Federation of Clean Air and Environmental Protection Associations - EFCA
International Union of Air Pollution Prevention and Environmental
Protection Associations - IUAPPA

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# CONTENT

## FOREWORD

The Croatian Air Pollution Prevention Association (CAPPA), the main organizer of „Air Protection" conferences, 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. Organized activities in the field of air protection started in Croatia 50 years ago, following the foundation of the Yugoslavian Association for Clean Air in 1973 in Zagreb. The Yugoslavian Association for Clean Air was divided into sections according to each Republic. After reorganization in 1983, the Republic Section for Croatia became the Croatian Association for Air Protection, within the Yugoslavian Union of Air Protection Associations. When Croatia declared independence from Yugoslavia, the Association changed its name to the Croatian Air Pollution Prevention Association (CAPPA) and in the coming years joined the International Union of Air Pollution Prevention and Environmental Protection Association (IUAPPA) and The European Federation of Clean Air and Environmental Protection Association (EFCA). Over the years, CAPPA has had numerous activities related to air protection, among which we would like to point out twelve successful „Air Pollution" national conferences (since 1997, every odd year), the 14th International Conference on Air Quality – Assessment and Policy at Local, Regional and Global Scales organized in cooperation with IUAPPA in Dubrovnik in 2003, and ten workshops abroad (every even year since 2000). CAPPA members regularly offer professional help during the preparation of air pollution protection legislation.

On the 50th anniversary of organized activities in the field of air protection in Croatia and the 30th anniversary of CAPPA, it was our great pleasure to organize again an international conference, together with the 13th national „Air Protection" meeting. This 2023 conference was held in the Astarea hotel in Mlini near Dubrovnik and includes the following topics:

1 - Air quality management

2 - Air pollution sources and emissions

3 - Ambient air pollution monitoring

4 - Machine learning and air quality modelling

5 - Developing and testing measuring methods

6 - Health impacts of air pollution

7 - Indoor air quality, energy efficiency, and healthy buildings

8 - Climate and environmental impacts of air pollution

During the "Air Protection 2023" conference the following special events took place: the session "*New regime on air protection in Europe*" organised under the auspices of the EFCA, a special session organized by IUAPPA entitled "*Air quality strategies for liveable cities in a changing climate*" as well as the workshop "*A spotlight on indoor air quality*" organized by EDIAQI ("*Evidence driven indoor air quality improvement*") project consortium.

As in previous years, abstracts of all presentations of the International conference and 13th Croatian scientific and professional meeting "Air Protection 2023" were published in the Book of Abstracts. At the end of the Conference, all of the authors were invited to submit their presentations as full papers for the Proceedings of "Air Protection 2023". It is our great pleasure to present to you this Proceedings, which contain 16 full paper manuscripts presented at the Conference, as well as appendix with presentations and posters.

The successful organization of the "Air Protection 2023" Conference and the publishing of these Proceedings would not have been possible without the great effort of the members of the Organizing, Scientific-Expert and Advisory Committee. We are particularly grateful to the Ministry of Environmental Protection and Green Transition and the Ministry of Science, Education and Youth, and express great appreciation to our co-organizers and sponsors, as well as to all who helped the organization of the Conference.

*Gordana Pehnec and Ranka Godec*

# FULL PAPERS

Oral presentation

**Darijo Brzoja, Jadranka Škevin-Sović**

# AIRQ – EXPANSION AND MODERNISATION OF THE NATIONAL NETWORK FOR CONTINUOUS AIR QUALITY MONITORING

## Abstract

*The project AIRQ – Expansion and Modernization of the National Network for Continuous Air Quality Monitoring aimed to enhance and optimize the air quality monitoring and management system in urban areas, designated zones, and agglomerations in Croatia. The primary beneficiary of the initiative was the Croatian Meteorological and Hydrological Service (DHMZ), with the Institute for Medical Research and Occupational Health (IMROH) as the project partner. The project was designed to support the implementation of air quality and environmental protection legislation, particularly Directive 2008/50/EC and the Air Protection Act (Official Gazette 127/19, 57/22). Its objectives included the development of integrated strategies and methodologies to evaluate, plan, and execute effective air quality control measures through the systematic measurement of key atmospheric parameters. Additionally, the project sought to advance monitoring programs for short-lived climate forcers (SCLFs) and to promote climate-sensitive measures aimed at reducing air pollution. Modernization efforts focused on meeting the mandatory minimum number of monitoring stations in designated zones and agglomerations and fulfilling obligations for the installation of EMEP (European Monitoring and Evaluation Programme) level 1 and level 2 stations to monitor a comprehensive range of pollutants. Furthermore, the project addressed the need to comply with data quality standards, including the replacement of non-compliant equipment with type-approved instruments (where such equipment is available) and ensuring the minimum required data coverage.*

**Keywords:** *air quality, national network, AIRQ*

## INTRODUCTION

Air pollution is recognized as one of the most significant environmental risks to human health, contributing to a wide range of adverse effects. It is a leading cause of cardiovascular and respiratory diseases, which, in severe cases, result in premature mortality. Despite substantial efforts to reduce anthropogenic emissions, polluted air remains a pressing concern, particularly in urban areas across Europe, including Croatia. The key pollutants impacting air quality in the region are particulate matter (PM), nitrogen dioxide ($NO_2$), and ground-level ozone ($O_3$). These pollutants are especially harmful to vulnerable population groups, such as the elderly, children, and individuals with pre-existing health conditions. Moreover, socio-economic disparities exacerbate exposure levels, with lower-income communities often disproportionately affected.

Beyond its impact on human health, air pollution has significant economic consequences, including reduced life expectancy, increased healthcare costs, and decreased productivity due to lost workdays. Air pollution also poses serious risks to vegetation and ecosystems. Pollutants such as ground-level ozone ($O_3$), ammonia ($NH_3$), and nitrogen oxides ($NO_2$) damage flora and fauna, degrade soil and water quality, and disrupt ecosystems. For instance, ground-level ozone inhibits the growth and development of crops and forests, reducing biodiversity. Nitrogen compound deposition contributes to acidification and eutrophication, altering species composition and enabling invasive species to thrive. These combined effects underscore the urgency of effective air quality monitoring and management systems (EEA, 2024).

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## DISCUSSION

The rising concentration of air pollutants is closely tied to increased anthropogenic activities. Addressing this challenge requires a systematic approach to air quality monitoring and management, particularly in urban areas, zones, and agglomerations. In Croatia, this need is met by the national network for continuous air quality monitoring, which has been significantly expanded and modernized through the project *AIRQ – Expansion and Modernization of the National Network for Continuous Air Quality Monitoring*. This comprehensive initiative, valued at €16,606,740, was co-financed by the European Regional Development Fund (85%) under the Operational Programme Competitiveness and Cohesion 2014-2020 and the Environmental Protection and Energy Efficiency Fund (15%). The primary objective was to improve Croatia's air quality management and monitoring system in line with Directive 2008/50/EC, ensuring compliance with European and national standards for environmental and public health protection. The primary beneficiary of the initiative was the Croatian Meteorological and Hydrological Service (DHMZ), with the Institute for Medical Research and Occupational Health (IMROH) as the project partner (AIRQ, 2024).

The *AIRQ* project addressed several critical needs:

1. **Expansion of Monitoring Infrastructure**: The project facilitated the modernization of 18 existing air quality monitoring stations and the construction of 6 new ones. This ensured compliance with the mandatory minimum number of monitoring points per zones and agglomerations, thereby enhancing spatial coverage.
2. **Data Quality Improvements**: Outdated equipment was replaced with type-approved instruments for pollutants where such standards exist. This upgrade was crucial for ensuring accurate, reliable, and internationally traceable data.
3. **Development of Modeling Capabilities**: A modeling system for estimating ground-level concentrations of pollutants was developed and operationalized. This system provides essential insights into pollutant dispersion patterns and enables more effective air quality management strategies.
4. **Laboratory Modernization**: The chemical laboratories of DHMZ and IMROH were equipped with advanced analytical instruments and auxiliary equipment. These upgrades support detailed analyses of particulate matter, air and precipitation samples, aiding compliance with the national monitoring program.
5. **Calibration and Standardization**: The calibration laboratory at DHMZ was equipped with state-of-the-art devices to ensure the traceability of air quality measurements to international standards. This step was instrumental in meeting data quality requirements and enhancing the credibility of monitoring results.

These interventions collectively established a robust air quality measurement and control system in Croatia, meeting European and national criteria for protecting human health and the environment.

## RESULTS AND ACHIEVEMENTS

The *AIRQ* project achieved several key outcomes, marking a significant improvement in Croatia's air quality monitoring capacity:

- **Comprehensive Population Coverage**: The share of the population in urban areas covered by air quality monitoring data increased from 50% to 100%.
- **Infrastructure Development**: Six new air quality monitoring stations were constructed, and eighteen existing stations were upgraded with modern, type-approved equipment (Figure 1, Figure 2).
- **Operational Modeling System**: A pollutant concentration estimation model was developed and implemented, providing valuable tools for forecasting and managing air quality (Figure 3).
- **Enhanced Laboratory Capabilities**: The chemical laboratories at DHMZ and IMROH were outfitted with new instruments for analyzing the chemical composition of suspended particles and precipitation, enabling more detailed environmental assessments.
- **Calibration Excellence**: The calibration laboratory was equipped to ensure that all air quality measurement devices meet international traceability standards, ensuring high-quality data.

One notable outcome of the project is Croatia's first official air quality forecast, derived from the applied modeling systems. This forecast, along with real-time and historical air quality data, is accessible to the public through dedicated platforms:

- Air Quality in the Republic of Croatia - portal of the Ministry of Environmental Protection and Green Transition (MEPGT, 2024)
- Air Quality Portal of the Croatian Meteorological and Hydrological Service (DHMZ, 2024)

**Figure 1.** Opuzen measuring station – National Network for Continuous Air Quality Monitoring


**Figure 2.** Modernized and newly built measuring stations as part of the National Network for Continuous Air Quality Monitoring

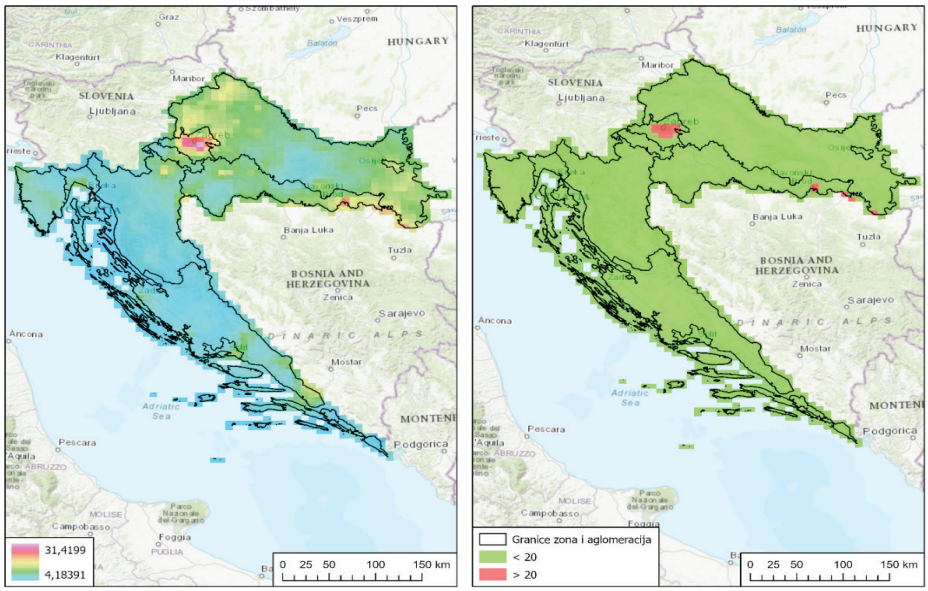


**Figure 3.** Left: $PM_{2.5}$ modeled annual mean concentration. Right: areas of $PM_{2.5}$ aceedances (limit value - 20 µg/m$^3$) given in red color. LOTOS - EUROS chemical transport model.

## CONCLUSIONS

Successfully completed in September 2023, the *AIRQ* project represents a milestone in advancing Croatia's capacity to monitor and manage air quality. All project indicators were met, including:

- Achieving full urban population coverage with air quality data.
- Constructing six new monitoring stations and modernizing eighteen existing ones.
- Developing and operationalizing a pollutant concentration estimation model.
- Equipping laboratories at DHMZ and IMROH with advanced analytical tools.
- Establishing a calibration laboratory capable of ensuring international traceability of air quality measurements.

The project's outcomes extend beyond compliance with EU directives, offering critical tools for mitigating air pollution and protecting public health. By integrating advanced monitoring technologies with public access to data, the project supports informed decision-making and fosters transparency. Moving forward, the insights and infrastructure developed through the *AIRQ* project will play a pivotal role in Croatia's efforts to address air quality and climate challenges effectively.

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Oral presentation

**Lucia Bustin, Torsten Tritscher, Sebastian H. Schmitt, Juergen Spielvogel, Oliver F. Bischof**

# ULTRAFINE PARTICLES (UFP) - RECENT TRENDS AND REGULATORY ACTIVITIES

## Abstract

*Recent studies reported that ultrafine particles (UFP) which are defined as particles equal or smaller than 0.1 µm, seem to be a better indicator of harmful air pollution in urban areas. Therefore, the measurement of the particle number concentration (PNC), which is most representative of UFP has gained much interest and importance. Based of scientific evidences World Health Organization (WHO) Global Air Quality Guidelines published in 2021 pointed out the need to expand the common air quality monitoring networks by integrating UFP measurements. It recommends to include size-segregated particle size distributions (PSD) and real-time PNC measurements in addition to simultaneous measurements with other airborne pollutants and characteristics of particulate matter. In order to harmonize and standardize these measurements, the European Committee for Standardization (CEN) has published the technical specification CEN/TS 16976:2016 for PNC measurements in ambient air using a Condensation Particle Counter (CPC). In addition, the CEN/TS 17434 technical specification for measuring the particle size distribution of ambient air by Scanning Mobility Particle Sizers (SMPS, or 'Mobility Particle Sizer Spectrometer', MPSS, in regulatory terms) was published in 2019. Finally, the proposal for a Directive of the EU Parliament and of the Council on ambient air quality and cleaner air for Europe (COM/2022/542 final) was published in 2022 with the intention to align EU air quality standards much more closely with WHO the aforementioned recommendations. In this paper, against the background of all these regulatory activities, the technical solution for reproducible sampling, conditioning and measurement of UFP, as well as the necessary data handling are presented.*

**Keywords**: *ultrafine particles, particle number concentration, particle size distribution, monitoring*

## INTRODUCTION

For many years, mass-based particulate matter $PM_{2.5}$ and $PM_{10}$ measurements have been standardized (DIN EN 12341:2014) for the regulatory quantification and monitoring of particles in ambient air. These larger particles have been relatively easy to measure and there is evidence of an association between particulate mass and health effects. However, recent studies reported that ultrafine particles, which are defined as particles equal or smaller than 0.1 µm, seem to be a better indicator of harmful air pollution in urban areas. Therefore, the measurement of the particle number concentration (PNC) which is most representative of ultrafine particles (UFP) has gained much interest and importance.

Reports such as Clean Air Copenhagen from 2014 or Leipzig Environmental Zone from 2017 focusing on UFP and their harmful effects that have been made publicly available helped spread the word on the relevance of UFP monitoring (Loeschau et al., 2017). In 2019, a team of renown expert summarized the current knowledge on UFPs in a white paper on ambient ultrafine particles (Cassee et al., 2019). This report has been cited by the World Health Organization in the WHO Global Air Quality Guidelines published in September 2021 (WHO, 2021). For the first time, these guidelines mention the need to expand the common air quality monitoring networks by integrating UFP measurements. It recommends to include size-segregated particle size distributions (PSD) and real-time PNC measurements in addition to simultaneous measurements with other airborne pollutants and characteristics of PM. The WHO report from 2021 also offers guidance what low and high UFP concentrations are to guide decisions on the priorities of UFP source emission control.

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## METHODS

In order to harmonize and standardize these measurements, the European Committee for Standardization (CEN) has published the technical specification CEN/TS 16976:2016 for PNC measurements in ambient air using a Condensation Particle Counter (CPC). Based on it, a European standard prEN 16976:2023 'Ambient air Determination of the particle number concentration of atmospheric aerosol' is currently being finalized and is published in preliminary form. In addition, the CEN/TS 17434 technical specification for measuring the particle size distribution of ambient air by Scanning Mobility Particle Sizers (SMPS, or 'Mobility Particle Sizer Spectrometer', MPSS, in regulatory terms) was published in 2020.

Finally, the proposal for a Directive of the EU Parliament and of the Council on ambient air quality and cleaner air for Europe (COM/2022/542 final) was published in October 2022 (EU Directive, 2022). The intention of this document is to align EU air quality standards much more closely with WHO the aforementioned recommendations. The proposal recommends UFP monitoring at supersites and states "Measurements at all monitoring supersites at urban background locations shall include fixed or indicative measurements of size distribution of ultrafine particles….".

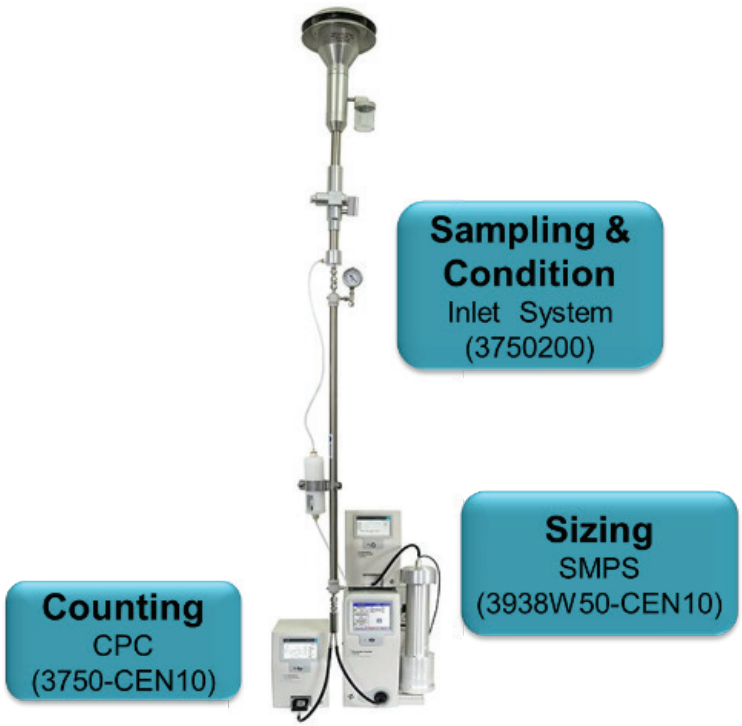


**Figure 1.** CEN-compliant solution for UFP measurements of PSD and PNC including the dedicated sampling system.

## CONCLUSIONS

Against the background of all these regulatory activities, we present the technical solution for reproducible sampling, conditioning and measurement of UFP as well as the necessary data handling. The complete measurement solution from TSI (see Figure 1) enables the continuous monitoring of UFP compliant with the aforementioned CEN technical specifications and it meets all current requirements of the ACTRIS European Research Infrastructure Consortium. We will share and highlight exemplary results from UFP monitoring at representative measurement sites from across Europe.

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Oral presentation

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# EXPERIENCES IN FIELD CALIBRATION ON SENSOR SYSTEMS WITHIN THE EUROPEAN AIRSENSEUR PROJECT

## Abstract

*In 2020, the project "Deployments of lower cost ambient air quality sensor systems in urban environments" was initiated, co-funded by the European Union and involving 4 institutions (JRC, VITO, NILU and IMROH) from 4 countries (Italy, Belgium, Norway and Croatia). As part of the project, 100 sensor sets (AirsensEUR type) were installed in 4 cities (City of Zagreb, 17 sets) to test their reliability and ability to measure air quality in different weather conditions and different locations. The paper presents the field calibration results of the AirSensEur sensor systems. Calibration consists of establishing a deterministic relationship between the known measured values and raw sensor responses. Multiple Linear Regression (MLR) was mostly used for the calibration method in the project. Most of the MLR models use covariates such as meteorological parameters, e.g., air temperature (Tair) and relative humidity (RH), and cross-sensitivities from gaseous interferons, e.g., $NO_2$, NO, and $O_3$, to improve calibration. This dependency is related to the physicochemical properties of sensors according to the type of electrolyte, electrode, semiconductor material, etc. The PM-sensors are sensitive to RH, which can be modelled by using the so-called Kohler theory to account for particle growth due to high RH. The sensor time-drift is rarely included in calibration covariates, since calibration is carried out over a few weeks and therefore the long-term drifting information is generally scarce. The calibrations were performed on CO, NO, $NO_2$, $O_3$, $PM_{10}$, $PM_{2.5}$ and $PM_1$ sensors.*

**Keywords:** *AirSensEur, calibration, MLR, air quality sensors*

## INTRODUCTION

Low-cost air pollution sensors are attracting more and more attention. They offer air pollution monitoring at a lower cost than conventional methods, in theory making air pollution monitoring possible in many more locations. At this point in time, measurements with low-cost sensors are clearly of lower and more questionable data quality (Castell et al., 2017; Lewis and Edwards, 2016; Spinelle et al., 2015a, 2017a) than the results from official monitoring stations carried out by EU Member States in accordance with European legislation and international standards.

If the quality of the data provided by low-cost sensing systems can be improved, they could become a game changer in monitoring air pollution, traffic management, personal exposure and health assessment, as well as citizen science and air pollution assessment. The purposes of the Pilot Project were to improve the data of low-cost sensor systems.

The calibration models were developed using the data collected in Ispra, Antwerp, Oslo and Zagreb in order to compare with each other for checking site effect, namely rural versus urban/traffic sites. The predictions using these calibration models in the urban sites were compared to reference data in order to investigate the sampling site effect at different urban settings including concentration ranges, meteorological parameters and sampling site types.

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Out of the experience gained from the Pilot Project, a guidance report describing the AirSensEur sensor system (ASE), deployment, network design, QA/QC and data management for air quality experts is also available (Yatkin et al., 2022).

The site descriptions including the reference air quality monitoring methods used in the city air quality monitoring stations (AQMSs), where the Pilot Project was conducted can be found elsewhere (Van Poppel et al., 2023).

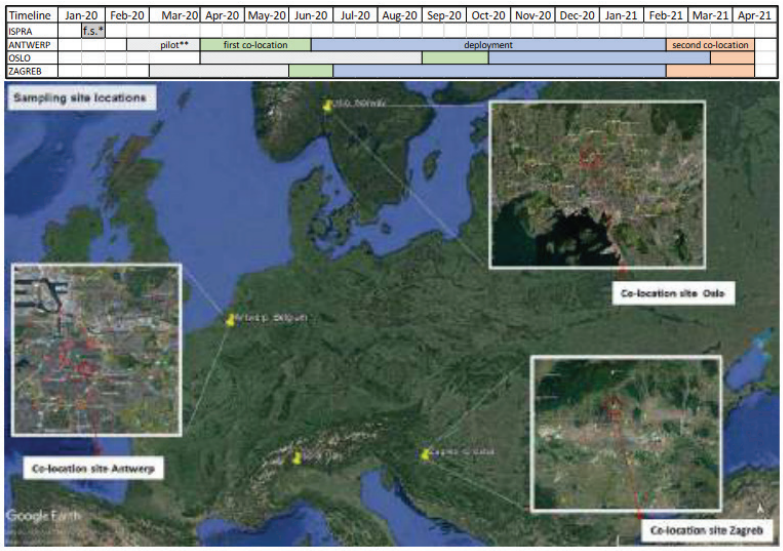
All computations in this project were performed using R language (R Core Team, 2021).

## MATERIALS AND METHODS

The sampling sites used in the Pilot Project are illustrated in Figure 1.

Initially, a feasibility study lasting for two weeks was carried out by co-location of ten ASEs with reference analysers in Ispra (called f.s. in Figure 1), The ASEs were co-located at one AQMS of each city (hereinafter called the 1st co-location), subsequently dispatched to the deployment sites, except in Ispra, among which some corresponded to other AQMSs, and finally co-located again at the AQMS used for the 1st co-location (hereinafter called the 2nd co-location).

Two weeks of data drawn from either the 1st co-location studies in Antwerp and Oslo, and the 2nd co-location in Zagreb were utilized for calibration of ASEs. The reason of using the 2nd co-location in Zagreb was the unavailability of minute reference data during the 1st co-location. The remaining sensor data corresponding to co-location at AQMS were utilized to evaluate the prediction performance of calibration models. The details of sampling sites, reference air monitoring methods and the exact time intervals of calibration and prediction can be in found elsewhere (Van Poppel et al., 2023).




* f.s.: feasibility study including small scale co-location in Ispra with ten ASEs.
** pilot in the cities with the same ten ASEs.

Source: Van Poppel, M. et al. SensEURCity: A multi-city air quality dataset collected for 2020/2021 using open low-cost sensor systems. Sci Data 10, 322, 2023

**Figure 1.** Overview of the sampling with the locations and timeline

The details of reference analysers at the AQMSs where the co-location campaigns took place, including measured pollutants and reference analysers at each AQMS are given in Table 2.

Table 2. Reference analysers used at the Air Quality Monitoring Stations.

| Parameters | Technique used | Type | Units |
|---|---|---|---|
| **ISPRA** (JRC-EMEP-ABSIS-ICOS station: latitude 45.81469 and longitude 8.63587) | | | |
| $PM_{10}$ | Oscillating Microbalance | Thermo Environment TEOM 1405 FDMS | µg/m³ |
| NO | Chemiluminescence | Thermo Environment 42i | ppb |
| $NO_2$ | Cavity attenuated phase shift spectroscopy (CAPS) | Aerodyne caps NO2 | ppb |
| CO | Non-dispersive Infrared Gas-Filter Correlation Spectroscopy | Horiba APMA - 370 | ppm |
| $O_3$ | Ultraviolet photometry | Thermo Environment 49i | ppb |
| $CO_2$, sampling at 30 meter high | Wavelength-Scanned Cavity Ring Down Spectroscopy (WS-CRDS) | Picarro G2401 | ppm |
| **ANTWERP** (Borgerhout R801 AQMS: latitude 51.2097 and longitude 4.4318) | | | |
| $PM_{10}$ | Optical particle counter | Palas Fidas 200 | µg/m³ |
| $PM_{2.5}$ | Optical particle counter | Palas Fidas 200 | µg/m³ |
| $PM_1$ | Optical particle counter | Palas Fidas 200 | µg/m³ |
| $NO/NO_2$ | Chemiluminescence | Thermo Environment 42i | ppb |
| CO | Non-dispersive IR spectroscopy | Teledyne API T300 | ppm |
| $O_3$ | Ultraviolet photometry | Teledyne API T400 | ppb |
| $CO_2$ | Non-dispersive IR absorption spectroscopy | Sick Sidor | ppm |
| **OSLO** (Kirkeveien-Marienlyst AQMS: latitude 59.93232 and longitude 10.72458) | | | |
| $PM_{10}$ | Oscillating Microbalance | Thermo TEOM 1405 FDMS (1) | µg/m³ |
| $PM_{2.5}$ | Oscillating Microbalance (equivalent method) | Thermo TEOM 1405 FDMS (1) | µg/m³ |
| $PM_{10}$ | Light scattering (equivalent method) | Palas Fidas 200 (1) | µg/m³ |
| $PM_{2.5}$ | Light scattering (equivalent method) | Palas Fidas 200 (1) | µg/m³ |
| $PM_1$ | Light scattering (equivalent method) | Palas Fidas 200 (1) | µg/m³ |
| $NO/NO_2$ | Chemiluminescence (reference method) | Opsis Serinus 40 | µg/m³ |
| CO | NDIR spectroscopy (reference method) | Opsis Serinus 30 | ppm |
| $O_3$ | UV photometry (reference method) | Teledyne API T400 (1) | ppb |
| **ZAGREB** (IMI AQMS: latitude 45.8354 and longitude 15.9784) | | | |
| $PM_{10}$ | Gravimetry | Sven Leckel SEQ47/50-CD | µg/m³ |
| $PM_{2.5}$ | Gravimetry | Sven Leckel SEQ47/50-CD | µg/m³ |
| $NO/NO_2$ | Chemiluminescence | Horiba APNA -370 | µg/m³ |
| CO | Non-dispersive IR spectroscopy | Horiba APMA - 370 | µg/m³ |
| $O_3$ | Non-dispersive ultraviolet absorption (NDUV) | Horiba APOA – 370 | µg/m³ |

(1): The Palas Fidas 200 was deployed only in the 1st co-location. During the deployment at Oslo_REF_KVN and the 2nd co-location, the data from the TEOM instrument are reported instead of the Fidas data.
All coordinates are in decimal degrees.

Source: Van Poppel, M. et al. SensEURCity: A multi-city air quality dataset collected for 2020/2021 using open low-cost sensor systems. Sci Data 10, 322, 2023

Calibration consists in establishing a deterministic relationship between the known measurand values and raw sensor responses (JCGM, 2012), which is most often proportional and/or can be defined by a mathematical model. In the literature, the Linear Regression (LR) and Multiple Linear Regression (MLR) models are the most common calibration techniques (Spinelle et al., 2015b, 2017b) used to calibrate the raw sensor data against reference data. Calibration can be established using either laboratory experiments under controlled conditions (Spinelle et al., 2017a) or field experiments (Spinelle et al., 2015b, 2017b). Other calibration techniques establish exponential, logarithmic (Spinelle et al., 2016a), and quadratic models, the Köhler theory of particle growing factor used for Optical Particulate Counters (OPC) sensors (Crilley et al., 2018, 2020; Di Antonio et al., 2018). However, sensor responses are generally influenced by several independent variables (hereinafter called covariates), one of them being the pollutant of interest. Among the relevant covariates, temperature in ambient air (Tair) and relative humidity (RH) have significant effect on almost any sensor types (Spinelle et al., 2017a) while $O_3$ has an effect on NO2-B43F sensors and vice versa (Knake et al., 2005).

Most of the MLR models use covariates such as meteorological parameters, e. g., Tair and RH, and cross-sensitivities from gaseous interferents, e.g., $NO_2$, NO, and $O_3$, to improve calibration. This dependency is related to the physico-chemical properties of sensors according to the type of electrolyte, electrode, or semiconductor material etc. The PM-sensors are sensitive to RH, which can be modelled by using the so-called Köhler theory to account for particle growth due to high RH. The sensor time-drift is rarely included in calibration covariates since calibration is carried out over few weeks and therefore the long-term drifting information is generally scarce.

The critical point of MLR method is to include covariates into the calibration model and to determine the starting values when fitting the coefficients of non-linear calibration models. The decision of adding covariates to field calibration models can be made according to the results of laboratory experiments (Spinelle et al., 2013, 2014, 2015a, 2016a, 2016b, 2017a, 2020). There are several statistical methods to assess the significance of covariates added into calibration models.

The automated procedure given in Figure 2 was applied to establish the calibration models using the sensor and reference data with minute resolution. The calibration method was packed in a single R script, where the following modelling parameters must be selected/ entered by user. The step-by-step instructions of running the R script and selecting the parameters can be found elsewhere (Yatkin et al., 2022).

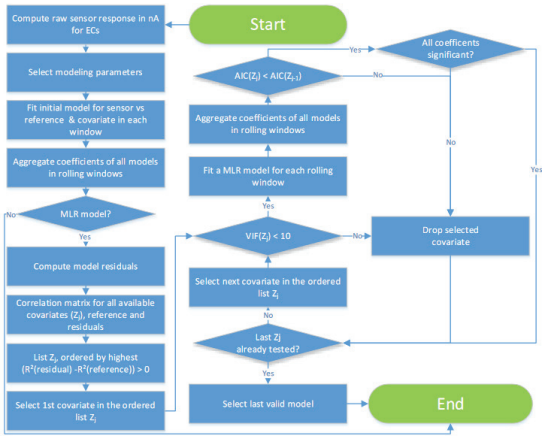



**Figure 2.** Flow chart of the procedure for the automatic calibration of sensors

## RESULTS AND ACHIEVEMENTS

The box and whisker plots of the model coefficients of CO-A4 sensors calibrated in the four cities ware shown in Figure 3 along with the ranges (min, median, 98th percentile and max) of reference CO concentrations. The within-city variabilities of coefficients were relatively small for Ispra and Oslo, indicated by narrow boxes and almost no outliers. The variation of coefficients in Antwerp for $a_0$ and Zagreb for $a_1$ were relatively large.

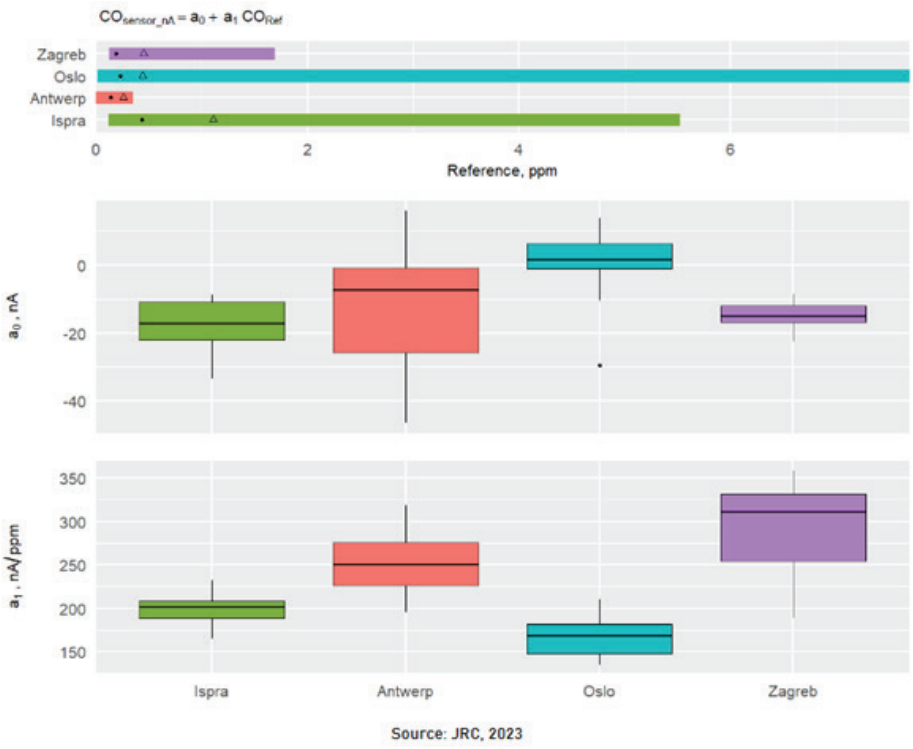



**Figure 3.** up: The range (min-max in bars, median in dot and 98th percentile in triangle) of reference CO concentrations in the four cities; down: Box and whisker plots of the coefficients of CO-A4 models

The box and whisker plots of the model coefficients of NO-B4 sensors calibrated in the four cities were shown in Figure 4 along with the ranges (min, median, 98th percentile and max) of reference NO concentrations. Note that the NO-B4 sensors were calibrated using data of the 2nd co-location in Antwerp, Oslo and Zagreb, see below for further information on the selection of calibration period. The within-city variabilities of coefficients were relatively small, as indicated by narrow boxes and few outliers. The largest variabilities were observed for $a_2$ in Antwerp and $a_1$ in Oslo.

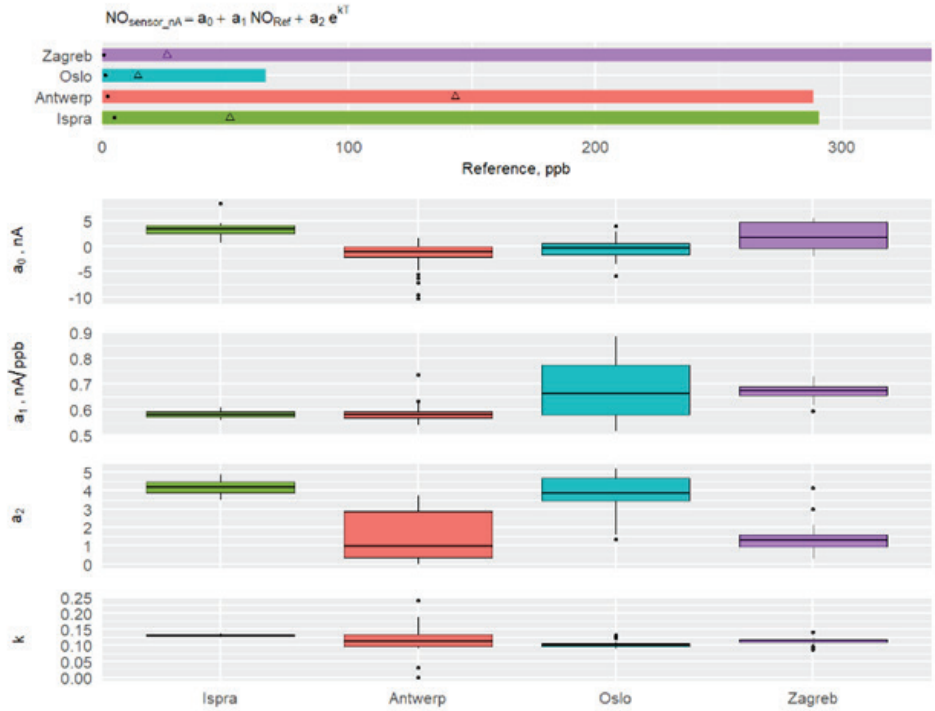



**Figure 4.** up: The range (min-max in bars, median in dot and 98th percentile in triangle) of reference NO concentrations in minute resolution in the four cities; down: Box and whisker plots of the coefficients of NO-B4 models

The box and whisker plots of the model coefficients of OX-A431 sensors for the models with the sole covariate of NO2-B43F sensor response were shown in Figure 5 along with the ranges (min, max, median and 98th percentile) of reference $O_3$ concentrations. The within-city variabilities of coefficients were relatively small, indicated by narrow boxes and occasional outliers.

The box and whisker plots of the Köhler model coefficients of CAT PM10 were shown in Figure 6 along with the ranges (min, max, median and 98th percentile) of reference $PM_{10}$ concentrations. The reference $PM_{10}$ method in Zagreb AQMS was the filter-based gravimetric measurement with 24-h resolution (EN, 2014), which makes the calibration of PM sensors impossible. Instead, a model derived from the medians of model coefficients in Antwerp was utilized for the calibration of PM sensors in Zagreb. The *k* value was found to be close to the literature one in Oslo (median 0.36), and lower in Antwerp (median 0.27) and in Ispra (median 0.04). The within-city variabilities of coefficients were relatively small except for *k* in Oslo, indicated by narrow boxes and occasional outliers.

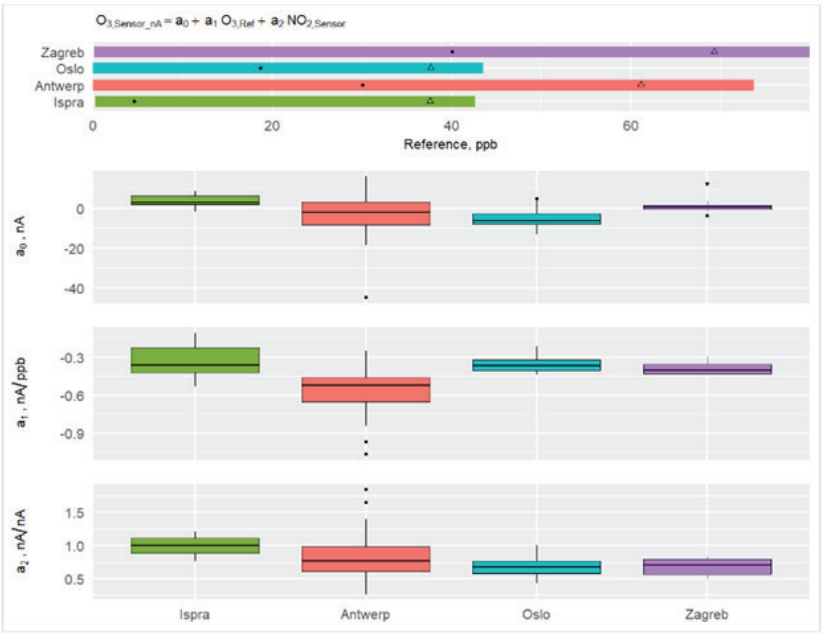



**Figure 5.** up: The range (min-max in bars, median in dot and 98th percentile in triangle) of reference $O_3$ concentrations in minute resolution in the four cities; down: Box and whisker plots of the coefficients of OX-A431 models with the sole covariate of NO2-B43F sensor response

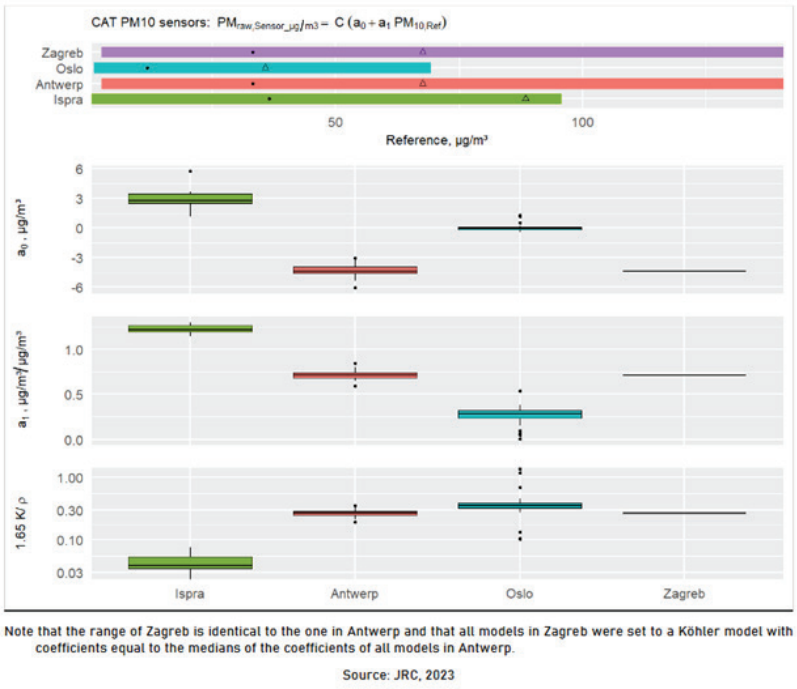



**Figure 6.** up: The range (min-max in bars, median in dot and 98th percentile in triangle) of reference $PM_{10}$ concentrations in minute resolution in the cities.; down: Box and whisker plots of the coefficients of CAT $PM_{10}$ Köhler models.

## CONCLUSIONS

The study conducted in the four cities with different geographical, meteorological and pollution characteristics is unique without equivalent studies in terms of time span covering different seasons and the content, e.g., two co-location along with reference methods before and after deployment, several gas and PM sensors etc. For each sensor, several calibration scenarios were examined to determine the best calibration model. The calibration model equations and evaluation of prediction are open to users. The methodology and outputs of this study such as the model equations/coefficients are directly applicable by sensor users, so-called calibration transfer. For example, the calibration PM models generated in Antwerp were transferred to Zagreb to predict the PM concentrations using non-calibrated sensors. In addition, the uncertainties arising from calibration transfer to employ for non-calibrated sensors anywhere were estimated allowing the user to evaluate deploying the new sensors with or without a prior field calibration study.

In fact, based on the findings of this study, only for CO and PMS $PM_{2.5}$ sensors (and $PM_1$ which does not currently have data quality objectives and limit values) the harmonized models of this study can be directly implemented to non-calibrated sensors. The proposed CO and $PM_{2.5}$ calibration models can be applied to sensor deployment anywhere and anytime with high probability of meeting the data quality objectives and limit values. For the other sensors, the decision of conducting a prior calibration would be based on the uncertainty objective of planned monitoring study. There is no further planned study after the Pilot study.

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Poster presentation

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# DEVELOPMENT AND OPTIMIZATION OF A TD-GC/MS METHOD FOR MEASUREMENT OF VOCs IN INDOOR AIR

## Abstract

*In today's increasingly urbanized societies, people spend the majority of their time in indoor environments. Their activities influence indoor air quality, emitting various organic pollutants such as volatile organic compounds (VOCs). VOCs comprise different chemical substituents such as alcohols, ketones, aldehydes, esters, halogens, amines, etc., emitted to the atmosphere from natural and anthropogenic sources. The most common indoor sources of VOCs are domestic products like cosmetics and sprays, cleaning solutions, cooking, smoking, off-gassing from building materials, renovation, and wood products for furniture or parquet. Concentrations in households mostly depend on ventilation and season. Some VOCs are important pollutants due to their carcinogenic and mutagenic impact on human health. Currently, regulations on the maximum allowed concentrations of VOCs in indoor air do not exist in the European Union. The aim of this study was to develop and optimize an analytical method for the determination of nineteen VOCs ($C_1$ – $C_9$) in indoor air by thermal desorption coupled with gas chromatography and mass spectrometry (TD-GC/MS). Thermal desorption multi-bed tubes were used for the method development. For the purpose of achieving better chromatography peak resolution and responses of nineteen VOCs, method parameters such as carrier gas flow were optimized.*

**Keywords:** *indoor air pollution, volatile organic compounds (VOCs), gas chromatography*

Volatile organic compounds (VOCs) are significant constituents of indoor air quality assessment due to their wide distribution and today's way of life. Their sources in the environment can be biogenic and anthropogenic. Many VOCs occur as components of naphtha and its derivatives and enter the atmosphere through the combustion of solid and liquid fuels and household heating. Consequently, the primary source of VOCs in the ambient air is traffic, while in the indoor environment, smoking, domestic and cleaning products, renovation, and furniture are also stated as indicative origins (Kozielska and Kaleta, 2020; Martellini et al., 2020; Vera et al., 2022). Since indoor air contains traces of many organic pollutants, their analysis is an interesting analytical challenge. Analysis of VOCs are possible using separation techniques such as gas chromatography (GC) coupled with an appropriate detector. It is characterized by high sensitivity for low concentrations of the analytes under investigation (Vallecillos et al., 2019). The advantage of the method is that it is fast, can separate very complex mixtures, and requires small sample volumes for determination. For this study, a mass spectrometer was used as the detector due to its possibility of achieving lower quantification limits compared to photoionization or flame ionization detectors. In this work, a thermal desorption (TD) unit was used in conjunction with the GC-MS system. The TD unit is a direct extension of gas chromatography, designed for automated sample introduction. It facilitates the preparation of organic substances for analysis, streamlining the process. Sampling of VOCs was performed by the adsorption of compounds present in the gaseous phase on tubes filled with adequate sorbents. Adsorbed gases are concentrated on a sorbent tube and are later released from the sorbent in TD unit by programmed heating in a flow of inert gas. This TD-GC/MS technique represents an alternative, high-sensitivity, solvent-free gas extraction process. As with GC, the key parameters are temperature, carrier gas flow rate, desorption time, and the selection of sorbent as the stationary phase. Method optimization included choosing the optimal desorption

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temperature and carrier gas flow rate is usually easy, considering the volatility and thermal stability of the compounds of interest and the temperature limitations of the selected sorbents in the tube and trap. The main goal of this study was to develop and optimize chromatographic conditions such as carrier gas flow for the determination of nineteen VOCs in indoor air.

## MATERIALS AND METHODS

Stock solutions of the target analytes were prepared by diluting a certified standard mixture of nineteen volatile organic compounds (2000 μg $mL^{-1}$) with methanol. The mixture included 2-methylpentane, dichloromethane, methylcyclopentane, chloroform, 2-methylhexane, cyclohexane, benzene, heptane, trichloroethene, methylcyclohexane, toluene, tetrachloroethene, ethylbenzene, *m*-xylene, *p*-xylene, *o*-xylene, styrene, 1,3,5-trimethylbenzene, and 1,4-dichlorobenzene (CRM4877) and was procured from Supelco, Bellefonte, USA. The stock solutions were stored at 4°C. Working standard solutions were prepared by appropriately diluting the stock solutions in methanol and stored under refrigeration. Methanol, with GC and MS grade purity (98–99.9%), was obtained from Merck, Germany. The analysis of adsorbed VOCs was conducted using TD-GC/MS. The thermal desorption system used was a UNITY-xr equipped with an ULTRA-xr autosampler (Markes, Llantrisant, United Kingdom). Gas chromatography was performed on an Agilent 8890 system, paired with an Agilent 5977B mass spectrometry detector. A DB-624 UI capillary column (6% cyanopropyl/phenyl, 94% polydimethylsiloxane; 60 m length, 0.32 mm internal diameter, 1.80 μm film thickness, Agilent Technologies, Santa Clara, CA, USA) was used for the analysis. Helium (99.9999%) was employed as the carrier gas. The MS operated in positive electron impact ionization (EI) mode under the following conditions: transfer line and ion source temperatures were set at 230°C, while the quadrupole temperature was maintained at 150°C. For sample preparation, manual analytical procedures were replaced with multi-bed TD tubes. The TD tubes were packed with a combination of porous polymer, graphitized carbon black, and carbonized molecular sieves (Markes, Llantrisant, United Kingdom). Preconditioned TD tubes were spiked with a standard mixture (CRM4877, Supelco) and heated in the desorber up to 320°C, with a helium flow rate of 50 mL $min^{-1}$ applied.

## RESULTS

During the development and optimization of the method for determining VOCs in indoor air, the chromatograms shown in Figures 1 to 5 were obtained. Figure 1 presents a chromatogram of mixed VOC standards in full-scan mode (SCAN), while Figures 2, 3, and 4 present total ion current (TIC) chromatograms of mixed VOC standards in the SIM mode with a different flow rate. Figure 5 presents an extracted ion current (EIC) chromatogram of mixed VOC standards in the SIM for all ions. The determined compounds are marked with numbers from 1 to 19 in the following order: methylene chloride, 2-methylpentane, methylcyclopentane, chloroform, 2-methylhexane, cyclohexane, benzene, heptane, trichloroethylene, methylcyclohexane, toluene, tetrachloroethylene, ethylbenzene, *m*- and *p*-xylenes, o-xylene, styrene, 1,3,5-trimethylbenzene, 1,4-dichlorobenzene.

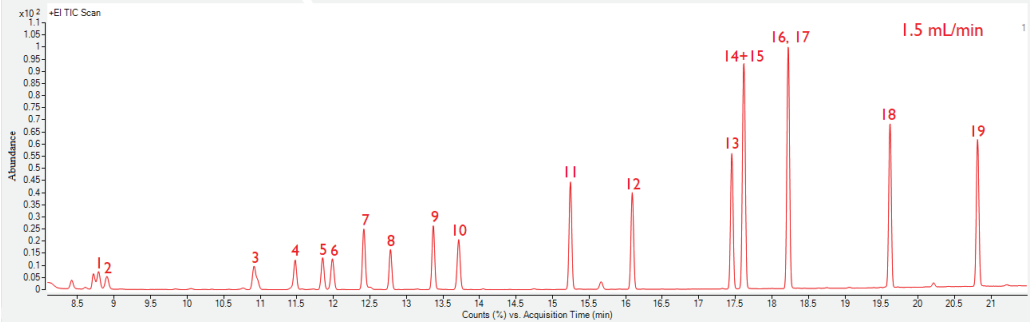


**Figure 1**. TIC chromatogram of mixed VOC standards in full-scan mode with TD-GC-MS. The selected flow rate is 1.5 mL min$^{-1}$.

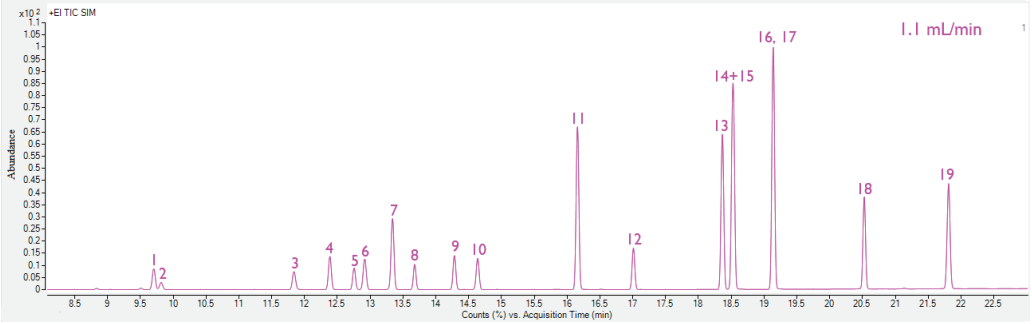


**Figure 2**. TIC chromatogram of mixed VOC standards in the SIM mode with a flow rate of 1.1 mL min$^{-1}$.

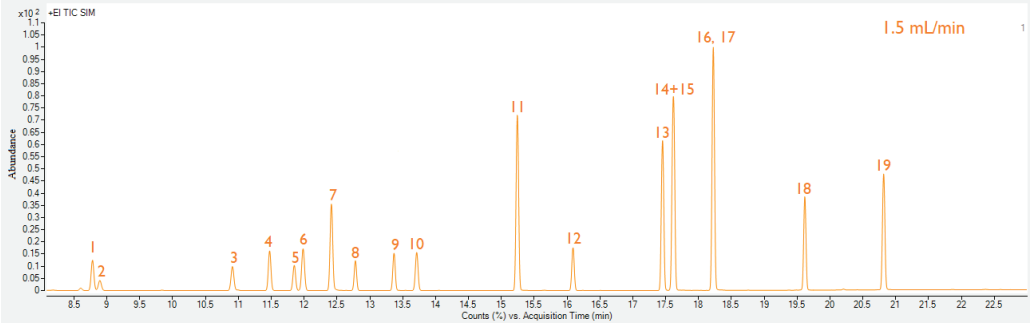


**Figure 3**. TIC chromatogram of mixed VOC standards in the SIM mode with a flow rate of 1.5 mL min$^{-1}$.

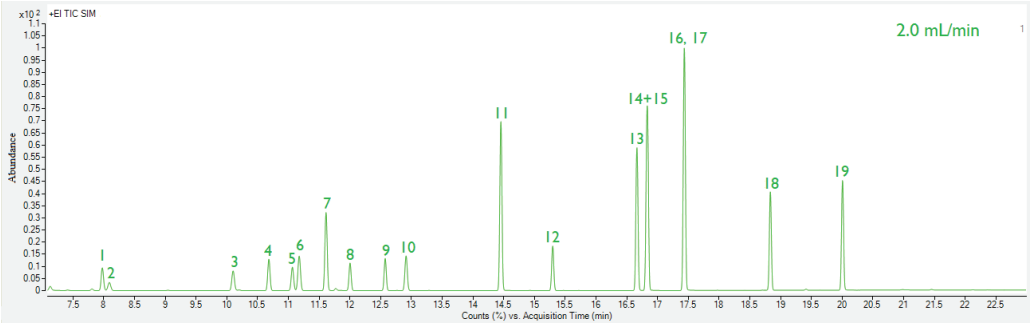


**Figure 4**. TIC chromatogram of mixed VOC standards in the SIM mode with a flow rate of 2.0 mL min$^{-1}$.

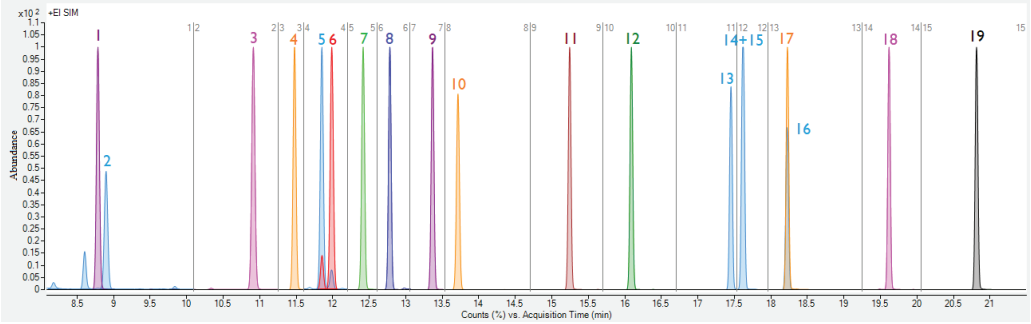


**Figure 5**. EIC chromatogram of mixed VOC standards in the SIM with TD-GC-MS.

## DISCUSSION

A mixed standard solution of VOCs was initially analyzed in full scan mode to identify and confirm the analytes using mass spectra from the library. The initial flow rate of 1.5 mL $min^{-1}$ is shown in Figure 1. Using the SCAN mode, ions corresponding to volatile organic compounds were selected, and retention times were determined for all of the analytes. These findings were further confirmed using the NIST Library.

Once the exact retention times of all compounds were determined, the SIM mode was used for targeted analysis, as it is more efficient for monitoring specific ions of interest. In this mode, the MS scans a narrow range of mass-to-charge ratios (*m*/*z*) for each chromatographic peak, rather than scanning the entire mass spectrum for every peak. Figures 2, 3, and 4 show the optimization of the selected flow rate (1.1, 1.5 and 2.0 mL $min^{-1}$) in SIM mode. The flow rate that was selected as the most suitable for the method is 1.5 mL $min^{-1}$.

Figure 5 shows an EIC chromatogram of the mixed VOCs standard in EI SIM mode. This mode provides easy identification, including their names and structures at the isomer level. The figure also illustrates the sequence in which individual analytes elute from the chromatographic column, numbered from 1 to 19: methylene chloride, 2-methylpentane, methylcyclopentane, chloroform, 2-methylhexane, cyclohexane, benzene, heptane, trichloroethylene, methylcyclohexane, toluene, tetrachloroethylene, ethylbenzene, *m*-,*p*-xylenes, *o*-xylene, styrene, 1,3,5-trimethylbenzene, and 1,4-dichlorobenzene.

As shown in Figure 5, 17 VOCs were successfully separated (peak resolution > 1.2), with *m*- and *p*-xylenes presented as the sum of isomers. *o*-Xylene and styrene eluted at the same retention time (18.2 minutes) but were detected with different mass-to-charge ratios (*m*/*z*). The *m*/*z* ratio for *o*-xylene was determined to be 91.1, while for styrene it was 104, allowing them to be identified as two distinct analytes despite having the same retention time.

## CONCLUSIONS

An analytical method, TD-GC/MS, for determining nineteen volatile organic compounds, was developed to monitor indoor air quality. Ultimately, 1.5 mL $min^{-1}$ proved to be the best flow rate of the carrier gas proved. All compounds were identified based on their retention time and the relative abundances of qualifier ions. Parameters such as the oven temperature program on the GC instrument will be optimized in future work.

## ACKNOWLEDGEMENT

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Poster presentation

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# CARCINOGENIC ACTIVITY OF PAHs AT THREE URBAN LOCATIONS IN CROATIA

## Abstract

*Polycyclic aromatic hydrocarbons (PAHs) are a big class of semi-volatile chemical compounds containing two or more aromatic rings. In this work, the mass concentrations of ten detected PAHs in the $PM_{10}$ particle fraction were assessed, as well as their carcinogenic activity. At three locations in Croatia, 24-hour samples of $PM_{10}$ particle fraction were collected on quartz filters from approximately 55 $m^3$ of air over 60 days during the cold and warm seasons. PAH concentrations were measured using high performance liquid chromatography (HPLC) and a fluorescence detector. Fluoranthene (Flu), pyrene (Pyr), benzo(a)anthracene (BaA), chrysene (Chry), benzo(b)fluoranthene (BbF), benzo(k) fluoranthene (BkF), benzo(a)pyrene (BaP), dibenzo(a,h)anthracene (DahA), benzo(ghi)perylene (BghiP), and indeno(1,2,3-cd)pyrene (IP) were analyzed. At all of the locations, the mass concentrations of all assessed PAHs and their carcinogenic activity were higher in the cold than in the warm period. Total carcinogenic activity was the highest at the urban industrial site with an average of 8.310 ng $m^{-3}$ and 0.173 ng $m^{-3}$ during the cold and warm periods, respectively, while at the urban residential site, it was 3.244 ng $m^{-3}$ during the cold and 0.119 ng $m^{-3}$ during the warm period, whereas at the urban background site, this was 4.425 ng $m^{-3}$ and 0.084 ng $m^{-3}$ for the cold and warm periods, respectively.*

**Keywords:** *$PM_{10}$, benzo(a)pyrene, HPLC*

## INTRODUCTION

Exposure to air contaminants that pose health concerns is more common in metropolitan areas because of the greater density of human activity there. The overall ambient concentrations of particulate matter (PM) are influenced by both natural and human activities, such as industry, power generation, transportation, domestic energy use, and the burning of agricultural waste (Ahmadipour et al., 2020; Dejchanchaiwong et al., 2020).

Polycyclic aromatic hydrocarbons (PAHs) are present in the atmosphere in the gaseous phase or are bound to suspended particles. The phase in which PAHs are found depends on their volatility under atmospheric conditions. Previous research has shown that PAHs with two or three aromatic rings are stable in the gaseous phase and their concentration in the air increases with temperature. In contrast, PAHs with more aromatic rings are found in the air mainly bound to particles (Dat and Chang, 2017; Liu et al., 2015). PAHs can also be degraded in the atmosphere by oxidation and photooxidation and can react with other atmospheric pollutants, such as sulfur dioxide, nitrogen dioxide, and ozone (Dat and Chang, 2017).

PAHs are formed as a result of natural processes such as carbonization, during large forest fires or volcanic eruptions, but the most significant source of PAHs is human activity (Dejchanchaiwong et al., 2020). They are produced during burning waste and various plastics in uncontrolled conditions or by pyrolysis of organic substances and during various industrial processes (production of coal, crude oil, heavy and light metals, etc.), and are also present in car exhaust gases and cigarette smoke (Ahmadipour et al., 2020).

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Benz(a)anthracene (BaA), chrysene (Chry), benzo(b)fluoranthene (BbF), benzo(k) fluoranthene (BkF), benzo(a)pyrene (BaP), dibenzo(a,h)anthracene (DahA), benzo(ghi) perylene (BghiP), indeno(1,2,3-cd)pyrene (IP) belong to the 16 PAHs priority pollutants listed by the US EPA (Keith, 2015). BaP is categorized as carcinogenic to humans (group 1) by the International Agency for Research on Cancer (IARC), while certain PAHs are classed as probable human carcinogens (group 2A) and possible human carcinogens (group 2B) by the IARC (Famiyeh et al., 2021; Rezaei et al., 2018).

## MATERIALS AND METHODS

### Site description

Location A was an urban background station in the residential area with moderate traffic density in central Croatia and a population of 790,017 inhabitants. Location B was an urban background station in the north-east of Croatia with a population of 35,312, while and location C was an urban industrial station in the eastern Croatia with 50,039 inhabitants.

### $PM_{10}$ and PAH analysis

Daily $PM_{10}$ sampling was carried out for 60 days in each season on quartz filter by a low-volume sampler with a flow of approximately 55 $m^3$ per day. Mass concentrations of $PM_{10}$ particle fraction were determined gravimetrically. After sampling filters were wrapped in aluminum foil and kept at -18 ˚C until analysis. PAHs from $PM_{10}$ particles were extracted with a solvent mixture (toluene:cyclohexane, 7:3) in an ultrasonic bath for one hour, centrifugated, evaporated to dryness and re-dissolved in acetonitrile. The Agilent Infinity II high-performance liquid chromatography system (HPLC) with a fluorescence detector and programmed changes in excitation and emission wavelengths was used for PAH determination. The following PAHs: fluoranthene (Flu), pyrene (Pyr), benzo(a)anthracene (BaA), Chrysene (Chry), benzo(b)fluoranthene (BbF), benzo(k) fluoranthene (BkF), benzo(a)pyrene (BaP), dibenzo(a,h)anthracene (DahA), benzo(ghi) perylene (BghiP), and indeno(1,2,3-cd) pyrene (IP) were analyzed (Jakovljević et al., 2015; Pehnec and Jakovljević, 2018).

### Assessment of carcinogenic activity

The carcinogenic activity of each PAH was calculated by multiplying the mass concentration of individual PAHs and their toxic equivalent factor (TEF). In this study, Nisbet and LaGoy (1992) TEF factor were used.

## RESULTS

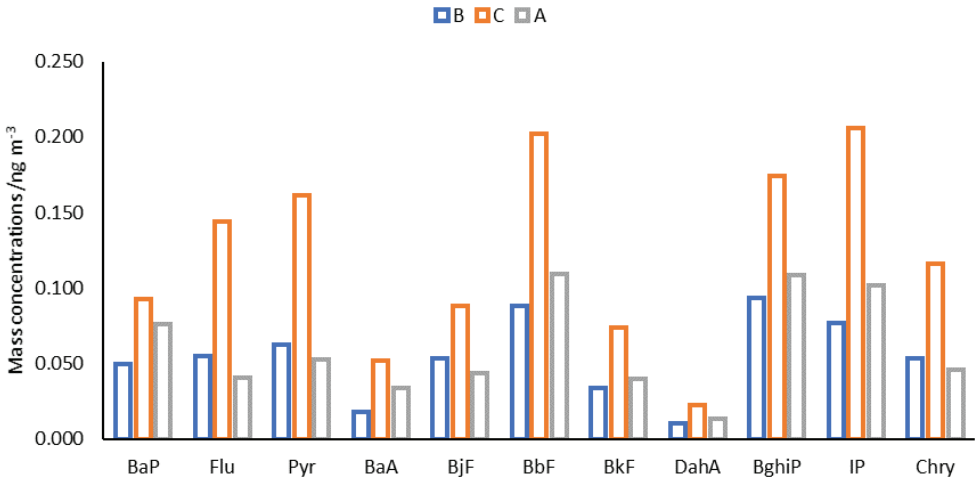


**Figure 1.** Mass concentrations of PAHs in the warm period

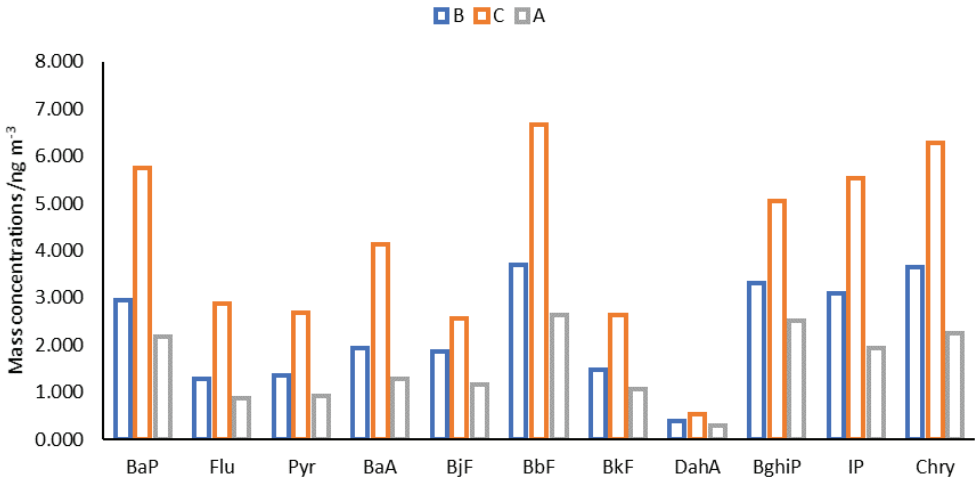


**Figure 2.** Mass concentrations of PAHs in the cold period

Figures 1 and 2 show the average mass concentrations of PAHs at the three measured locations during the warm period and cold period, respectively.

Figure 3 shows the mass concentrations of $PM_{10}$ particle fraction in warm and cold periods for all measured locations.

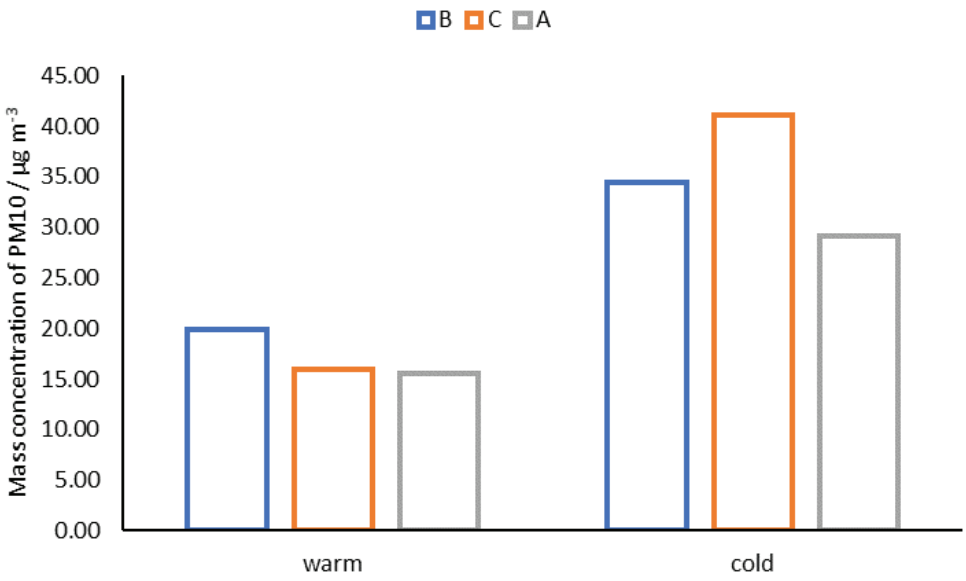


**Figure 3.** Mass concentrations of $PM_{10}$ particle fraction

## DISCUSSION

PAH and $PM_{10}$ concentrations were much lower in the warmer season than in the colder. In the warmer period, the highest concentration was recorded for BbF at location A, BghiP at location B and IP at location C. The average concentration of BaP was 0.076 ng $m^{-3}$, 0.05 ng $m^{-3}$ and 0.092 ng $m^{-3}$ at location A, B and C (Figure 1).

Concentrations of PAHs during the cold period showed variation between locations with the highest concentration of BbF and the lowest concentrations of DahA at all locations. The average BaP concentration was 2.183 ng $m^{-3}$, 2.947 ng $m^{-3}$ and 5.750 ng $m^{-3}$ at location A, B and C, respectively (Figure 2).

The highest average concentration of $PM_{10}$ particle fraction was measured at location C (41 µg $m^{-3}$) and location B (20 µg $m^{-3}$) in cold and warm periods, respectively (Figure 3). At location A, the traffic and population density are higher than at location B, but at location B populations probably use wood or other crude fuels for household heating which led to high concentrations at this location.

In every location, the carcinogenic activity was higher during colder times than during warmer ones. BaP contributed more than 50 % to the total carcinogenic activity at all locations while during the warm period, BaP contributed more than 65 %. These results confirm BaP as a good indicator of the health impact of the PAH mixture on human health but also show that some other PAHs contributed more significantly to the total carcinogenicity at location C during the warmer period. Carcinogenic activity in the colder period ranged from 0.261 ng $m^{-3}$ to 13.916 ng $m^{-3}$ with an average value of 3.244 ng $m^{-3}$ at location A. At locations B and C, the average values were 4.425 ng $m^{-3}$ and 8.310 ng $m^{-3}$, respectively, ranging from 0.525 ng $m^{-3}$

to 19.533 ng $m^{-3}$ at location B and from 0.534 ng $m^{-3}$ to 30.328 ng $m^{-3}$ at location C. During the warmer period, carcinogenic activity ranged from 0.017 ng $m^{-3}$ to 2.939 ng $m^{-3}$ at location A, from 0.021 ng $m^{-3}$ to 0.225 ng $m^{-3}$ at the location B and from 0.027 ng $m^{-3}$ to 0.725 ng $m^{-3}$ at location C. The average value of carcinogenic activity was 0.119 ng $m^{-3}$, 0.084 ng $m^{-3}$ and 0.173 ng $m^{-3}$ for locations A, B and C, respectively.

## CONCLUSIONS

At all three locations, the mass concentrations of all measured PAHs and their carcinogenic activity were higher in the cold than in the warm period. In the cold period, the highest concentrations of all PAHs were observed at location C, followed by location B and then A. In the warm period, the highest concentration of all PAHs was also at location C, while the lowest at location B. Total carcinogenic activity was estimated to be the highest at location C and was 8.310 ng $m^{-3}$ and 0.173 ng $m^{-3}$ during the cold and warm periods, respectively, while at location A it was 3.244 ng $m^{-3}$ during cold and 0.119 ng $m^{-3}$ during a warm period, at location B total carcinogenic activity was 4.425 ng $m^{-3}$ and 0.084 ng $m^{-3}$ for the cold and warm period, respectively. The highest values obtained during the winter period indicated the need for further measurements and estimations of possible pollution sources.

## ACKNOWLEDGEMENT

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Oral presentation

**Hrvoje Krapanić, Daikin Central Europe**

# INDOOR AIR QUALITY IN SCHOOLS IN SLOVAKIA

## Abstract

*The COVID-19 pandemic has brought the quality of the indoor environment to the centre of our attention. Both experts and the general public are realizing how important it is in our lives and how much the environment where we spend most of our time can affect human health. However, reconstructing public buildings remains a challenge, where schools and preschools are considered the most neglected. Children, one of the most vulnerable population group, spend more time at school than anywhere else, except at home. Indoor air quality (IAQ) impacts student concentration, their performance and health. This paper shows the results of IAQ monitoring in 20 schools all over Slovakia over the June, July, August and September 2021. It includes results of testing and comparing the classroom air quality with and without an air purifier and also with and without a ventilation unit installed. By measuring temperature and humidity, particulate matter (PM) concentration and $CO_2$ concentration, it was shown that IAQ in the classrooms without ventilation is poor and the measured values often exceeded the allowed and recommended thresholds and therefore is a health risk for students and staff. Especially poor situation was with $CO_2$ concentration. By installing heat recovery ventilation in one of the classrooms with one the worst measured values, significant improvement of $CO_2$ concentration level was achieved.*

**Keywords**: *monitoring, air purifier, ventilation, $CO_2$ concentration*

## INTRODUCTION

The quality of the indoor environment (IEQ) has been brought to the centre of our attention, especially through the COVID-19 times. Both experts and the general public are realizing how big of a role it plays in our lives and how much the indoor environment where we spend most of our time can affect human health. In the private sector, the pressure to improve the indoor environment has grown and its higher importance, which is now also supported by building certification programs (e.g. BREEAM, LEED, WELL or DGNB), is contributing in no small part to certified buildings being more marketable. Here, the market tends steer things in the right direction, having in mind effectiveness of the people working in buildings, their health (thus less absence) and their well-being (keep the good people on board). However, reconstructing public buildings remains a challenge, as new construction is sporadic. School and pre-school facilities are considered the most neglected even though school children are a particularly vulnerable population group. Children spend more time at school than anywhere else, except at home. Since the negative effects of some airborne pollutants on human health are scientifically proven, it is unfortunate that such pollutants are also widely found in school environments. Indoor air quality (IAQ) basically impacts: a) student concentration and performance and b) health. The appeals to the governments and ministries are heard, but due to a lack of budget, sometimes also lack of a good will to make a strategic plan of school renovations, result in the lagging behind some other target groups, keeping the schools indoor environmental quality (IEQ) on a low level.

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## MATERIALS AND METHODS

### Indoor environmental quality and indoor air quality

The indoor environmental quality (IEQ) of which indoor air quality (IAQ) is a part, may be defined as conditions inside the building, or building indoor conditions, consisting of: lightning (including the daylight and other visual conditions), acoustic conditions, comfort with thermal conditions and mentioned IAQ. Humas have perfectly 'built in' systems to help us recognizing threats, but our human organism stops sensing the quality of indoor air after a while and our olfactory organs tend to adjust to the environment - thus we stop recognizing potential threats occurring around us. This phenomena can be even life threatening, so by recognizing IAQ to having a strong impact on our health, and deal with this problem, we already make the first step towards the solution.

### Indoor air quality parameters

This project was focused on IAQ and will report on monitoring following parameters:

a) $CO_2$ concentration in ppm – measuring without and with countermeasures (air purifier and ventilation). As shown in Figure 1, concentration of $CO_2$ has strong impact on a human body, which increase is particularly difficult to notice, since there are no odours or other visible signs of increased concentration. When human body reacts and the symptoms are becoming visible, the concentration is already too high, therefore it is necessary to establish a constant monitoring and measuring.

| $CO_2$ concentration(PPM) | Up to 1000 | 1000 - 1500 | 1500-2000 | 2000-3000 | 3000 to 5000 |
|---|---|---|---|---|---|
| Details | Recommended $CO_2$ level in indoor environment for good indoor air quality | Max. $CO_2$ limit recommended in indoor environment | Symptoms: Fatigue & decreased concentration | Symptoms: Drowsiness, headache, increase in blood pressure | Highest exposure limit! It is not recommended to stay indoors for a longer time under these conditions |

**Figure 1.** Human body reactions to different concentrations of $CO_2$ in the indoor spaces (CO2METER, 2024)

b) Spatial temperature – temperature in the classroom during testing without and with countermeasure (air purifier). Operative temperature is based on the set of values, out of which only simple spatial temperature will be monitored

c) Particulate matters $PM_1$, $PM_{2.5}$ and $PM_{10}$, also measuring with and without countermeasure (air purifier).

d) Humidity and volatile organic compounds (VOCs) – it will be measured but will not be addressed in detail in this paper.

### Schools

In Slovakia there are more than 6.700 schools with 1.1 million pupils and students and 165.000 teachers which implicates there are more than 46.000 classrooms (CVTISR, 2021).

If this is scaled up to European figures, we talk about 630.000 schools (WONDER, 2024) with 79,7 million pupils and students (EUROSTAT, 2022) and 5.4 million teachers of primary and secondary schools (EUROSTAT, 2020). By extrapolating the number of students per classrooms from Slovakian situation to European, we could say there are around 3,32 million classrooms in Europe, where problems with IAQ can occur, impacting vulnerable group – children. It is fair to mention, that IAQ is European wide problem, so Slovakian sample could be also used in other European countries, especially in central and eastern Europe.

When choosing representative schools in Slovakia, the researchers did try to respect the Slovakian geographical diversity and school locations in cities. As shown in Figure 2, it is visible that schools are spread evenly throughout regions of Slovakia. Cities are mentioned in the Figure 3, together with photos of schools. In lots of cases, chosen school locations were in the parts of the cities next to busy roads or/and railway traffic (outdoor pollution) which has highly negative impact on IAQ. This increases the need for IAQ control and quick countermeasures.

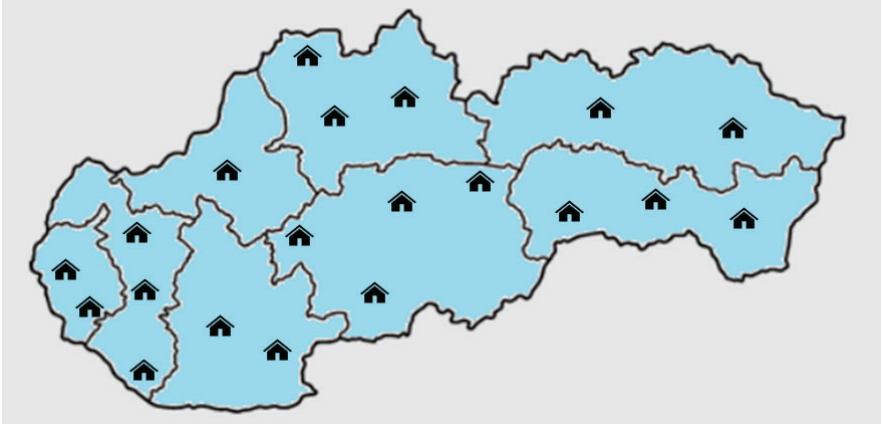

**Figure 2.** Map of Slovakia with locations of schools participating in the research


**Figure 3.** Photos of participating schools

## Conditions and specifications

The first phase of monitoring was executed from 1st June until 31st June 2021, divided in two parts:

a) Monitoring of status quo - IAQ sensors were installed in the classrooms. In order not to get a IAQ sensor spoiled and touched, it was often used masked and protected (i.e. in the hamster cage.
b) Monitoring after implementing air purifiers, which was introduced in the second half of June – installed air purifiers were AAF AstroPure 2000 or Daikin Air Purifier MC55W. In the graphs, the moment of introducing air purifier was marked as "event" and then compared PM and VOC values measured before and after installation of the air purifiers.
c) Installation of heat recovery ventilation unit Daikin VAM-J as the third phase over the summerbreak and measuring in September 2021.

## RESULTS AND DISCUSSION

Comparison of results gathered by measuring temperature, humidity, particulate matter (PM) concentration and $CO_2$ concentration are described in the below section.

### Temperature

From so called operative temperature, the uniform temperature of an enclosure where a person would exchange the same amount of heat by radiation plus convection as in the actual non-uniform environment (ISO EN 7730), only spatial temperature will be measured, because this would be enough to show there is an environmental problem. In the Figure 4, the temperature development was shown. It was noticed, that the temperature is constantly increased, since there is no natural ventilation when school is closed (e.g. over night).

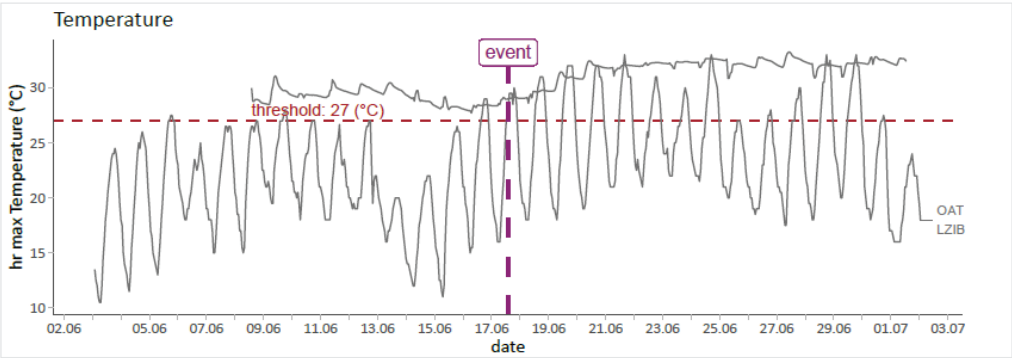


**Figure 4.** Example of the temperature measured in June 2021, where 'event' marks the moment where air purifier was installed

What is also visible from the graph in Figure 4, the introduction of air purifier had no influence on the temperature. Similar was also with humidity – again no influence from air purifier.

## Particulate matter (PM)

None of 20 measuring sites in schools show problem with PM. Though it is visible from the Figure 5, that air purifier reduces average PM (by at least 30%), PM concentration rarely cross the WHO thresholds (EEA, 2023) as shown in Figure 5. True value of the air purifier would be shown in winter time, when PMs are being used as transportation means for viruses, and air purification plays more important role.

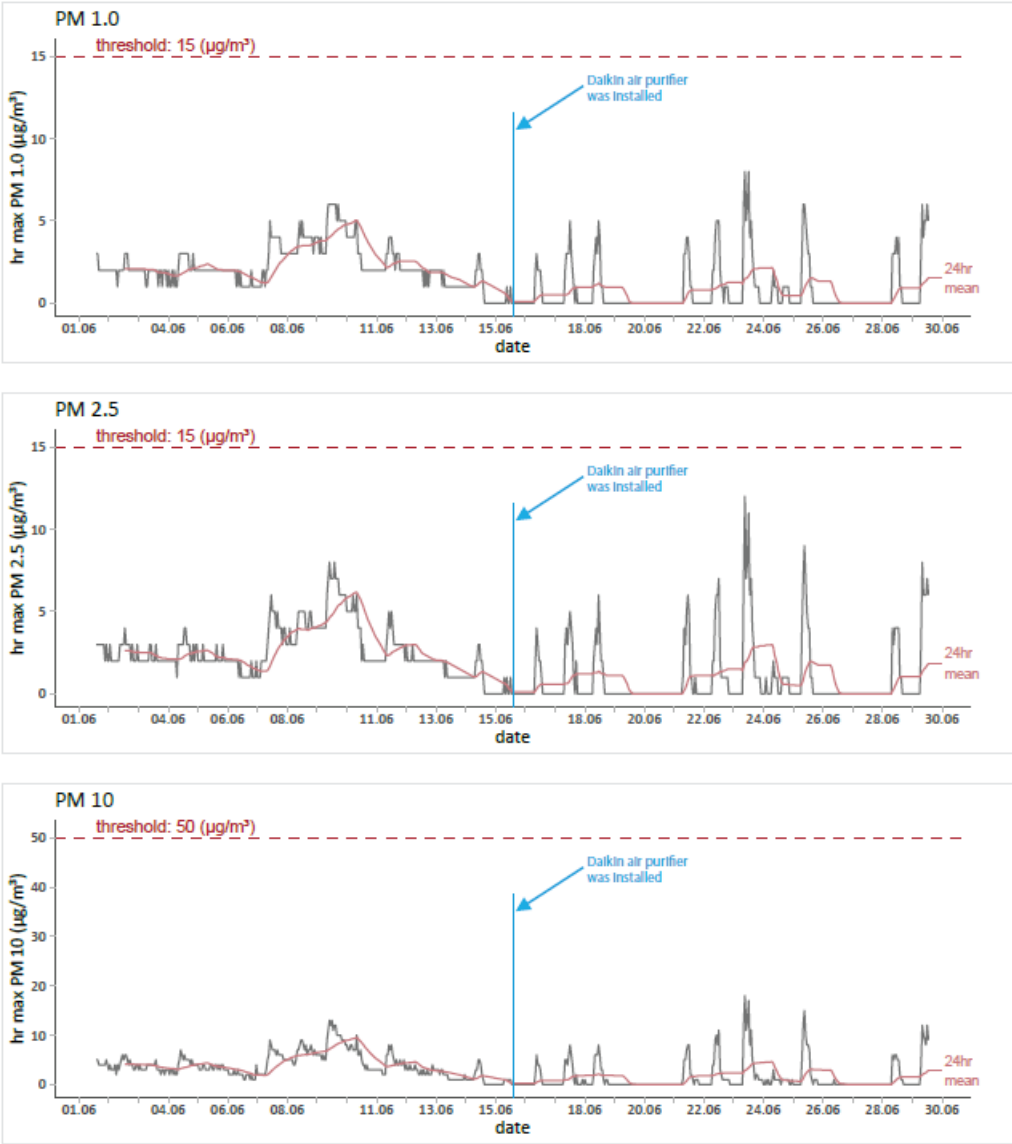


**Figure 5.** Concentration of $PM_1$, $PM_{2.5}$ and $PM_{10}$ with the moment of installation of air purifier, with WHO thresholds (EEA, 2023)

## Results of $CO_2$ concentration measurement

Measured $CO_2$ concentrations were the most interesting ones from the research point of view, since measured values gave a lot of valuable (and somehow expected) insights which prove the threat for pupils and students of poor IAQ conditions in the classrooms. The Figure 6 shows the school classification based on average $CO_2$ concentrations in the classrooms. Results showed that almost all schools struggle with increased $CO_2$ concentrations and more than 11 out of 20 definitely have sick building syndrome (SBS), with concentrations higher than 2000 ppm of $CO_2$ (US-EPA, 1991).

It is important to repeat that the measurements took place in the summer period where airing the classrooms is more convenient. It is fair to predict, that in winter periods the situation will be even worse, which asks for clear and quick countermeasures.

| $CO_2$ concentration(PPM) | Up to 1000 | 1000 - 1500 | 1500-2000 | 2000-3000 | 3000 to 5000 |
|---|---|---|---|---|---|
| Details | Recommended $CO_2$ level in indoor environment for good indoor air quality | Max. $CO_2$ limit recommended in indoor environment | Symptoms: Fatigue & decreased concentration | Symptoms: Drowsiness, headache, increase in blood pressure | Highest exposure limit! It is not recommended to stay indoors for a longer time under these conditions |

**Figure 6.** Results of grouping of schools according to measured average $CO_2$ concentration

The measurement results are shown in the Figure 7, where occurence of very high concentration is obvious. Air purifier meant no difference to the concentration levels, so there is a need of a different countermeasure.

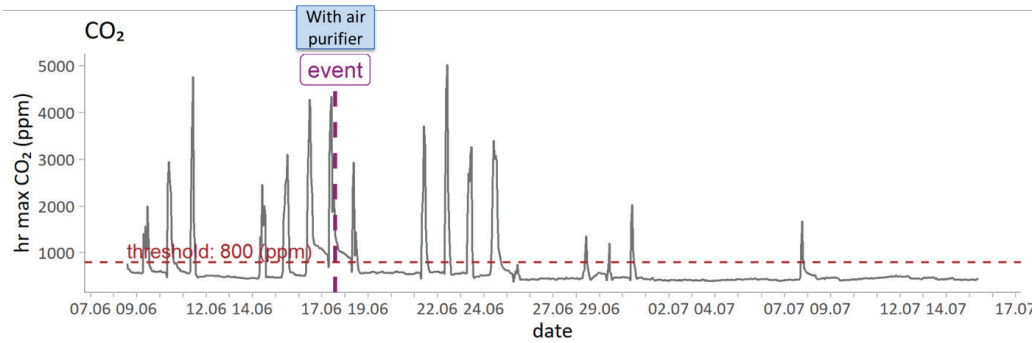


**Figure 7.** Example of one of the worst measured values of $CO_2$ concentration in one school

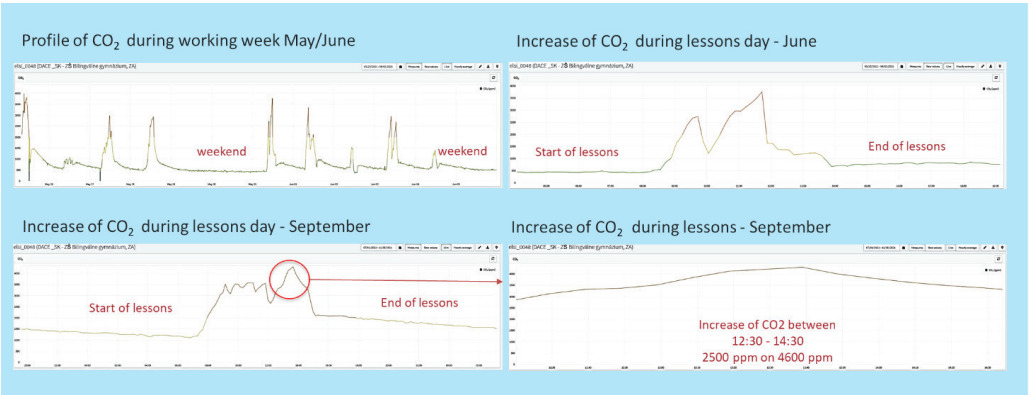


**Figure 8.** Example of measured $CO_2$ concentration in a week, one day and specific hours

Further results shown in Figure 8 present the $CO_2$ concentration development during one week in in May/June, one day in June, one day in September and the specific time between 12:30 and 14:30. $CO_2$ concentration development in one day between 12:30 and 14:30 show already high concentration of 2500 ppm increasing to 4600 ppm, where we can see that $CO_2$ concentration, once risen during the day, never drops to recommended $CO_2$ levels, not even with natural ventilation (opening windows bring also polluted air from the outside, so the benefits of natural ventilation should be separately investigated).

In the primary school ZŠ Nová Dedinka, during summer break, heat recovery ventilation unit was installed. The results of the $CO_2$ concentration are shown in the Figure 9.

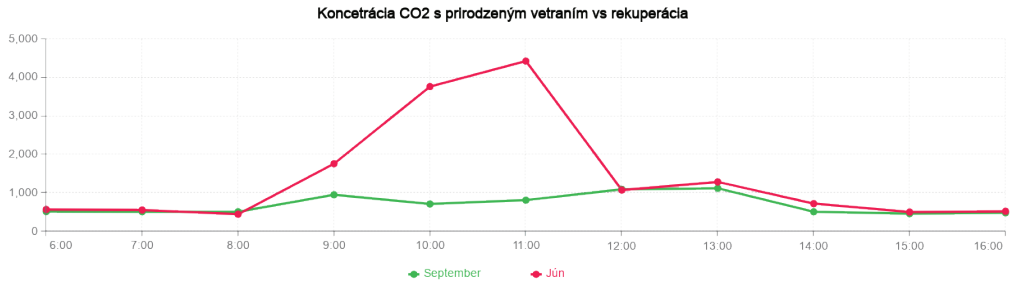


**Figure 9.** $CO_2$ concentration in primary school ZŠ Nová Dedinka before and after installing heat recovery ventilation unit VAM J

Comparing measured values before (red line) and after the installation of heat recovery ventilation unit (green line), the successful countermeasure with the installation of heat recovery ventilation unit was achieved. During September, the recommended WHO $CO_2$ concentration threshold was successfully kept throughout the whole time, which showed that ventilation is key tool to keep $CO_2$ concentration in the recommended limits.

## CONCLUSION

Indoor air quality research done in Slovakia on 20 schools did show in practice how poor is the air quality in the classrooms all over Slovakia, and similar conclusion could be made on majority of schools in central and eastern Europe, perhaps even wider. With too high humidity and temperatures (measurements took place in summer), the comfort in schools is on a very low level. Particulate matters measured are in most schools in the frames of WHO threshold (EEA, 2023) which is 15 $\mu g/m^3$ for $PM_{2,5}$, while $CO_2$ concentrations were far above acceptable levels, which means that health of school children, but also teachers and other staff working in schools, is threatened for long years, and it is right time to finally do something about it.

European Commission has published in April 2024 the Directive (EU) 2924/1275 on the energy performance of buildings (usually known by the abbreviation EPBD). In this directive it is clearly mentioned that IAQ plays an important role, and that EU member states should require that non-residential buildings should have IAQ sensors and provide high indoor air quality in buildings. REHVA (2024) published position paper on Indoor environmental quality (IEQ) which part is IAQ for above mentioned EPBD, urging to include ventilation as a separate point next to heating and cooling, tackling the poor IAQ in buildings even after the renovation. At the end, the Directive leaves this to member states to decide on requirements.

With simple countermeasure like ventilation (which should include filtration) IAQ can be significantly improved, schools could finally become comfortable and healthy place to spend time and work in. So, overall advice given, in order to ensure better or even maintain good indoor air quality, is to consider installing forced (mechanical) ventilation. There is a strong need to speed up the renovation process overall, and schools should be top of the priority for all of us, not to further jeopardize health of one of the most vulnerable groups – children.

## ACKOWLEDGMENTS:

This study was realised in by Vladimir Orovnický and Daikin Slovakia team, and the results were part of the bigger project, done together with their partners in the association 'Buildings for Future' in Slovakia.

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Poster presentation

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# PRELIMINARY COMPARISON OF AIR QUALITY SENSOR MEASUREMENTS WITH DATA FROM REFERENT MONITORING STATIONS – EDIAQI PROJECT

## Abstract

*Over the past few years, there has been a significant increase in the use of low-cost sensors for air quality monitoring. The relationship between the concentration of pollutants and their sources is one of the main topics of interest in environmental and health studies. The impact of air quality on human health has been widely researched with the conclusion that monitoring air quality is more important than ever, whereas recent studies have become more focused on indoor air quality monitoring. For the purposes of the Zagreb – pilot part of the EDIAQI (Evidence Driven Indoor Air Quality Improvement) project, two outdoor air quality sensors were placed in Zagreb, the capital of Croatia, for testing the sensors in real conditions. The sensors were placed at reference monitoring stations that are part of the Zagreb air quality monitoring network. One sensor was placed in the northern part of the city, at the Institute for Medical Research and Occupational Health (IMROH), which is an urban background station, and another one at the air quality monitoring station Peščenica in the eastern part of Zagreb with an industrial background. Considering the fact that sensor measurement accuracy and precision in previous studies have shown significant dependency on the location of the sensor, the purpose of this work was to determine the correlation between sensor measurements and the data collected at the reference monitoring stations. Particulate matter ($PM_{2.5}$ and $PM_{10}$), $NO_2$ and meteorological data (temperature, humidity, and atmospheric pressure) were chosen as relevant air quality parameters that can be used to determine data correlations. Hourly and daily averaged data were collected from both sources for a time period of two months (April/May 2023). Statistical analysis was performed using Python libraries for data analysis. All of the results in this work are part of preliminary testing and further research will be carried out through the EDIAQI project.*

**Keywords:** *air quality, low-cost sensor measurements, pollutants, particulate matter, meteorological data*

## INTRODUCTION

The impact of ambient air quality on human health has become an increasingly prominent area of research in recent years. With growing concerns over air pollution and its detrimental effects on public health, monitoring air quality has never been more crucial. As a result, there has been a significant surge in research exploring the potential use of low-cost sensors for air quality monitoring (Bush et al., 2022). These sensors have garnered considerable attention due to their numerous advantages over traditional, more expensive air quality monitoring instruments. Some of the key benefits of low-cost sensors include lower operational expenses, ease of deployment, and reduced administrative complexities, making them more accessible and scalable for widespread use.

However, while low-cost sensors offer these advantages, they also come with their own set of challenges. Air quality sensors are designed with hardware that is sensitive to specific air pollutants, and to ensure that they generate reliable and accurate data, they require careful calibration and robust data processing methods. One of the main challenges associated with these sensors is that calibrations performed in controlled

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laboratory settings often do not fully reflect the dynamic and variable environmental conditions encountered in real-world scenarios. This discrepancy between laboratory and field conditions can lead to inaccuracies in sensor measurements, highlighting the importance of applying advanced data analysis techniques to improve the quality and reliability of sensor-generated data.

In previous studies, the accuracy and precision of sensor measurements have been shown to be highly dependent on the sensor's location. Environmental factors such as temperature, humidity, wind speed, and local pollution sources can all influence the performance of low-cost sensors. Therefore, it is essential to conduct a thorough data analysis to identify and correct these location-specific biases, optimizing the sensor's data to be as accurate and representative as possible.

The primary objective of this study was to investigate the correlation between the measurements provided by low-cost sensors and the data collected at reference monitoring stations. By comparing sensor data to more accurate and validated reference data, the aim was to better understand how well low-cost sensors can replicate traditional air quality measurements and identify factors that influence their performance. Through this analysis, we hope to enhance the calibration and deployment strategies for low-cost sensors, ultimately improving their utility in real-world air quality monitoring applications.

## MATERIALS AND METHODS

Particulate matter ($PM_{2.5}$ and $PM_{10}$), $NO_2$ and meteorological data (temperature, humidity, and atmospheric pressure) were chosen as relevant air quality parameters that can be used to determine data correlations. Measurements conducted by AIRWINGS outdoor sensors, developed by WINGS ICT SOLUTIONS were compared to reference measurements. Reference measurements of ambient $NO_2$ were performed using HORIBA APNA 370 according to norm EN 14211:2012, while referent PM values were determined using gravimetric methods accredited by norm EN 12341:2014. The sensors were placed at reference monitoring stations that are part of the Zagreb air quality monitoring network and funded by the City of Zagreb. One is located in the northern part of the city, at the Institute for Medical Research and Occupational Health (IMROH), which is categorized as an urban background station, and the second one at the air quality monitoring station Peščenica (PES) in the eastern part of Zagreb with an industrial background. Hourly and daily averaged data for a time period of two months (April/May 2023) was collected from both sources. Prior to machine learning, collected data was optimized by outlier removal, and statistical analysis was performed. The data was then normalized by Min – Max Scaling and the dataset was split into training and testing subsets using an 75/25 % split.

Random Forest (RF) models have demonstrated considerable potential as an effective tool for the calibration and validation of low-cost air quality sensors. Specifically, Random Forest regression, a supervised machine learning technique, has gained traction due to its robustness and versatility in handling complex datasets, which makes it particularly well-suited for sensor data analysis. This approach involves the use of an ensemble of

decision trees, where each tree is trained on a random subset of the data. During the training process, the trees learn to make predictions based on different combinations of input features, which allows the model to capture a wide range of patterns in the data. This random selection of features and data subsets helps to avoid overfitting, which can be particularly problematic when working with noisy or highly variable sensor data. Once the model has been trained, the predictions from all individual decision trees are aggregated, typically using a simple average (in the case of regression tasks), to provide a final output. This ensemble approach leads to improved accuracy, as the errors made by individual trees are likely to be offset by others in the forest. As a result, Random Forest regression is particularly effective in reducing variance and bias, making it a potential choice for calibrating low-cost sensors that might otherwise produce noisy or inconsistent data.

## RESULTS AND DISCUSSION

Meteorological data collected from the IMROH station and the sensors placed there was investigated, and pressure, relative humidity and temperature all showed a high correlation between sensor and referent data, as can be seen in Figure 1. The same could not be reproduced for the PES station because the station lacked meteorological referent data.

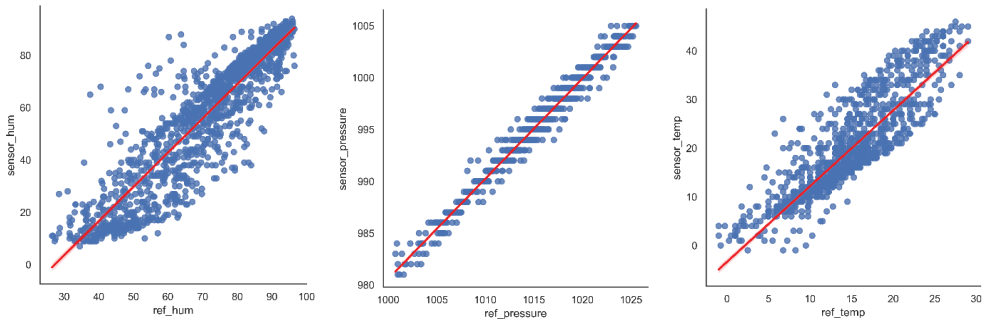


**Figure 1.** Meteorological data correlation plots for the IMROH station

Looking into $NO_2$ measurements presented in the heatmap plots in Figure 2, we can see that the predicted values at both stations had a high correlation with values measured by the sensor but little to none with referent $NO_2$ values. We can see that the sensor-measured $NO_2$ values correlated both with the humidity and pressure measured by the sensor and the referent measurements.

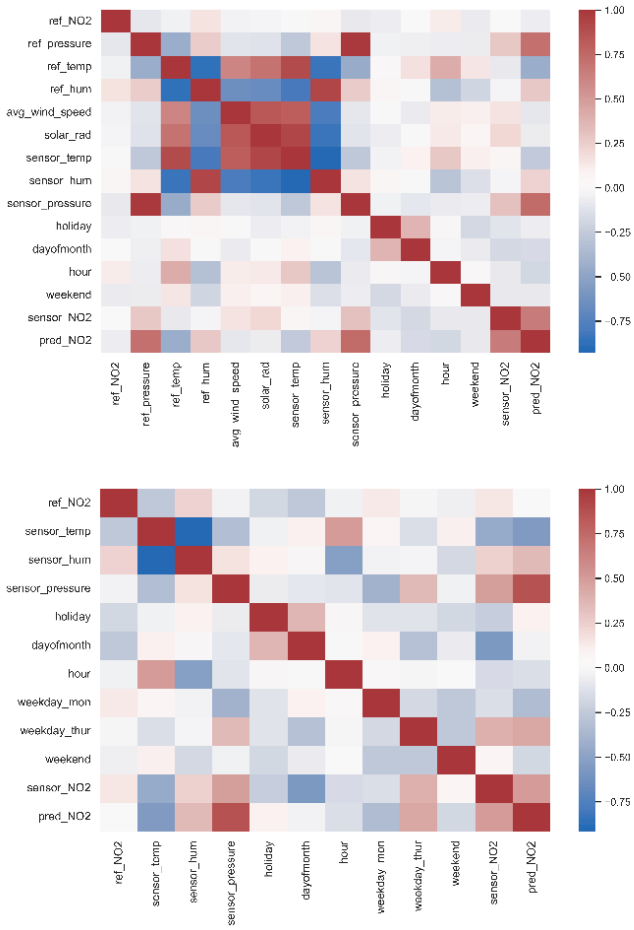


**Figure 2.** Heatmap plots of $NO_2$ values after RF modeling: a) IMROH station, b) PES station

The IMROH station only has the $PM_{10}$ and $PM_{2.5}$ referent measurements, while the PES station has $PM_{10}$ referent measurements. Using RF, predicted values based on the 75/25 split were determined for a 2-week test set. Considering the limitations and restrictions of the dataset size, the correlation of the predicted and referent PM concentrations can be seen, but the effect of the offset of sensor values from the referent values is evident in Figure 3.

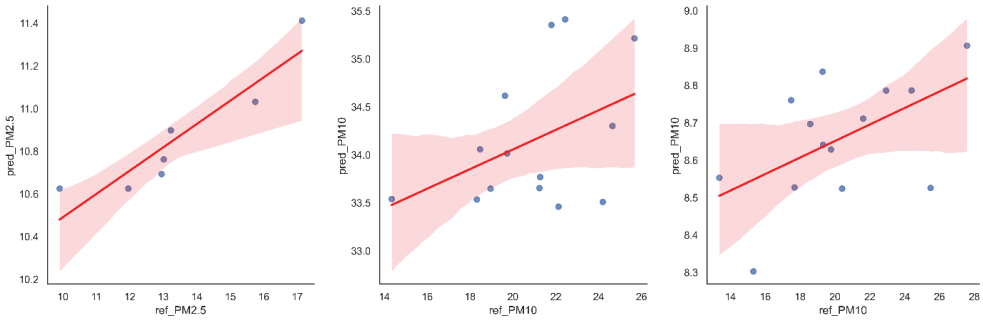


**Figure 3.** Correlation plots of predicted PM values after RF modeling on a 2-week test set: a) IMROH station $PM_{10}$, b) IMROH station $PM_{2.5}$, c) PES station $PM_{10}$

## CONCLUSIONS

Meteorological sensor data showed a correlation with meteorological data collected on the IMROH referent station with a significant offset. Since low-cost sensors base their measurements on meteorological data, a calibration of sensor meteorology based on local meteorological data is needed. Following RF modeling, the predicted PM values showed a correlation to referent data, but the effect of the offset was visible. The heatmap plots of $NO_2$ values after RF modeling show that the predicted $NO_2$ values followed the trend of determined sensor $NO_2$ values, but they did not show a correlation to referent $NO_2$ values. Since the PES station did not have meteorological data, it was not used in the training of the model, and the absence of the meteorological data had an impact on the model itself. Further analysis on a bigger dataset is necessary after the calibration of the sensors based on local meteorology.

## ACKNOWLEDGEMENT

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Oral presentation

**Gordana Pehnec**

# CURRENT AIR QUALITY LEGISLATION AND NEW WORLD HEALTH ORGANIZATION GUIDELINES – IMPACT ON AIR QUALITY ASSESSMENT IN ZAGREB, CROATIA

## Abstract

*Air quality in Croatia is assessed annually according to the Air Pollution Act (OG No. 127/19, 57/22) and Regulation on Levels of Pollutants in Ambient Air (OG No. 72/20). Since 2011, Croatian legislation has been fully harmonized with EU legislation. In 2021, based on the most recent scientific evidence, the World Health Organization (WHO) published new global air quality guidelines, with stricter recommendations on guideline levels for most pollutants. In October 2022, the EU Commission proposed a revision of the Ambient Air Quality Directives. The EU Directive Proposal set air quality standards that were more closely aligned with the latest WHO recommendations and should be reached by 2030. Measurements of ambient air quality in Zagreb, Croatia, have been carried out continuously within the local air quality monitoring network funded by the City of Zagreb since the 1960s. Currently, the network consists of six stations, located in different parts of the town. In this study, data on air quality from the Zagreb local monitoring network for the period 2018-2022 were analysed. Levels of pollutants are discussed with regard to current air quality legislation, the new EU Directive Proposal and WHO guidelines. Considering current legislation, during the observed five years, levels of $PM_{10}$, $NO_2$ and $O_3$ exceeded limit values only at some monitoring stations. However, taking into account the new EU Directive Proposal limit values, the air would be considered polluted at almost all of the stations regarding $PM_{10}$, $PM_{2.5}$, $NO_2$ and $O_3$. Although decreasing trends of pollutant concentrations were observed at most of the stations, it seems difficult to achieve the new EU objectives before 2030. Regarding the recommended WHO guidelines values, the air quality was assessed as even worse for all of these pollutants.*

**Keywords:** *air pollutants, air quality objectives, EU Directive Proposal, limit value, WHO*

## INTRODUCTION

Ambient air pollution currently presents the largest environmental health risk in Europe. It is estimated as the number one environmental cause of early death in the European Union (EU), causing around 275,000 premature deaths due to the exposure to $PM_{2.5}$ and around 64,000 by $NO_2$ each year (EEA, 2022a), among which over 1,200 deaths in people under 18 years of age (EEA, 2023). It especially affects vulnerable groups (children, elderly people and persons with pre-existing conditions, socioeconomically disadvantaged groups). A significant number of noncommunicable diseases is attributed to air pollution, including asthma, cardiovascular problems and lung cancer, but was also found to cause changes of the nervous system, and conditions such as dementia. Furthermore, polluted air presents a risk to the environment as well, through acidification, eutrophication, and ozone damage (EEA, 2022b).

The World Health Organization (WHO) has regularly integrated scientific evidence on air pollution's health impacts since 1987 and published recommendations in the form of Air Quality Guidelines (AQG). They are based on systematic literature reviews and subsequent rigorous evaluation methods as well as extensive consultation with experts and end-users of the guidelines from all regions of the world. The WHO AQG serves as a global target for national, regional and city governments to work towards improving air quality (WHO, 1987, 2006, 2021). The last issue of AQG published in September 2021,

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sets stricter recommendations on guideline levels for $PM_{2.5}$, $PM_{10}$, $O_3$, $NO_2$, $SO_2$ and CO and suggests the monitoring of some emerging pollutants such as ultrafine particles and black carbon (WHO, 2021).

The current EU ambient air quality legislation framework includes the following documents: Directive 2008/50/EC, Directive 2004/107/EC and Directive 2015/1480/EC of the European Parliament and of the Council (EC 2004, EC 2008, EC 2015) and implements limit values recommended by the WHO AQG from 2005, but not in full. In December 2019, within the European Green Deal, the European Commission committed to further improving air quality and aligning EU air quality standards more closely with the latest recommendations of the WHO. The Zero Pollution Action Plan entails a vision for 2050 to reduce air, water and soil pollution to levels no longer considered harmful to health and natural ecosystems. 2030 targets were introduced, of which two are related to air quality - to reduce the health impacts of air pollution (premature deaths) by more than 55%, and to reduce the share of EU ecosystems where air pollution threatens biodiversity by 25% (EC, 2023). In October 2022, the EU Commission proposed a revision of the Ambient Air Quality Directives with the goal to merge the current directives into one, further improve the legislative framework, especially in relation to penalties and public information, strengthen air quality monitoring, modelling and planning, and align EU air quality standards more closely with WHO recommendations by 2030 (EC, 2022).

The aim of this paper was to compare the limit values in guidelines and legislation as well as to compare air quality assessments based on current legislation, the Proposal of the Directive and WHO guidelines using the case of the city of Zagreb, Croatia.

## MATERIALS AND METHODS

Data on mass concentrations of pollutants in the air of Zagreb, Croatia, measured at six measuring stations of the local measuring network of the city of Zagreb over a five-year period (2018-2022), were analysed. The locations of the measuring stations and pollutants included in this study are shown on Figure 1. The network is funded by the City of Zagreb and measurements are contractually carried out by the Institute for Medical Research and Occupational Health, using reference, standardized methods in accordance with the requirements of the EU directives.

The air quality assessment was carried out with regard to the current Directive 2008/50/EC, the Proposal for the revised Directive from 2022 and the WHO 2021 air quality guidelines. The following pollutants were included in the study: $O_3$, $NO_2$, $PM_{10}$, and $PM_{2.5}$.

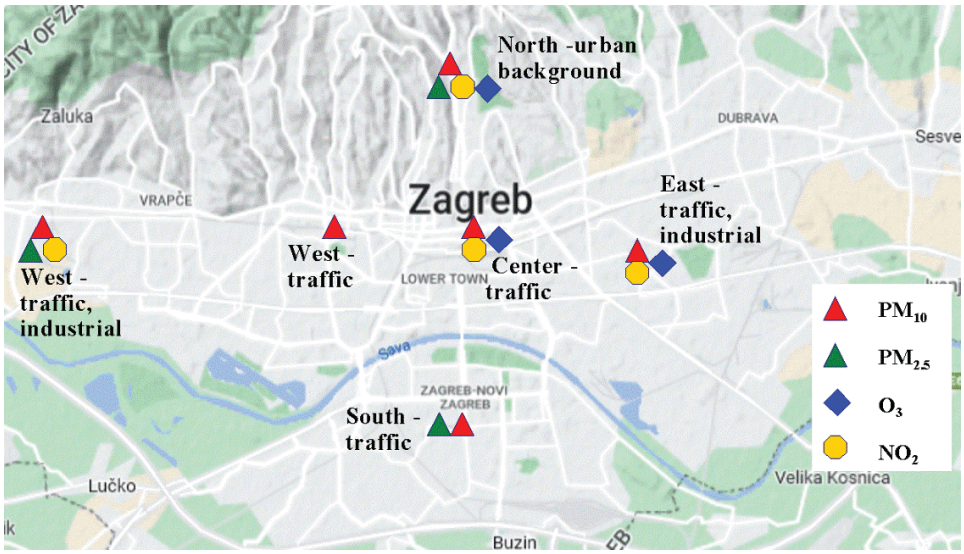


**Figure 1.** Locations of measuring stations within the Zagreb city monitoring network and the measured pollutants included in the study

## RESULTS AND DISCUSSION

Table 1 presents and compares limit and target values set by current EU legislation (EC, 2004; EC, 2008), the EU Directive Proposal (EC, 2022) and the WHO AQG from 2005 and 2021 (WHO, 2006; WHO 2021). It is evident that EU Directive Proposal from 2022 sets much lower limit values compared to the current ones, especially for $NO_2$, $PM_{10}$ and $PM_{2.5}$, but these air quality standards are still higher than the latest WHO recommendations.

Figure 2 shows number of days with $O_3$ exceedances for the period 2018-2022 with corresponding air quality standards and WHO recommendations. It is evident that the number of days with exceedances varied significantly from year to year, which is not surprising given the photochemical origin of tropospheric ozone and its dependence on meteorological parameters. At the traffic measuring station, there were no exceedances of the target values from the existing Directive or from the proposal for amending the Directive, while, observing the WHO guidelines, the air quality with regard to $O_3$ was not satisfactory at all of the stations.

The $NO_2$ concentrations at all four measuring stations were characterized by a decreasing trend, which was most pronounced at the measuring station with the highest traffic density in the city center (Figure 3). The limit value from the current Directive was not exceeded once during the observed five-year period, but if the limit values from the Directive Proposal were applied, then the air quality would be satisfactory during all five years only at the measuring station in the northern part of the city. However, given the pronounced decreasing trend in $NO_2$ concentrations, it is very likely that, if it continues, the air quality will also be satisfactory at the other measuring stations in the coming years. If the WHO guidelines are taken into account, the air quality was not satisfactory at any station, and given the large number of days with exceedances of the guidelines, it is unlikely that $NO_2$ levels in Zagreb will be in line with them in the near future.

**Table 1**. Limit and target values of pollutants in the ambient air with regard to the protection of human health

| | | Limit/target value | | Guideline value | |
|---|---|---|---|---|---|
| **Pollutant** | **Averaging time** | **Current EU legislation** | **EU Directive Proposal** | **WHO 2005** | **WHO 2021** |
| **$O_3$** | Maximum daily 8-h average | 120 µg/m³<br>not to be exceeded more than 25 times per calendar year** | 120 µg/m³<br>not to be exceeded more than 18 times per calendar year** | 100 µg/m³ | 100 µg/m³<br>not to be exceeded more than 3-4 times per year* |
| **$PM_{10}$** | 24 h | 50 µg/m³<br>not to be exceeded more than 35 times per calendar year | 45 µg/m³<br>not to be exceeded more than 18 times per calendar year | 50 µg/m³ | 45 µg/m³<br>not to be exceeded more than 3-4 times per year* |
| | Calendar year | 40 µg/m³ | 20 µg/m³ | 20 µg/m³ | 15 µg/m³ |
| $PM_{2.5}$ | 24 h | - | 25 µg/m³<br>not to be exceeded more than 18 times per calendar year | 25 µg/m³ | 15 µg/m³<br>not to be exceeded more than 3-4 times per year* |
| | Calendar year | 25 µg/m³ | 10 µg/m³ | 10 µg/m³ | 5 µg/m³ |
| **$NO_2$** | 1 h | 200 µg/m³<br>not to be exceeded more than 18 times per calendar year | 200 µg/m³<br>not to be exceeded more than 18 times per calendar year | 200 µg/m³ | 200 µg/m³ |
| | 24 h | - | 50 µg/m³<br>not to be exceeded more than 18 times per calendar year | - | 25 µg/m³<br>not to be exceeded more than 3-4 times per year* |
| | Calendar year | 40 µg/m³ | 20 µg/m³ | 40 µg/m³ | 10 µg/m³ |
| **CO** | 1 h | - | | 35 mg/m³ | 35 mg/m³ |
| | Maximum daily 8-h average | 10 mg/m³ | 10 mg/m³ | 10 mg/m³ | 10 mg/m³ |
| | 24 h | - | 4 mg/m³<br>not to be exceeded more than 18 times per calendar year | | 4 mg/m³ |
| **$SO_2$** | 1 h | 350 µg/m³<br>not to be exceeded more than 24 times per calendar year | 350 µg/m³<br>not to be exceeded more than ones per calendar year | 500 µg/m³<br>for 10-min averaging period | 500 µg/m³<br>for 10-min averaging period |
| | 24 h | 125 µg/m³<br>not to be exceeded more than 3 times per calendar year | 50 µg/m³<br>not to be exceeded more than 18 times per calendar year | 20 µg/m³ | 40 µg/m³<br>not to be exceeded more than 3-4 times per year* |
| | Calendar year | - | 20 µg/m³ | - | - |

*99th percentile; ** averaged over three years


**Figure 2.** Number of days with maximum 8-hour average (a) higher than 120 µg/m³ (the current EU Directive, EU Directive Proposal); (b) higher than 100 µg/m³ (WHO AQG)

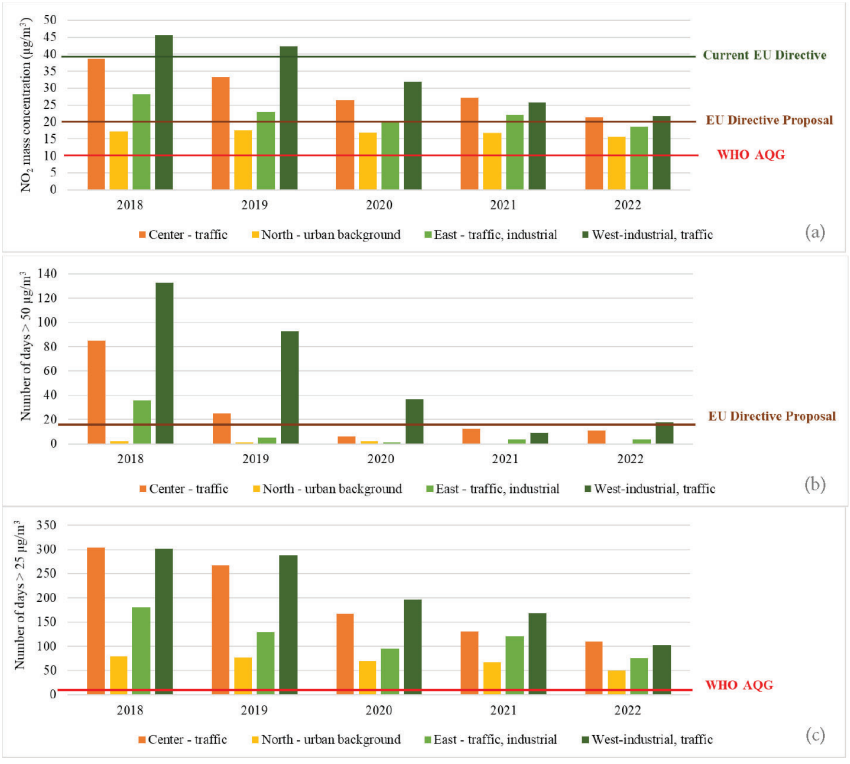


**Figure 3.** (a) $NO_2$ annual average with regard to the current EU Directive, EU Directive Proposal and WHO AQG; Number of days with 24-h $NO_2$ concentrations (b) higher than 50 µg/m³ (EU Directive Proposal); (c) higher than 25 µg/m³ (WHO AQG)

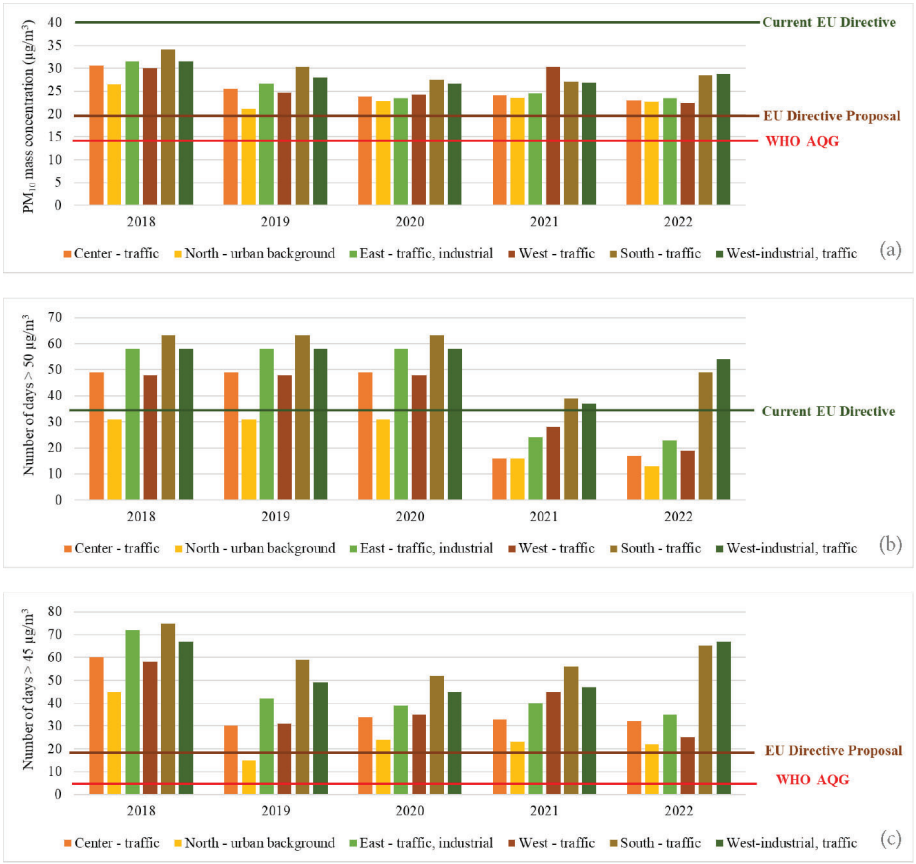


**Figure 4.** (a) $PM_{10}$ annual average with regard to the current EU Directive, EU Directive Proposal and WHO guidelines; Number of days with 24-h $PM_{10}$ concentrations (b) higher than 50 µg/m³ (current EU Directive); (c) higher than 45 µg/m³ (EU Directive Proposal and WHO guidelines)

At all six measuring stations for the period 2018-2022, a decreasing trend in $PM_{10}$ concentrations was observed, although for most measuring stations it was less pronounced compared to the decreasing trend of $NO_2$ (Figure 4). The limit value for the annual average from the current Directive was not exceeded at any measuring station, but if the limit value for the annual average from the Directive Proposal, and especially the WHO guidelines, were taken into account, then the air quality would not be in accordance with these values at all of the measuring stations. Considering the limit value for the 24-hour average from the current regulations, the air quality was satisfactory only at the measuring station in the northern part of the city during the whole observed period and, since 2021 in the city center, in the eastern part of the town and at a traffic location in the west. However, if the limit values from the Directive Proposal and from the WHO guidelines were applied to assess air quality, then the air quality would not be satisfactory at all of the measuring station. Although there was a downward trend in both the annual averages and the number of days with exceedances, it does not seem

likely that the targets set will be achieved at all of the measuring stations by 2030 without implementing additional measures.

A decreasing trend in $PM_{2.5}$ concentrations was evident at all three measuring stations and the limit value for the annual average from the current Directive was not exceeded at any station (Figure 5). However, if the air quality assessment were carried out on the basis of the limit value for the annual average from the Directive Proposal and WHO guidelines, then the air quality would not be satisfactory at all of the locations. Considering the number of days with $PM_{2.5}$ concentrations higher than 25 μg/m³ (Directive Proposal) and higher than 15 μg/m³ (WHO guidelines), the very large number of exceedances clearly show that the goals set will not be achieved until 2030. Croatia is an exception in Europe - according to the latest report of the European Environment Agency for 2022 (EEA, 2024), as many as 16 countries, mainly from central and south-eastern Europe, reported higher $PM_{2.5}$ concentrations than Croatia. Central-eastern Europe and Italy reported the highest concentrations of particulate matter, primarily due to the burning of solid fuels for domestic heating and their use in industry.

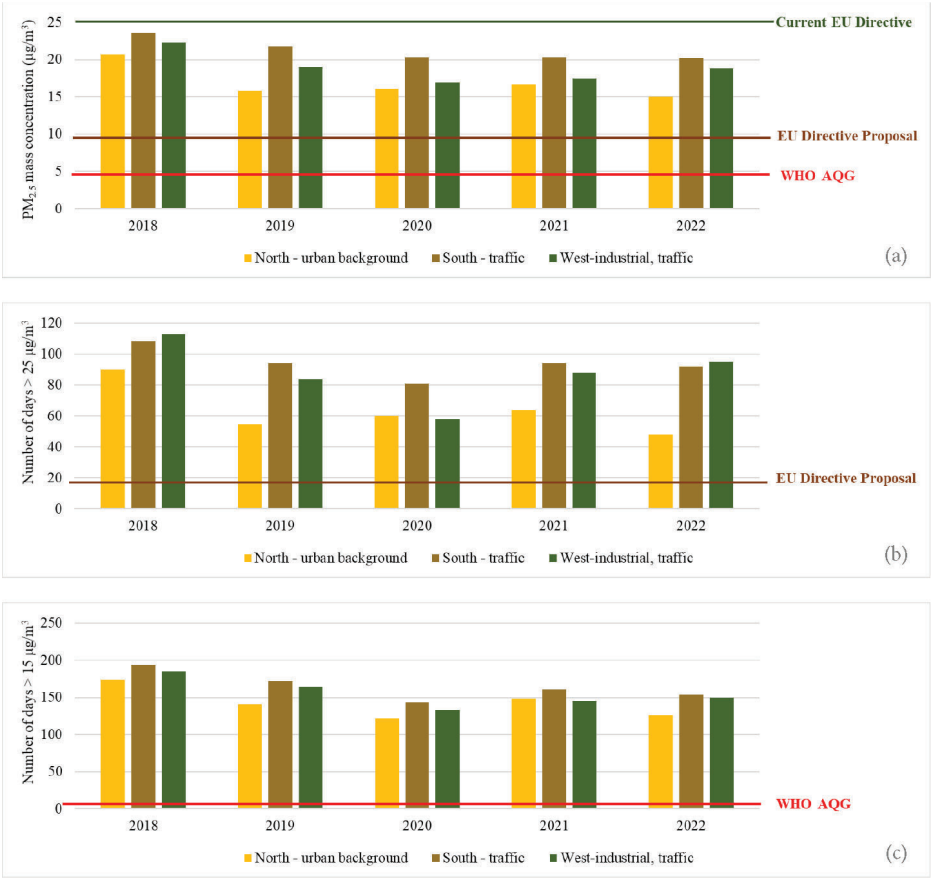


**Figure 5.** (a) $PM_{2.5}$ annual average with regard to the current EU Directive, Directive Proposal and WHO guidelines; Number of days with 24-h $PM_{2.5}$ concentrations (b) higher than 25 μg/m³ (EU Directive Proposal); (c) higher than 15 μg/m³ (WHO AQG)

## CONCLUSIONS

Taking into account current legislation, levels of $PM_{10}$, and $O_3$ exceeded limit values only at some monitoring stations, but considering the new EU Directive Proposal limit values, the air would be considered polluted at some stations regarding $NO_2$ and $O_3$, and at all stations regarding $PM_{10}$ and $PM_{2.5}$. Considering WHO guideline values, the air quality was unsatisfactory at all of the stations for all of the analysed pollutants ($O_3$, $NO_2$, $PM_{10}$, and $PM_{2.5}$). Although strong decreasing trends of pollutant concentrations were observed at most of the stations, it seems difficult to achieve the new EU objectives for $PM_{10}$ and $PM_{2.5}$ before 2030 without implementing additional measurement for the improvement of air quality, especially in the field of traffic emissions and emissions from household heating.

## ACKNOWLEDGEMENTS

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Poster presentation

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# THE RELATIONSHIP BETWEEN GAS CONSUMPTION AND AIR POLLUTION IN ZAGREB

## Abstract

*The polycyclic aromatic hydrocarbons (PAHs) and metals present in particulate matter (PM) significantly contribute to the health risks associated with air pollution. This paper presents a comprehensive analysis of the relationship between gas consumption and the concentrations of PAHs and metals in the $PM_{10}$ fraction of PM. By utilizing statistical techniques and Python models, the study investigated the potential associations and quantified the relationship between gas consumption patterns, meteorological conditions and measured concentrations of PAHs and metals in the atmosphere. A combination of statistical techniques was used, including Principal Component Analysis (PCA), correlation analysis and Non-Negative Matrix Factorization (NMF). Variables that were strongly correlated or had similar sources tended to cluster together in the PCA results. Gas consumption (kWh), mass concentrations of fluoranthene and arsenic in $PM_{10}$ were grouped together, indicating their potential relationship. Mass concentrations of cadmium and lead formed a cluster, suggesting a shared source or common factors influencing the concentrations of these metals in air pollution, while copper, iron, and manganese formed a separate cluster, indicating potential similarities in their sources or influencing factors. Additionally, NMF provided valuable information for understanding PAHs and metal pollution dynamics over the studied period. These findings can serve policymakers, urban planners, and environmental stakeholders in implementing effective strategies to mitigate air pollution and promote sustainable energy consumption practices in the city of Zagreb.*

**Keywords:** *air pollution, metals, NMF, PAHs*

## INTRODUCTION

Air pollution is a worldwide problem that harms human health, leading to serious illnesses and risks to well-being (Poulsen et al., 2023; Sørensen et al., 2022). The main components of particulate matter (PM) include organic compounds, metals, biological materials and water-soluble ions (Kampa and Castanas, 2008). Polycyclic aromatic hydrocarbons (PAHs) are organic compounds produced as the result of the combustion of fossil fuels, wood, organic materials, industrial processes, or agricultural activities (Krzyszczak and Czech, 2021). PAHs have been identified as potent carcinogens and mutagens (Dieme et al., 2012; Jakovljević et al., 2020a) and are known to induce oxidative stress and inflammation in the human body, processes that are associated with different health problems, including respiratory and cardiovascular diseases (Leclercq et al., 2016). Metals in PM come from both natural and anthropogenic sources like industrial emissions, burning fossil fuels, and the stirring up of dust and soil (Chen and Lippmann, 2009). This study explores air pollution and public health by examining the sources of PAHs and metals in $PM_{10}$, their relationship to gas consumption, and the impact of weather conditions on their levels. It also investigates gas usage, weather, and pollutants interact. This is the first study in the region to combine air quality, meteorology, and gas consumption data. The findings aim to improve air quality management and public health by identifying pollutant sources and relationships.

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## MATERIALS AND METHODS

This study focuses on the IMROH measuring station in Zagreb, Croatia, an urban residential site for air pollution monitoring, located at the Institute for Medical Research and Occupational Health. From 2017 to 2020, 24-hour $PM_{10}$ samples were collected and analyzed for metals, including arsenic (As), cadmium (Cd), lead (Pb), manganese (Mn), iron (Fe), copper (Cu), and zinc (Zn). The analyzed PAHs included benzo(a)pyrene (BaP), benzo(a)anthracene (BaA), benzo(ghi)perylene (BghiP), dibenzo(ah)anthracene (DahA), chrysene (Chry), benzo(k)fluoranthene (BkF), benzo(b)fluoranthene (BbF), benzo(j)fluoranthene (BjF), fluoranthene (Flu), and pyrene (Pyr).

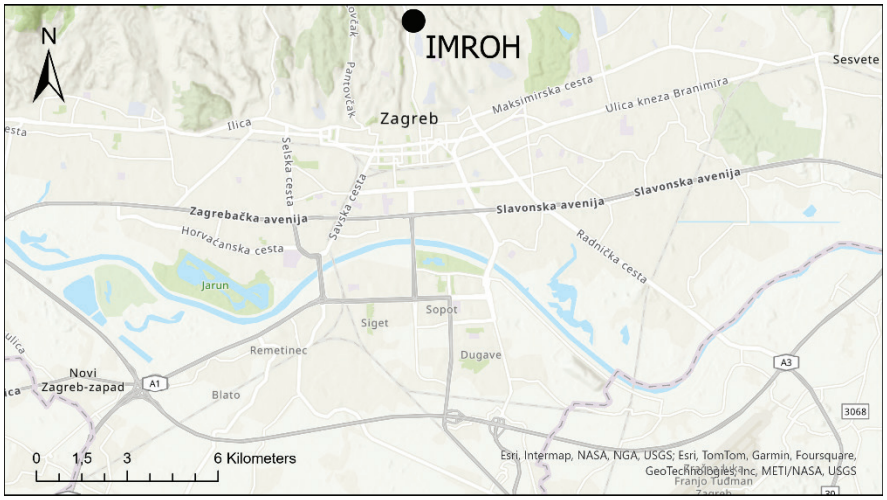


**Figure 1**. Study area with air quality measuring station (IMROH, N: 45º 50' 04"; E: 15º 58' 41")

$PM_{10}$ samples were collected using low-volume samplers (~55 $m^3$/day) and analyzed for metal content with inductively coupled plasma mass spectrometry (ICP-MS) after microwave digestion in nitric acid (Beslic et al., 2020). PAHs were extracted from filters in an ultrasonic bath using a solvent mixture of cyclohexane and toluene, centrifugated, evaporated to dryness and re-dissolved in acetonitrile. The analysis used a high-performance liquid chromatography (HPLC) system with a fluorescence detector (Jakovljević et al., 2020b). Additionally, monthly gas consumption data (provided by IMROH), along with meteorological data such as average temperature, pressure, precipitation, and wind speed (from Croatian Meteorological and Hydrological Service), were used to examine seasonal pollutant patterns and relationships with meteorology and energy use. In this study, Python (v3.10) was used for statistical analysis. Monthly means of pollutants were calculated to match the monthly gas consumption data, resulting in 48 data points over four years. A correlation matrix identified significant relationships between variables, guiding further analysis. Non-Negative Matrix Factorization (NMF) was applied to understand potential pollutant sources and temporal patterns by breaking the data into non-negative components (Boutsidis and Gallopoulos, 2008). Principal

Component Analysis (PCA) was used for the same purpose as NMF, to identify clusters of related variables (Souza et al., 2018). These methods together provided insights into pollutant sources and their influencing factors.

## RESULTS AND DISCUSSION

The correlation matrix was calculated to summarize relationships among pollutant variables, and helped identify highly correlated pollutants and understand their behavior and common origins. Furthermore, a heatmap was made to visually represent the complex variable correlations within the dataset (Figure 2).

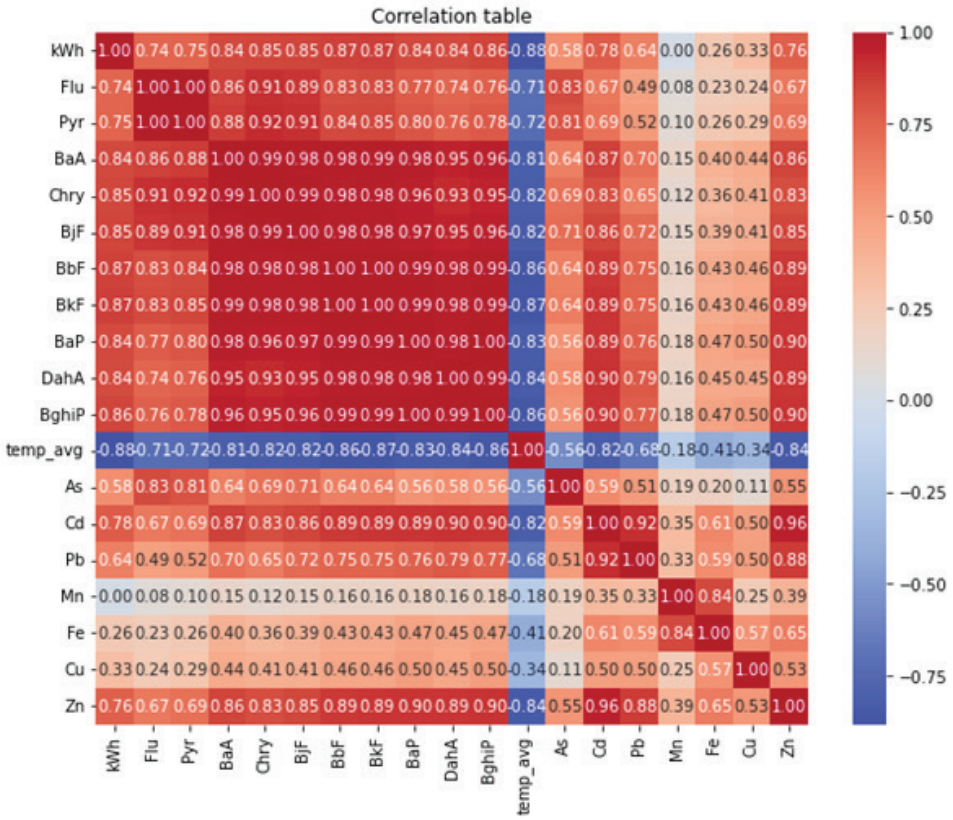


**Figure 2.** Heatmap illustrating pairwise correlations among dataset variables, with color intensity representing the strength and direction of associations

There were several instances of strong positive correlations, colored by darker red, which may indicate common sources or similar environmental behaviors. Conversely, strong negative correlations, indicated by dark blue, imply an inverse relationship, hinting at distinct sources or divergent environmental processes for the variables. The correlation matrix revealed strong positive relationships among PAHs such as BaP, BbF, DahA, and

BghiP, indicating shared sources like traffic or heating emissions. Similarly, metals like Pb, Zn, and Cd showed strong correlations, reflecting a mix of combustion and industrial activities. Gas consumption (kWh) was highly correlated with PAHs and moderately with metals, emphasizing its role in pollutant levels during colder months. A negative correlation between temperature and both PAHs and metals highlighted seasonal variations, with higher concentrations in winter due to increased heating. Metals like Mn and Cu showed weaker correlations with other pollutants, suggesting non-combustion sources like road dust or vehicle wear. NMF was used to understand the potential sources and the mutual relationships deeper, revealing temporal variability within the dataset (Figure 3).

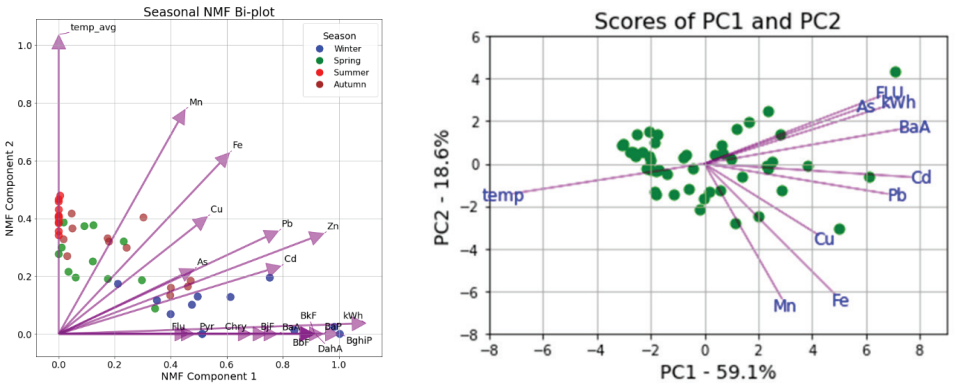


**Figure 3.** Seasonal NMF bi-plot and PCA bi-plot graphs for different variables

The seasonal NMF bi-plot (Figure 3) showed relationships between pollutants, temperature and gas consumption. PAHs and metals like Pb, Cd and Zn were strongly aligned with gas consumption (kWh) along Component 1, indicating their connection to heating activities during winter, as seen in the clustering of winter data points. Flu and Pyr were particularly related to the combustion of wood, grass, or coal (Jakovljević et al., 2015). Other PAHs (DahA, BghiP, BaP, BbF, and BkF) had vector directions similar to Flu and Pyr but were placed in a separate cluster with a potentially different pollution source, probably vehicle exhaust emissions (Jakovljević et al., 2020a). Metals such as Mn, Fe, and Cu were more influenced by Component 2, suggesting non-combustion sources like vehicle wear or industrial emissions. Temperature (temp_avg) aligned opposite heating-related pollutants along Component 2, reflecting a negative correlation, as these pollutants were more concentrated in colder months. The seasonal distribution demonstrated higher pollutant levels in winter due to heating, while summer and spring showed a weaker influence from heating sources and more dispersion due to higher temperatures. Findings from PCA confirmed these results, as similar patterns in pollutant groupings and source identifications were observed. To deepen this understanding, a linear regression model should be applied for further investigation into the relationships among pollutants, meteorology, and gas consumption.

## CONCLUSIONS

This study, conducted at the IMROH air quality station in Zagreb, examined the links between gas consumption, meteorological conditions, and atmospheric concentrations of PAHs and metals. By integrating air quality data with meteorological and gas consumption data, it identified key pollution dynamics using PCA and NMF. Findings showed seasonal variations, with higher pollutant levels during colder months due to increased heating and traffic emissions. PAHs like BaP, BghiP, and DahA were primarily linked to traffic, while Flu and Pyr were associated with residential heating. Metals such as Mn, Fe, and Cu were traced to vehicle wear and road dust, whereas Pb, Zn, Cd, and As reflected mixed sources, including traffic, heating, and industrial processes. This multidimensional approach enhances understanding of pollutant sources and seasonal patterns, providing a foundation for informed air quality management and public health strategies. Future research could refine these findings by incorporating additional data, measurement sites, or alternative statistical techniques.

## ACKNOWLEDGEMENT

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Poster presentation

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# MONITORING OF HYDROGEN SULPHIDE AND MERCAPTANS IN THE AIR IN THE VICINITY OF THE ZAGREB CENTRAL WASTEWATER TREATMENT PLANT

## Abstract

*The Central Wastewater Treatment Plant Zagreb (CWWTZ) is Croatia's first wastewater treatment concession, which ensures Zagreb's compliance with EU environmental and water protection standards. Daily samples of hydrogen sulphide ($H_2S$) and mercaptans were collected at five monitoring stations (CWWTZ and surrounding areas) over thirty days each during winters and summers from 2018 to 2022. Mass concentrations were determined spectrophotometrically. Average $H_2S$ concentrations at all stations ranged from 0.67 μg/m³ (2020) to 2.38 μg/m³ (2021) in winter, and from 0.63 μg/m³ (2019) to 10.78 μg/m³ (2021) in summer. From 2018 to 2020, $H_2S$ levels were below the limit value (LV) during both periods. However, in the summers of 2021 and 2022, the 24-hour $H_2S$ concentrations exceeded the LV at one station (18 times) and three stations (20, 11, and 11 times), respectively. For mercaptans, the average winter mass concentrations ranged from 0.38 μg/m³ (2018) to 1.41 μg/m³ (2021), and average summer mass concentrations from 0.31 μg/m³ (2018) to 1.13 μg/m³ (2022). The LV for mercaptans was never exceeded during the monitoring period. These occasional $H_2S$ exceedances highlight the need for continuous air quality monitoring in the area of possible influence of the wastewater treatment plant.*

**Keywords:** *air pollution, $H_2S$, R-SH, spectrophotometry*

## INTRODUCTION

Systematic monitoring of the quality of the Sava River began as early as 1933, and in 1939 the decision was made to build a wastewater treatment plant at its current location. Although Zagreb was among the first cities in the world to build a sewage system for wastewater collection, it was only in 2000 that the Project Concession Agreement was signed for the construction of a central wastewater treatment plant. The preparatory work, necessary documentation, permits and construction of the plant were completed in 2004 when the facilities for mechanical, and in 2007 for biological, wastewater treatment were put into operation (Tedeschi et al., 2014). The Central Wastewater Treatment Plant Zagreb (CWWTZ) is the first wastewater treatment concession in Croatia and it enables the City of Zagreb to comply with the European Union's ecological standards in the field of environmental and water protection (Schroder et al., 2001). The monitoring of specific air pollutants in the area of possible influence of the wastewater treatment plant on the surrounding air has been carried out since the plant began operating.

Hydrogen sulphide ($H_2S$) and mercaptans (R-SH) are significant sulphur-containing compounds commonly found in the atmosphere, particularly in areas influenced by industrial activities and wastewater treatment processes. $H_2S$ is a colourless gas, soluble in various liquids including water and alcohol, known for its characteristic odour, detectable at very low concentrations. Most of the atmospheric hydrogen sulphide has natural origins, it occurs around sulphur springs and lakes, and anaerobic decomposition of organic matter (WHO, 2000). Anthropogenic sources of $H_2S$ are mostly industrial processes such as petroleum refining, natural gas processing, and wastewater treatment.

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Mercaptans, also known as thiols, are organic compounds containing a sulfhydryl group (-SH). They are characterized by their strong, unpleasant odour and are often added to natural gas as odorants for leak detection due to their potent smell. They are introduced into the atmosphere through both natural processes, such as the reduction of sulphate in anaerobic waters and soils, and anthropogenic activities, including fossil fuel combustion, petrochemical industries, and municipal sewage systems (Moliner-Martinez et al., 2013).

Both $H_2S$ and mercaptans are of environmental and health concern due to their toxicity and potential to cause respiratory and neurological effects at elevated concentrations. Spectrophotometric methods are commonly employed to determine the mass concentrations of these pollutants in ambient air. Monitoring these compounds in the air is crucial for assessing air quality and ensuring compliance with environmental regulations.

Hydrogen sulphide and mercaptans belong to the group of compounds with unpleasant and irritating odours and their elevated concentrations in the air can significantly impact the quality of life. In Croatia, the Regulation on Levels of Air Pollutants (OG 72/2020) prescribes concentration limit values (LV) based on the quality of life (odour annoyance) for 24-hour concentration averages (5 μg/m$^3$ and 3 μg/m$^3$ for $H_2S$ and R-SH, respectively) as well as the frequency of permitted exceedances during the calendar year (≤ 7 times). The LVs are based on the Air Protection Act (OG 127/2019, OG 57/2022), and if there are more than 7 exceedances of the LV value for $H_2S$ and R-SH the air is classified as 2nd category (polluted air); otherwise, it is categorized as 1st category "clean or insignificantly polluted air".

This paper presents the results of a five-year monitoring of hydrogen sulphide and total mercaptans at the five stations within or in the vicinity of the Central Wastewater Treatment Plant Zagreb.

## MATERIALS AND METHODS

From 2018 to 2022, 24-hour samples of hydrogen sulphide ($H_2S$) and total mercaptans (R–SH) were continuously collected for one month each in winter and summer at five monitoring stations (MS 1 – MS 5) within and around the CWWTZ complex. The sampling periods for each season are detailed in Table 1.

Air samples for $H_2S$ and R–SH were collected using impregnated filter media. For $H_2S$ sampling, Whatman No. 41 filter paper was impregnated with mercury (II) chloride and urea as an antioxidant. The $H_2S$ concentration was then determined spectrophotometrically using molybdenum blue method (Vađić et al., 1980; Vađić, 1982; Vađić, 1983; Gluščić et al., 2020).

**Table 1.** Sampling period in winters and summers of each sampling year

| | sampling period | |
|---|---|---|
| | **winter** | **summer** |
| **2018** | 22th January - 22th February | 9th July - 10th August |
| **2019** | 18th February - 21st March | 8th July - 9th August |
| **2020** | 6th February - 8th March | 14th July - 13th August |
| **2021** | 8th February - 11th March | 1st July - 2nd August (MS 5 - 7th July - 6th August) |
| **2022** | 15th February - 17th March | 22nd July - 28th August |

Due to the interference of hydrogen sulphide during the sample collection of mercaptans, it was necessary to remove it beforehand. This was achieved by connecting the first holder with an impregnated filter to collect samples of $H_2S$, and the second holder with an impregnated filter to collect samples of R–SH. Mercaptans were collected on Whatman No. 41 filter paper impregnated with mercury(II) acetate and acetic acid. The concentration of R–SH was determined spectrophotometrically using N,N-dimethyl-p-phenylenediamine hydrochloride and Reissner's reagent. The method determines total mercaptans, with results expressed as mercaptan sulphur (R–SH) (Moore et al, 1960; Gluščić et al., 2020; IMROH, 2018; IMROH, 2019; IMROH, 2020; IMROH, 2021; IMROH, 2022).

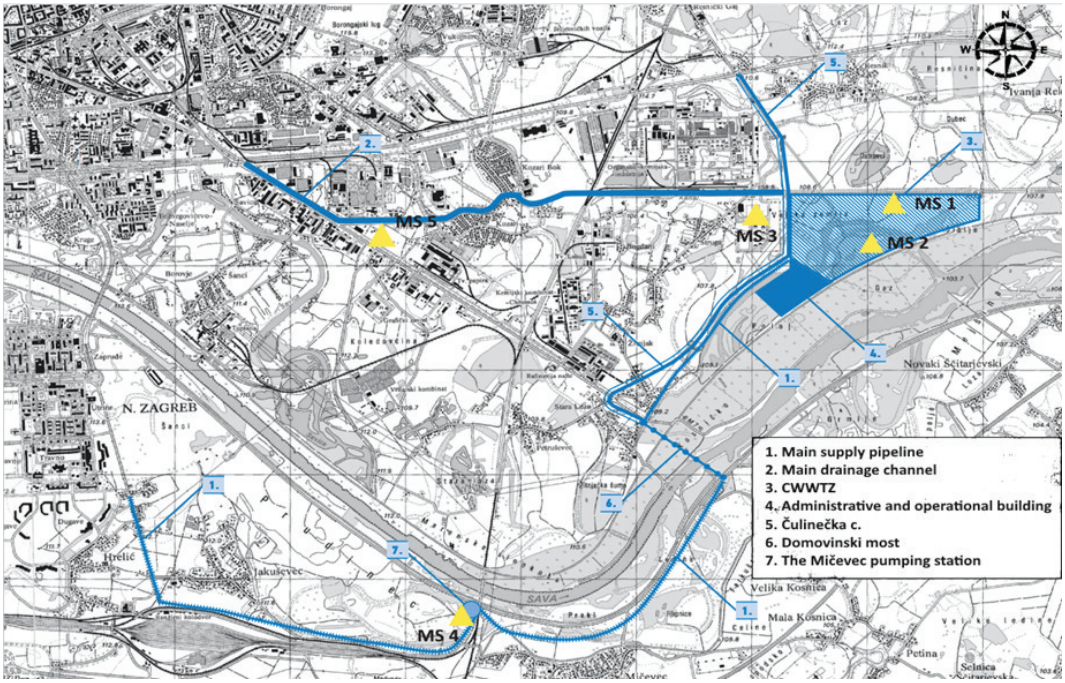


**Figure 1**. Locations of the monitoring stations (MS) – customized from (Tedeschi et al., 2014)

## RESULTS AND DISCUSSION

Daily (24-hour) mass concentrations of $H_2S$ at all five monitoring stations ranged from 0.07 μg $m^{-3}$ to 3.26 μg $m^{-3}$ in 2018, 0.10 μg $m^{-3}$ to 4.09 μg $m^{-3}$ in 2019, 0.09 μg $m^{-3}$ to 5.34 μg $m^{-3}$ in 2020, 0.13 μg $m^{-3}$ to 35.9 μg $m^{-3}$ in 2021 and 0.16 μg $m^{-3}$ to 65.0 μg $m^{-3}$ in 2022. Average mass concentrations of $H_2S$ at all sampling stations for the entire sampling period are shown in Figure 2. The highest average $H_2S$ mass concentration was measured in the summer at MS 3 in 2021, and the lowest in the summer of 2019 at MS 2. Average mass concentrations of $H_2S$ were mostly higher during the summer in the entire sampling period which is in accordance with the previous measurements done at this sampling sites (Kalinić et al., 2007; Godec et al., 2014).

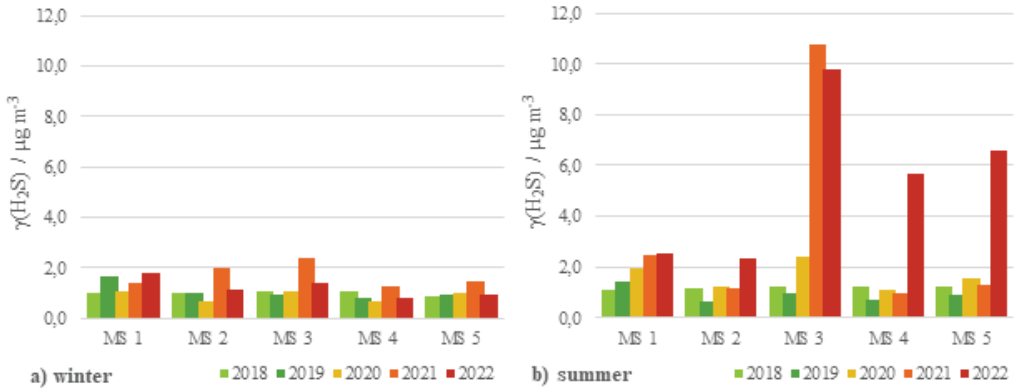


**Figure 2**. Average mass concentrations of hydrogen sulphide in winters (a) and summers (b) in the sampling period (2018 – 2022)

The Regulation on the Levels of Air Pollutants (OG 72/2020) prescribes concentration limit values (LV) for $H_2S$ and R–SH set with regard to the quality of life (odour annoyance), and not in regard to the protection of human health. According to the Regulation for $H_2S$, during a 24-hour averaging period the LV is 5 μg $m^{-3}$ and must not be exceeded more than seven times during a calendar year. Table 2 shows the number of exceedances of the 24-hour $H_2S$ mass concentrations at all monitoring stations in both seasons during the entire monitoring period. The exceedances occurred at monitoring station MS 3 in summer (2) of 2020, winter (2) and summer (18) of 2021, summer (20) of 2022, and at MS 1, MS 2, MS 4 and MS 5 in 2022 with the number of exceedances of 4, 4, 11 and 11, respectively (IMROH, 2018; IMROH, 2019; IMROH, 2020; IMROH, 2021; IMROH, 2022).

**Table 2.** Number of $H_2S$ exceedances in a five-year monitoring period (LV = 5 μg $m^{-3}$ for a 24-hour average)

| | 2018 | | 2019 | | 2020 | | 2021 | | 2022 | |
|---|---|---|---|---|---|---|---|---|---|---|
| | w | s | w | s | w | s | w | s | w | s |
| **MS 1** | – | – | – | – | – | – | – | – | – | 4 |
| **MS 2** | – | – | – | – | – | – | – | – | – | 4 |
| **MS 3** | – | – | – | – | – | 2 | 2 | 18 | – | 20 |
| **MS 4** | – | – | – | – | – | – | – | – | – | 11 |
| **MS 5** | – | – | – | – | – | – | – | – | – | 11 |

w – winter, s – summer

Daily (24-hour) mass concentrations of R–SH at all five monitoring stations ranged from 0.08 μg $m^{-3}$ to 2.55 μg $m^{-3}$ in 2018, 0.08 μg $m^{-3}$ to 1.58 μg $m^{-3}$ in 2019, 0.10 μg $m^{-3}$ to 2.96 μg $m^{-3}$ in 2020, 0.20 μg $m^{-3}$ to 2.99 μg $m^{-3}$ in 2021 and 0.10 μg $m^{-3}$ to 2.62 μg $m^{-3}$ in 2022.

Average mass concentrations of R–SH at all sampling stations for the entire sampling period are shown in Figure 3. The highest average R–SH mass concentration was measured

in the winter of 2021 at MS 3, and the lowest in the summer of 2018 at the MS 2. Average mass concentrations of R–SH were mostly higher during the winter, unlike the $H_2S$ mass concentrations in the entire sampling period (Kalinić et al, 2007; Godec et al, 2014).

According to the Regulation for R–SH, the LV for a 24-hour average is 3 μg $m^{-3}$ and must not be exceeded more than seven times during a calendar year. The limit value for mercaptans was never exceeded during winters and summers in the five-year monitoring period.

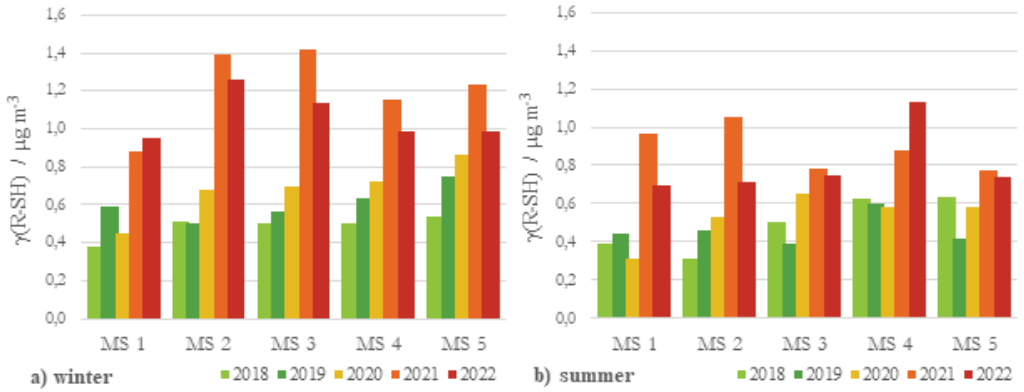


**Figure 3**. Average mass concentrations of R-SH in winters (a) and summers (b) in the sampling period (2018–2022)

## CONCLUSIONS

Exceedances of limit value for $H_2S$ occurred less than 7 times during the monitoring period 2018-2020. However, during the summer periods of 2021 and 2022, 24-hour $H_2S$ mass concentrations exceeded limit values at MS 3 (18 times) and MS 3, MS 4 and MS 5 (20, 11 and 11 times) stations, respectively. Since up to 7 exceedances of the limit value are allowed during the year, the air quality at these monitoring stations was considered unsatisfactory, i.e. the results indicated that the air quality was of the 2nd category (polluted air) with regard to $H_2S$. During the five-year monitoring of mercaptans, the limit value was never exceeded for winter and summer periods.

Occasional exceedances of $H_2S$ limit values indicated the need for further continuous monitoring of air quality in the area of possible influences of the wastewater treatment plant.

## ACKNOWLEDGEMENT

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Poster presentation

**Riva Elena, Malcevschi Alessio, Buschini Annamaria**

# *TRADESCANTIA ANDERSONIANA*: A NEW PLANT SPECIES FOR *IN SITU* BIOMONITORING OF AIR QUALITY

## Abstract

*The Tradescantia micronucleus assay is one of the most widely used bioassay to detect genotoxins in the environment by identifying micronuclei in pollen tetrad cells. This study aimed to compare two specific species: Tradescantia clone #4430 and Tradescantia andersoniana, the latter had not previously been evaluated for this purpose. The interspecies difference in the spontaneous mutation rate was evaluated. Then, the plants were exposed to two known mutagens, maleic hydrazide (MH) and ethyl methanesulfonate (EMS) at different concentrations to better understand their sensitivity to different genotoxins. Results showed a linear increase in the number of micronuclei as MH concentration increased in both species analyzed. An interesting response was found for EMS: it showed toxic effects and inhibition of tetrads production at the highest tested concentration (1 mM) in T. andersoniana and a slight decrease in tetrad production in the case of the clone #4430 indicating that the two Tradescantia species have different characteristics and thus, responses. Subsequently, the two species were used in an in situ biomonitoring study in Italy to evaluate air quality. Results showed a good level of air quality, and this study allowed us to indicate T. andersoniana as one of the most suitable species for environmental biomonitoring.*

**Keywords**: *Tradescantia, TRAD-MCN assay, Micronucleus, Interspecies differences*

## INTRODUCTION

Increasing environmental pollution is further deteriorating the world. To study environmental alterations comprehensively, it is not enough to analyze emissions from a purely chemical-physical point of view: it is necessary to assess the damage done to the entire ecosystem (Aryal et al., 2020; Lin et al., 2023). Although knowledge about the toxicological properties of many compounds has increased, environmental risk levels are still uncertain. For these reasons, there is an increasing focus on the effects, or rather the damage, that certain substances cause to the living (Kim et al., 2013; Kumar et al., 2021). Reading and interpreting the changes to which organisms are subjected is a useful strategy for qualifying and quantifying pollution: by studying the morphological, anatomical and physiological alterations of organisms, assessing any rarefaction in the number of individuals and reporting the disappearance of species, it is possible to identify environmentally compromised areas (Li et al., 2019; Li et al., 2023; Mherzi et al., 2020). Biomonitoring allows the use of various species to detect a range of pollutants and can provide valuable historical information, as symptoms may persist even after a pollution event has occurred. The ability of a living organism to respond to complex and sometimes unknown stimuli provides more complete information about the quality of an environment than that provided by traditional methods (AL-Alam et al., 2019; Ferreira et al., 2023; Mahapatra et al., 2019). In biomonitoring studies, plants play an important role because of their capacity to always react to environmental stimuli (Picó et al., 2023; Saxena and Ghosh, 2013). Plant air quality biomonitoring is a method that has established itself in many fields of application and provides fundamental information on air grade. Air pollution is a major threat to human health, and it impairs genetic stability, contributes to mutations in the DNA, and increases the risk of cancer (Rocha et al., 2018) and for these reasons, air quality

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biomonitoring is essential. Different types of tests can be used to investigate air quality but to detect genotoxins in the environment, the micronucleus (MN) assay with early tetrad cells of *Tradescantia* (Trad-MCN assay) is the most widely used (Rodrigues et al., 2024). The Trad-MCN assay involves counting micronuclei in pollen grain mother cells during the tetrad phase. These micronucleus structures form from whole or fragmented chromosomes that are lost during cell division and are left in the cytoplasm of interphasic cells instead of being incorporated into the nuclei of the daughter cells (Meireles et al., 2009; Mišík et al., 2013). Several species belong to the genus *Tradescantia (Commelinaceae),* but the most used in these types of tests is the #4430 clone, a hybrid between *Tradescantia hirsutiflora* and *Tradescantia subacaulis*. These plants can be exposed to chemical and complex mixtures differently, but *in situ* biomonitoring is the most widely used. *Tradescantia andersoniana* has never been used before for these types of studies and in our work we wanted to better understand interspecies differences in spontaneous mutation rate and single species reaction to two known mutagens. These results helped us to better understand which species was best suited for our future air quality biomonitoring study.

## MATERIALS AND METHODS

### Plants species

The genus *Tradescantia* belongs to the *Commelinaceae* family. Plants and clones of this genus have been used to study the genotoxicity of chemical compounds, polluted soils, wastewater, or drinking water, and to monitor pollutants gaseous. The most frequently employed species for genotoxicity studies is the #4430 clone, which is obtained by crossing *T. subacaulis* and *T. hirsutiflora*, but we analyzed another interesting species which is *Tradescantia andersoniana*. *Clone #4430* is sterile, thus genetically stable, and has an herbaceous appearance with a spike-like inflorescence composed of 16 to 20 blue or blue-purple flowers. *T. andersoniana* is a vigorous perennial plant that forms tufts with long arched leaves, light, and many varieties vary in flower colours.

### Cultivation and maintenance of *Tradescantia* plants

For successful cultivation of *Tradescantia*, it is crucial to regulate ventilation, temperature, and air quality, as these factors can influence the formation of micronuclei. During the multiplication phase and in winter, it is recommended to grow the plants in greenhouses with a day/night temperature of 24°C, relative humidity of 65% during the day and 70% at night, and a 16-hour daylight cycle. The plants were grown in a mixture of potting soil, sand, and peat moss (4:2:1 ratio) in 12-15 cm pots, regularly watered, and fertilized twice a month. These conditions were also used to assess the frequency of spontaneous reversion in the plants.

### *In vitro* exposure

To investigate the answer of the plants to known mutagens, we performed a stem absorption experiment: plant cuttings were exposed to two different molecules in 10 mL tubes. After severing the cuttings, they were partially immersed in the liquid. In this case, we utilized two known mutagens: maleic hydrazide (MH) and ethyl methanesulfonate (EMS) dissolved

in DMSO. We decided to use the final concentration of 0.4 vol.% (Klumpp et al., 2004) of DMSO to avoid the toxic effects that can result from a too-high concentration. Different concentrations were used to test both molecules: for maleic hydrazide, we decided to use 1.0, 2.0, and 4.0 mM; and for ethyl methanesulfonate 0.25, 0.5, 1.0, and 2.0 mM. After 6h treatment, the plants were subjected to a 24 h recovery time in Hoagland solution to allow the formation of MN in tetrads. Untreated plants immersed in Hoagland's solution were used as negative controls. Following recovery, inflorescences were fixed in a 3:1 ratio of pure ethanol and acetic acid ("Carnoy solution") for 24h and then stored in 70% ethanol until the time of slide preparation.

### *In situ* exposure

To conduct the *in situ* experiment, we exposed several *T.andersoniana* and *T.clone* #4430 plants in different locations in an area that was known to have good air quality in Italy. These plants were placed two metres above the ground in supports that would allow proper exposure and were watered regularly twice a week. For this type of experiment, it was decided to expose plants for a period of time that was about 3-4 weeks. During the sampling process, inflorescences were cuts and immediately immersed in "Carnoy solution" (as described above) for 24 h and then stored in 70% ethanol until the time of slide preparation.

### Slide preparation

To prepare slides, inflorescences were dissected under a stereo microscope to isolate the flower buds. The buds were placed in a glass slide, dissected to expose the anthers, which were then crushed. Two to three drops of 2% acetocarmine were added, and a coverslip was placed in top. Cytogenetic analysis to estimate the number of micronuclei was performed under an optical microscope (400X), 300 tetrads per slide were counted and five slides were prepared from individual inflorescences for each exposure, thus scoring 1,500 tetrads per treatment. Structures measuring 1/3 to 1/5 of the nucleus size, with similar chromatin distribution and clear separation from the nucleus, were considered micronuclei ("MCNs") (Meireles et al., 2009; Roberto et al., 2009). Test results were expressed as frequency of micronuclei related to the number of tetrads observed (MCN/100 tetrads).

## RESULTS AND DISCUSSION

### *In vitro* study

In our study, we aimed to investigate interspecies variations in spontaneous mutation rates and sensitivity of different species to two known mutagens (EMS and MH).

Following treatment, slides were prepared, and micronuclei were counted under an optical microscope. For each treatment, test results are expressed as the frequency of micronuclei related to the number of tetrads observed (MCN/100 tetrads). From our *in vitro* studies we can conclude that the spontaneous mutation rate is different but similar between the two plants: 0.53 ± 0.28 MCN/100 tetrads in the case of *T.clone* #4430 and 0.90 ± 0.23 MCN/100 tetrads for *T.andersoniana.* In the case of MH, we noted a response in both plants: a clear increase in the number of micronuclei directly proportional to the increase of mutagen

concentration was seen in the case of *T. andersionana* (Figure 1A). *T. clone #4430* resulted in a higher sensitivity to the treatment at the lowest MH concentration compared to *T. andersoniana*, indicating a more sensitivity of this plant to this known mutagen (Figure 1C). In the case of EMS, it was noted a toxic effect and an inhibition of tetrads production already at 1 mM for *T. andersioniana* and a decrease production of tetrads at 2 mM for *T. clone #4430* (Figure 1B, D).

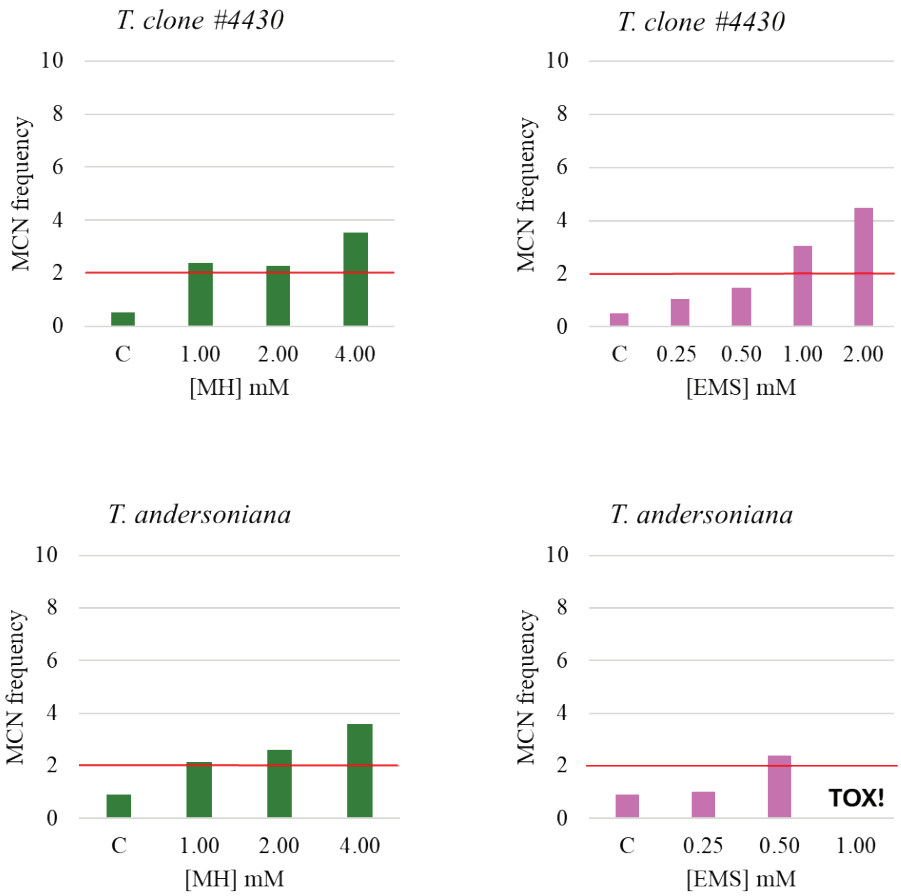


**Figure 1.** Results of the treatments of *T. andersioniana* and *T. clone #4430* with different concentration of EMS and MH. Results are expressed as the frequency of micronuclei related to the number of tetrads observed (MCN/100 tetrads).

*T. andersoniana* showed greater sensitivity to both mutagens, with a dose-dependent increase in micronuclei number after MH treatment. Both plants showed toxic effects and inhibited tetrad production following treatment with EMS, at 1 mM for *T. andersoniana* and 2 mM for *clone #4430*. EMS was found to be more toxic and mutagenic than MH, which is used in agriculture for growth regulation. *T.clone #4430* showed higher sensitivity to low MH concentrations, highlighting differences between the species.

## *In situ* study

In order to investigate the different response of these plants in an *in situ* study, we exposed our plant samples in different points in an area with good air quality. Sampling 01 was carried out before the plants were exposed to analyse the spontaneous mutation rate and it resulted similar with values between 0.30 and 0.35 MCN/100 tetrads (*T.clone #4430* and *T.andersoniana* respectively). Following 20 and 30 days, the two *Tradescantia* species resulted in a comparable micronuclei frequency, always below 2 micronuclei per 100 tetrads analysed (MCN/100 tetrads), a threshold generally used, as can be seen from the graphs (Klumpp et al. 2006; de Moralis et al., 2019). The analysis of the inflorescences carried out in successive samples of the same plants has allowed to highlight a lack of induction of genotoxic events, confirming that the sampling area had a good air quality. Although small variations, present more in *T. andersoniana* analysis, in the number of micronuclei are observed, they remain within a biological variability of the spontaneous frequency of mutation (Figure 2).

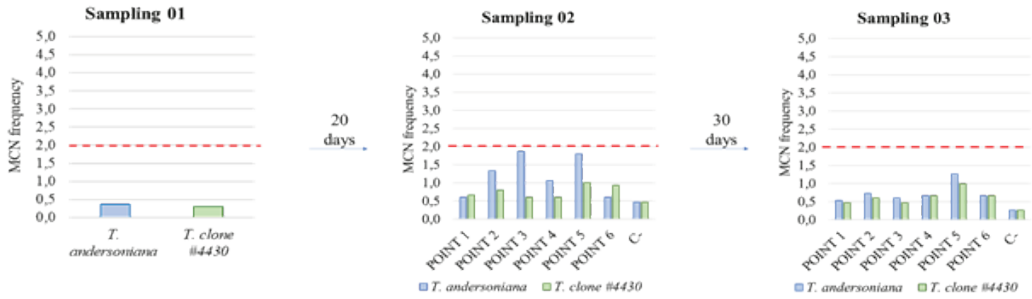


**Figure 2.** Results of *in situ* biomonitoring studies. Results are expressed as the frequency of micronuclei related to the number of tetrads observed (MCN/100 tetrads).

From these graphs we can conclude that the two *Tradescantia* species have a comparable micronuclei frequency and that both plants can be used for *in situ* biomonitoring studies thus allowing a more in-depth assessment using two different species.

## CONCLUSIONS

Biomonitoring with plants, particularly *Tradescantia*, is essential because it provides a natural, cost-effective way to detect and assess environmental pollutants. This plant is highly sensitive to genotoxic substances, making it a valuable bioindicator for measuring the mutagenic effects of different pollutants on living organisms. This study serves as a starting point for further analysis aimed at deepening our understanding of the response of these two plant species to different environmental stimuli. The findings provide a foundation for future investigations into how these plants can be utilized in *in situ* applications.

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Poster presentation

**Zdravka Sever Štrukil, Ivana Jakovljević, Gordana Pehnec, Ivan Bešlić**

# LEVELS OF POLYCYCLIC AROMATIC HYDROCARBONS IN URBAN AREAS OF OSIJEK AND RIJEKA

## Abstract

*Polycyclic aromatic hydrocarbons (PAHs) are a group of chemicals that occur naturally in coal, crude oil, gasoline, fossil fuels and can be released into the air during the incomplete combustion of wood, biomass or fossil fuels. As long-term exposure to PAHs can cause cataracts, kidney and liver damage, jaundice and in some cases cancer, it is very important to give PAHs high priority when considering air quality management and the reduction of their impacts. Sampling of the $PM_{10}$ particle fraction was carried out at two locations, in the city of Osijek in eastern, continental Croatia and the city of Rijeka in western, coastal Croatia. At both locations, 24-hour samples were collected continuously for 30 days in every season in 2022 and concentrations of 11 measured PAHs were determined by high performance liquid chromatography (HPLC) with a fluorescent detector. In Osijek, the average mass concentrations of PAHs were 2 to 3 times higher than those measured in Rijeka, except in autumn, when they were as many as 5 times higher in Osijek compared to Rijeka. A similar seasonal variation was observed at both locations, following the decreasing trend winter > autumn > spring > summer and winter > spring > autumn > summer in Osijek and Rijeka, respectively.*

**Keywords:** *$PM_{10}$ fraction, PAHs, HPLC*

## INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a class of semi volatile organic chemicals composed of at least two fused benzene rings. Over 200 PAHs have been identified in various ecological environments. Because of their stable chemical structure (Haritash and Kaushik, 2009), they are highly persistent pollutants and harmful to ecosystems (Møller et al., 1982). The United States Environmental Protection Agency (US EPA) has listed 16 PAHs as priority pollutants based on their pronounced toxicity, mutagenic properties, and potential carcinogenic effects. Benzo(a)pyrene (BaP) belongs to the first group of carcinogenic substances and can be identified as a key marker of PAH toxicity (IARC, 2010). The European air quality standard for BaP is established at 1 ng/m$^3$ (annual target value). Emission of PAHs to an ecosystem can occur by volcanos and fires but mostly by anthropogenic activities such as domestic heating, vehicle exhausts, waste combustion, etc. (Jesus et al., 2022). The less efficient the burning process is, the more PAHs are released. In coastal regions, the potential anthropogenic origins of PAHs also include port and ship building activities, oil spills, sea transport as well as wildfires. The aim of this study was to determine whether there are differences in PAH levels between seasons and their potential origins in cities with similar populations but different geographical locations, climate and traffic density.

## MATERIALS AND METHODS

Daily concentrations of PAHs were simultaneously monitored at two sampling sites in Croatia, both of which are part of the national network for continuous air quality monitoring and were equipped as part of the AIRQ project ("Expansion and Modernisation of the National Network for Continuous Air Quality Monitoring", KK.06.2.1.02.0001).

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Sampling site 1 was located in eastern continental Croatia, in the city of Osijek. Geographically, it is situated on the right bank of the Drava River with a population of 96,313 (CBS, 2021), which makes it the largest city in Slavonia and the fourth largest city in Croatia. Osijek has a typical continental climate with cold and relatively long winters and warm and even hot summers. Location 2 was in the city of Rijeka in western costal Croatia. Rijeka is the largest Croatian port and the third-largest city in the Republic of Croatia with a population of 107,964 (CBS, 2021) and a moderately warm humid climate (Figure 1).


**Figure 1.** Sampling locations

The $PM_{10}$ particle fraction was sampled by 24-hour collection of approximately 55 $m^3$ of air on quartz fiber filters (Whatman QMA), and a total of 120 samples were collected at each location. Samples were collected during four sampling periods in 2022 as follows: January 1–30 (winter), April 1–30 (spring), July 1–30 (summer), and November 1–30 (autumn) using low volume samplers (MicroPNS LVS 17, MCZ).

After sampling, the filters with the samples were stored wrapped in aluminum foil and kept in a dark place at a temperature below 20°C until analysis. The extraction of the sample filters was carried out using a Dionex ASE 350 accelerated solvent extractor system (Thermo Fisher Scientific, USA) with a solvent mixture of toluene and cyclohexane (7:3) (Horvat et al., 2024). The obtained extracts were evaporated to dryness using a Rocket evaporator (Thermo Fisher Scientific, USA) and then dissolved in a known volume of acetonitrile. The analysis was performed using high-performance liquid chromatography (HPLC) with a fluorescence detector equipped with variable excitation and emission wavelengths. The following PAHs were determined: fluoranthene (Flu), pyrene (Pyr), benzo(a)anthracene (BaA), chrysene (Chr), benzo(j)fluoranthene (BjF), benzo(b) fluoranthene (BbF), benzo(k)fluoranthene (BkF), BaP, dibenzo(a,h)anthracene (DahA), benzo(ghi)perylene (BghiP), and indeno(1,2,3-cd)pyrene (IP). Chromatographic separation was performed using a Zorbax Eclipse PAH column (100 × 2.1 mm) with a mobile phase flow rate (acetonitrile:water 60:40) of 200 µL/min. Calibration solutions

prepared from the Supelco EPA 610 PAH primary standard were used to calibrate the HPLC. In order to determine differences between the measuring sites for all PAHs and between seasons non-parametric Kruskal-Wallis test was applied in the program *Statistica ver.14.0.*

## RESULTS AND DISCUSSION

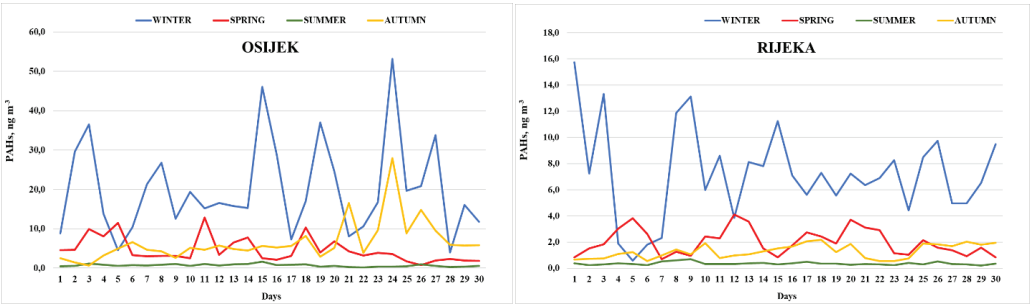


**Figure 2.** The sum of eleven measured PAHs in each season at both locations

The seasonal PAH distribution was observed reaching highest values in winter period and minimum values in summer period at both locations. In Osijek, the sum of 11 PAHs (∑11 PAHs) ranged from 53.23 ng/m³ in winter to 0.19 ng/m³ in summer, while in Rijeka, the range was 15.75 – 0.21 ng/m³. The most significant difference between the two locations was observed in the autumn, with Osijek recording a maximum ∑11 PAHs value of 27.91 ng/m³, compared to 2.17 ng/m³ in Rijeka (Figure 2).

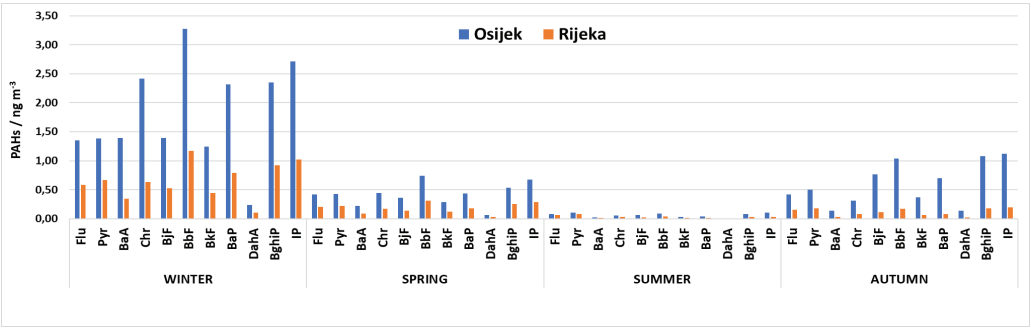


**Figure 3.** Average mass concentrations of PAHs in each season at both location

Average mass concentrations of PAHs during four seasons exhibited a typical U-shaped pattern at both locations. In Osijek the following pattern was observed for all PAHs except for Flu, BaA and Chr: winter – spring – summer – autumn. Statistically differences were found for all measured PAHs between all seasons, except there were no differences between spring and autumn for Flu, Pyr, BaA, Chr, BjF, BbF and BkF. In Rijeka the U-shaped pattern was in order: winter – autumn – summer – spring for all PAHs, except for Flu. There were no statistically differences only between spring and autumn for most

PAHs, except for BaA and Chr. Regarding the average PAHs concentrations within each season, all measured PAHs were statistically significantly higher in Osijek compared to Rijeka. Generally, the highest average values were measured for BbF and IP at both locations, while DahA had the lowest concentrations. BaP had relatively high levels in winter, with average mass concentration of 2.32 ng/m³ in Osijek and 0.79 ng/m³ in Rijeka, which was almost 56 and 43 times higher than the values registered in summer in Osijek and Rijeka, respectively (Figure 3).

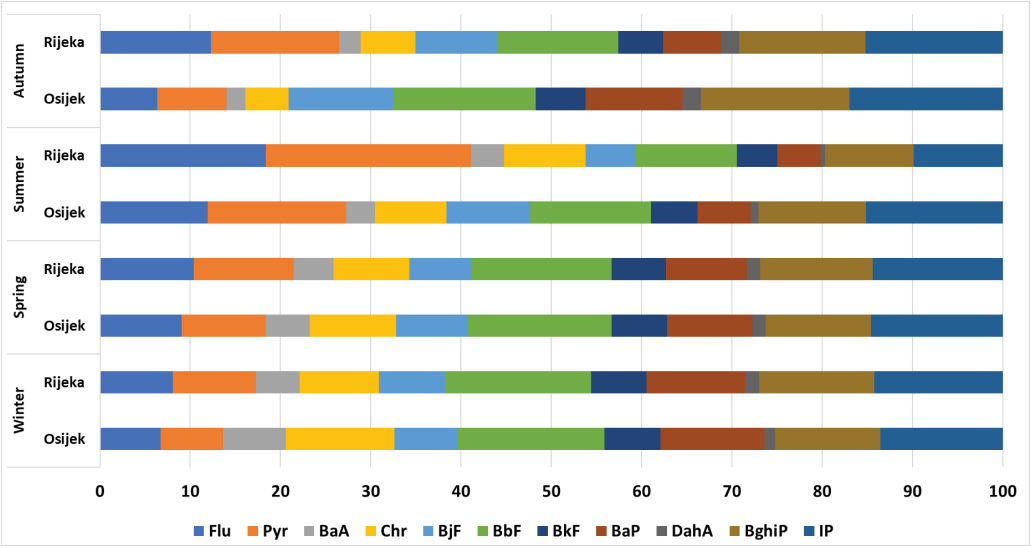


**Figure 4.** Contribution of each PAH in the sum of PAHs at both locations

The contribution of each measured PAH in the sum of total PAHs was calculated in order to study potential differences between the two locations. PAHs are mainly grouped in low molecular weight PAHs (2- and 3-ring PAHs) and high molecular weight PAHs (4-, 5-, and 6-ring PAHs) according to the number of aromatic rings in their molecular structure which determines their volatility, reactivity and toxicity. It is known that heavy PAHs with 4 or more rings are identified with high-temperature combustion processes (Stogiannidis and Laane, 2015). In Osijek, the contribution of high molecular weight PAHs (BjF, BbF, BkF, BaP, DahA, BhgiP, IP) was predominant in autumn (79%), followed by winter and spring both with 67% and summer 62% of the total PAHs. In Rijeka, the highest contribution of 5-ring and 6-ring PAHs occurred primarily in winter (69%), followed by spring (66%), autumn (65%) and summer (47%). Medium molecular weight PAHs (Flu, Pyr, BaA, and Chr) had a large contribution (38%) in summer, while in autumn their contribution to the total PAHs did not exceed 22% in Osijek. On the other hand, in Rijeka the contribution of 4-ring PAHs to the total sum of PAHs increased from 31% in winter to 54% in summer possible as a result of photochemistry, urban traffic, and shipping emissions (Figure 4).

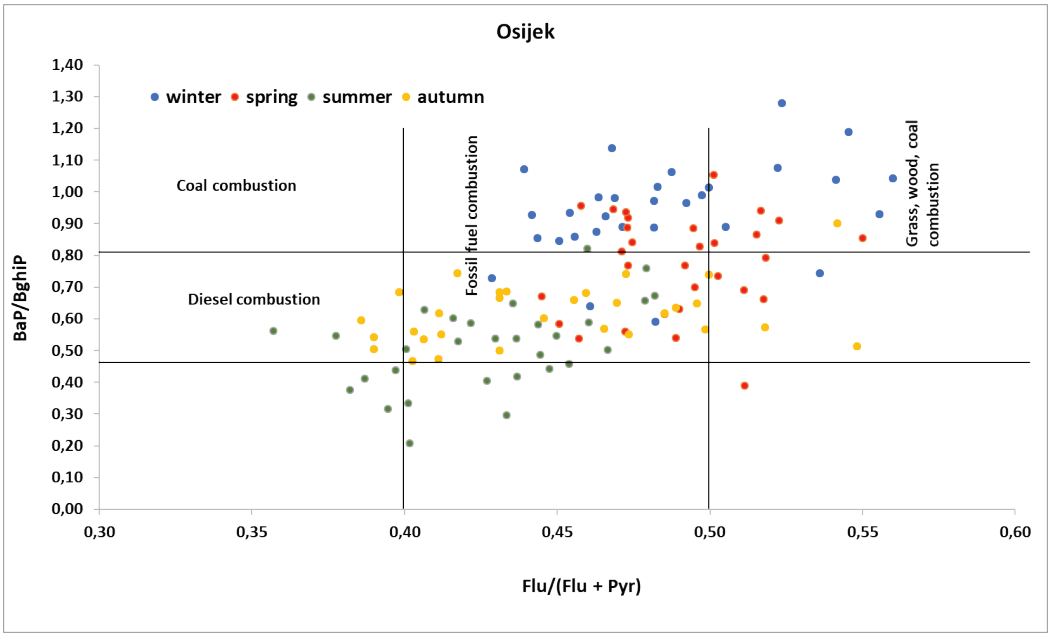


**Figure 5.** Seasonal differences of PAH diagnostic ratios in Osijek

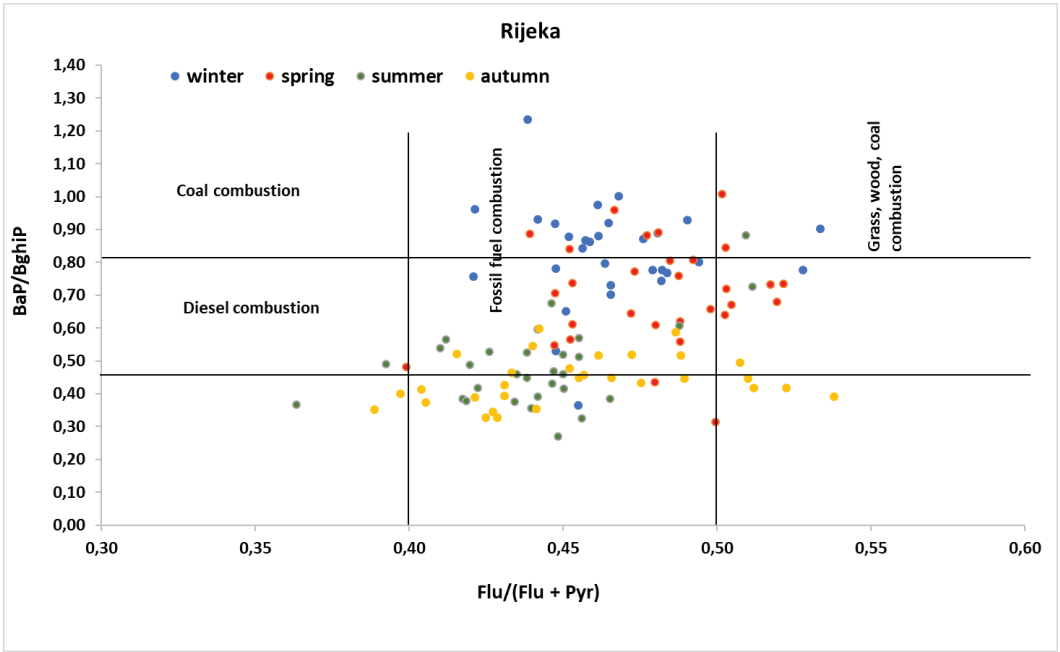


**Figure 6.** Seasonal differences of PAH diagnostic ratios in Rijeka

Furthermore, to identify the potential origins of the PAH compounds, diagnostic ratios were chosen as widely acceptable and used toll (Tobiszewski and Namieśnik, 2012). The BaP/BghiP ratio is used to evaluate the contribution of vehicular emissions (Agudelo-Castañeda and Teixeira, 2014) and the ratio Flu/(Flu+Pyr) as a useful marker for biomass burning (De La Torre-Roche et al., 2009). In Rijeka, the BaP/BghiP ratio increased from 0.44 in autumn to 0.71 in spring, while in Osijek the lowest BaP/BghiP was in summer (0.51) and the highest in spring (0.77) showing a predominance of diesel combustion through spring and summer at both locations (Figure 5). The highest BaP/BghiP ratio was seen in winter; 0.95 in Osijek and 0.83 in Rijeka, suggesting wood or coal combustion as a major source of PAHs. In Osijek, only in winter and spring the Flu/(Flu+Pyr) diagnostic ratio was 0.50 showing a predominance of pollution by grass, wood or coal, while that was not the case in Rijeka (Figure 6).

## CONCLUSIONS

The average PAHs concentrations in Osijek were much higher in winter (1.83 ng/m$^3$), followed by autumn (0.59 ng/m$^3$) and spring (0.42 ng/m$^3$). At Rijeka the average PAHs concentrations followed the similar order: winter (0.66 ng/m$^3$), spring (0.18 ng/m$^3$) and autumn (0.12 ng/m$^3$). In the summer period, the total average concentrations did not exceed 0.07 ng/m$^3$ at both locations. The contribution of individual PAHs to the sum of total PAHs ranged from 21% for 4-ring PAHs to 46% of 5-ring PAHs in autumn at Osijek with the biggest contribution of BbF in winter and spring. At Rijeka, 6-ring PAHs contributed with a minimum of 20% in summer, while the biggest contribution was for 4-ring PAHs (54%). The BaP/BghiP and Flu/(Flu+Pyr) diagnostic ratios indicated mixed sources at both sites with the predominance of diesel combustion from traffic at all seasons, except in winter. In winter, potential PAH sources also arose from wood and coal combustion, especially in Osijek. The observed differences in PAH levels, which were 2 to 3 times higher in Osijek compared to Rijeka, highlight important spatial and seasonal variations.

## ACKNOWLEDGEMENT

This study was performed using the facilities and equipment funded within the European Regional Development Fund project KK.01.1.1.02.0007 “Research and Education Centre of Environmental Health and Radiation Protection – Reconstruction and Expansion of the Institute for Medical Research and Occupational Health” and using instruments acquired through the project AirQ - “Expansion and Modernization of the National Network for Continuous Air Quality Monitoring” (K.K.06.2.1.02.0001, granted by the European Regional Development Fund, Croatian Environmental Protection, and Energy Efficiency Fund).

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Poster presentation

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# TEMPORAL VARIATIONS OF SEMIVOLATILE ORGANIC COMPOUNDS IN $PM_{10}$ PARTICLE FRACTION

## Abstract

*Air pollution causes 4.2 million premature deaths annually, with particulate matter (PM) posing significant health risks, including respiratory and cardiovascular diseases. Semi-volatile components of PM, such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and organochlorinated pesticides (OCPs), are known for their carcinogenic and mutagenic properties. Despite bans on PCBs and OCPs under the Stockholm Convention, their persistence ensures their continued environmental presence. In the European Union, PAH monitoring in the $PM_{10}$ particle fraction (particles with an equivalent aerodynamic diameter < 10 µm) is legally mandated, but data on PCBs and OCPs in PM are scarce, particularly in Croatia. This study was conducted through a year-long campaign in 2022 at an urban background station in Zagreb to examine the temporal variations of PAHs, PCBs, and OCPs in the $PM_{10}$ particle fraction. Weekly samples from ~700 $m^3$ of ambient air were collected on pre-fired quartz fiber filters, gravimetrically analyzed for $PM_{10}$ mass concentrations, and extracted using a hexane-dichloromethane solvent mixture. This study provides the first simultaneous measurements of PAHs, PCBs, and OCPs in the $PM_{10}$ particle fraction in Zagreb, offering insights into their levels, and temporal trends, alongside comparisons with similar urban environments globally.*

**Keywords:** *PAHs, OCPs, PCBs, temporal distribution*

## INTRODUCTION

Air pollution in both cities and rural areas, according to the latest data from the World Health Organization, causes 4.2 million premature deaths worldwide. Particulate matter (PM) is recognized as a special risk to human health, causing respiratory and cardiovascular diseases such as cancer of the respiratory tract, with increasing evidence of effects on other organ systems as well (Kim et al., 2015). Polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and organochlorinated pesticides (OCPs) are among the semivolatile components of PM known for their carcinogenic and mutagenic potencies. Although PCBs and OCPs were banned decades ago under the Stockholm Convention, their levels are still being detected in all environmental compartments due to their persistence and long-distance transport (Othman et al., 2022; Shen and Wania, 2005). In the European Union, there is a legal obligation to monitor PAHs in the $PM_{10}$ particle fraction in ambient air, but the measurements are limited to a comparatively smaller number of measuring stations than for the other parameters that are monitored. PCBs and OCPs are not covered by air protection regulations, and data on their concentrations in PM in Croatia are scarce (EEA, 2024). This study involves a one-year campaign conducted at an urban background station located in Zagreb, Croatia, in order to investigate the temporal variations of PAHs, OCPs, and PCBs in the $PM_{10}$ particle fraction.

## MATERIALS AND METHODS

Weekly $PM_{10}$ samples were collected continuously throughout 2022 from approximately 700 $m^3$ of ambient air on quartz fibre filters (Pall, 90 mm) pre-fired at 400 °C for 4 hours.

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Mass concentrations of $PM_{10}$ were determined gravimetrically. Filters were extracted in the solvent mixture of hexane and dichloromethane by accelerated solvent extraction, concentrated under a gentle nitrogen stream, and analyzed. Analysis of 12 PAHs (fluoranthene, pyrene, benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*j*]fluoranthene, benzo[*a*]pyrene, benzo[*e*]pyrene, indeno[1,2,3-*cd*]pyrene, dibenz[*a*,*h*]anthracene and benzo[*ghi*]perylene) was performed by gas chromatography coupled with triple quadrupole mass spectrometry (GC-MS/MS) and analysis of 17 PCBs (PCB-28, PCB-52, PCB-74, PCB-60, PCB-101, PCB-123, PCB-118, PCB-114, PCB-153, PCB-105, PCB-138, PCB-167, PCB-156, PCB-157, PCB-180, PCB-170, and PCB-189) and 7 OCPs (α-hexachlorocyclohexane, β-hexachlorocyclohexane, γ-hexachlorocyclohexane, hexachlorobenzene, *p*,*p*'-DDT, *p*,*p*'-DDD and *p*,*p*'-DDE) by gas chromatography with electron capture detector (GC-μECD).

## RESULTS AND DISCUSSION

In weekly $PM_{10}$ particle fraction samples collected in Zagreb in 2022, mass concentrations of 12 PAHs, 17 PCBs, and 7 OCPs were determined. The results of total PAHs, PCBs, and OCPs are presented in Figures 1–4. Higher mass concentrations of PAHs (in ng $m^{-3}$) were observed in the $PM_{10}$ particle fraction compared to organochlorine compounds (in pg $m^{-3}$).

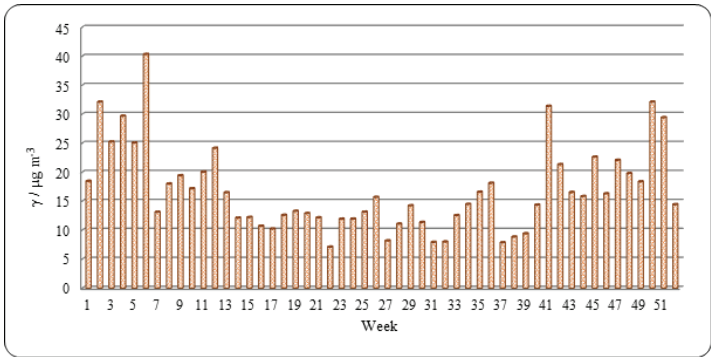


**Figure 1.** Mass concentrations of the $PM_{10}$ particle fraction in 2022 at an urban background station in Zagreb, Croatia

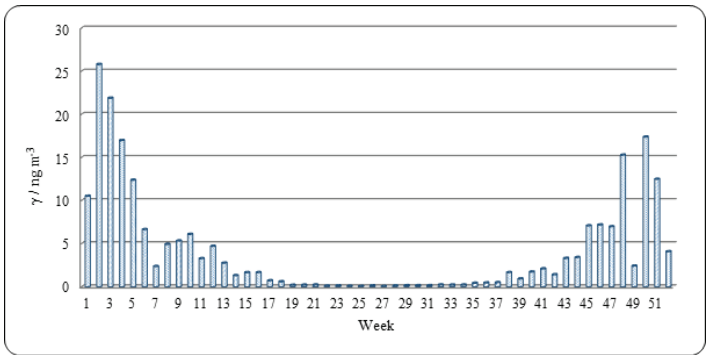


**Figure 2.** Mass concentrations of $\sum_{12}$PAHs measured in weekly samples of the $PM_{10}$ particle fraction in 2022 at an urban background station in Zagreb, Croatia

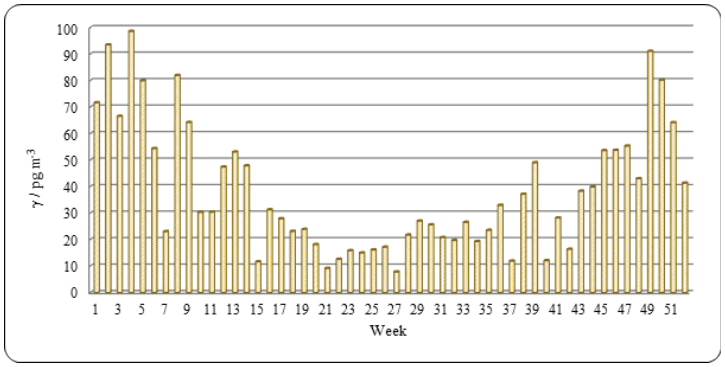


**Figure 3.** Mass concentrations of $\sum_7$OCPs measured in weekly samples of the $PM_{10}$ particle fraction in 2022 at an urban background station in Zagreb, Croatia

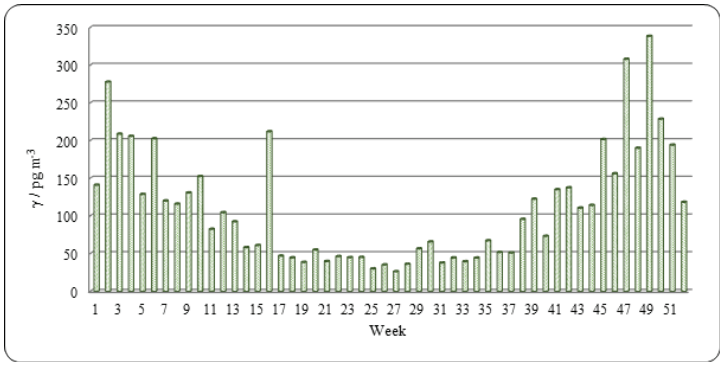


**Figure 4.** Mass concentrations of $\sum_{17}$PCBs measured in weekly samples of the $PM_{10}$ particle fraction in 2022 at an urban background station in Zagreb, Croatia

The mass concentrations of the $PM_{10}$ particle fraction ranged from 7.1 μg $m^{-3}$ to 40.3 μg $m^{-3}$, with an average of 16.9 μg $m^{-3}$. Compared to earlier studies conducted in central Zagreb between 2011 and 2013 at a high-traffic monitoring site, where the average $PM_{10}$ mass concentration was 36 μg $m^{-3}$ (Šimić et al., 2020), lower average $PM_{10}$ mass concentrations were obtained. These results align with findings by Lovrić et al. (2022), who reported a significant decline in $PM_{10}$ mass concentrations in Zagreb during the period 2009–2020. Examining the seasonal variations in $PM_{10}$ mass concentrations during 2022, the highest average values were recorded during the colder period of the year, while the lowest average weekly values were observed during the warmer period.

The weekly mass concentrations of $\sum_{12}$PAHs in the $PM_{10}$ particle fraction in Zagreb during 2022 ranged from 0.1 ng $m^{-3}$ to 25.8 ng $m^{-3}$ (average 4.2 ng $m^{-3}$), which is higher than the values obtained in studies conducted at the same location in 2013 (12.6 ng $m^{-3}$) (Jakovljević et al., 2018). In comparison with other urban environments, the mass concentrations of $\sum_{12}$PAHs measured in the $PM_{10}$ particle fraction in Zagreb in 2022 were higher than the mass concentrations of $\sum_{18}$PAHs determined in the $PM_{10}$ particle fraction in Malaysia in September 2019 (average daily mass concentration of $\sum_{18}$PAHs was

9.9 ng $m^{-3}$) (Najurudeen et al., 2023). However, they were lower than the mass concentrations of $\Sigma_{16}$PAHs measured in Belgrade in 2003 at an urban traffic monitoring site (5.5–52.9 ng $m^{-3}$) (Cvetković et al., 2015) and the mass concentrations of $\Sigma_{16}$PAHs measured in Iran in 2015–2016 at an urban traffic monitoring site (602.4–712.2 ng $m^{-3}$) (Jahedi et al., 2021).

The weekly mass concentrations of $\Sigma_{17}$PCBs in the $PM_{10}$ particle fraction ranged from 26.1 pg $m^{-3}$ to 338.3 pg $m^{-3}$ (average 110.8 pg $m^{-3}$). Looking at studies on other urban environments, we can observe that the mass concentrations of $\Sigma_{17}$PCBs measured in the $PM_{10}$ particle fraction in Zagreb's air in 2022 were higher than the mass concentrations determined in the $PM_{10}$ particle fraction in Beijing, China, in 2002–2003 (average mass concentration of $\Sigma_{37}$PCBs in five-day $PM_{10}$ samples was 89.2 pg $m^{-3}$) (Xu et al., 2005), but lower than the mass concentrations of $\Sigma_{26}$PCBs measured in İzmir, Turkey, in 2006 (average mass concentration of $\Sigma_{26}$PCBs in daily $PM_{10}$ samples was 153 pg $m^{-3}$) (Odabasi et al., 2015).

The weekly mass concentrations of $\Sigma_{7}$OCPs in the $PM_{10}$ particle fraction ranged from 7.7 pg $m^{-3}$ to 98.6 pg $m^{-3}$ (average 38.5 pg $m^{-3}$). Compared to other urban environments, the mass concentrations of $\Sigma_{7}$OCPs measured in the $PM_{10}$ particle fraction in Zagreb in 2022 were lower than those determined in the $PM_{10}$ particle fraction in Taiyuan, China, in 2006 (median mass concentration of $\Sigma_{21}$OCPs in daily $PM_{10}$ samples was 180 pg $m^{-3}$) (Fu et al., 2009) and Izmir, Turkey, in 2006 (average mass concentration of $\Sigma_{9}$OCPs in daily $PM_{10}$ samples was 90.2 pg $m^{-3}$) (Odabasi et al., 2015). However, they were higher than the mass concentrations of $\Sigma_{7}$OCPs measured in Mexico in 2014 (median mass concentration of $\Sigma_{7}$OCPs in six-day $PM_{10}$ samples was 13.6 pg $m^{-3}$) (Beristain-Montiel et al., 2020).

## CONCLUSIONS

The median mass concentrations of $PM_{10}$ particle fraction, $\Sigma_{12}$PAHs, $\Sigma_{7}$OCPs, and $\Sigma_{17}$PCBs were 15.1 μg $m^{-3}$, 1.7 ng $m^{-3}$, 30.3 pg $m^{-3}$, and 93.9 pg $m^{-3}$, respectively with maximum values in the cold period of the year for all three groups of compounds. These results are in accordance with the concentration levels of semivolatile organic compounds in $PM_{10}$ particle fraction found in the literature. This study represents the first results of simultaneous measurements of PAHs, PCBs, and OCPs in the $PM_{10}$ particle fraction in Zagreb, which in addition to the knowledge about levels and temporal changes, enable their intercomparison as well as comparison with similar locations around the world.

## ACKOWLEDGEMENT

This study was performed using the facilities and equipment funded within the European Regional Development Fund project KK.01.1.1.02.0007 "Research and Education Centre of Environmental Health and Radiation Protection – Reconstruction and Expansion of the Institute for Medical Research and Occupational Health", and as part of the project "Analysis of Organic Pollutants in Biological Systems and the Environment," supported by institutional funding for scientific activities.

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Poster presentation

**Suzana Sopčić, Ranka Godec, Ivan Bešlić, Gordana Pehnec**

# ANHYDROSUGAR DISTRIBUTION IN DIFFERENT PARTICULATE MATTER FRACTIONS AND THEIR SEASONAL PATTERN

## Abstract

*This study aimed to determine the mass concentrations of levoglucosan, mannosan, and galactosan in three different particle fractions, $PM_{10}$, $PM_{2.5}$, $PM_1$, in order to examine their seasonal pattern and to find their relationship between fractions. Results showed that the average mass concentrations of $PM_{10}$, $PM_{2.5}$, $PM_1$ decreased in the following order: winter, spring, summer, and autumn. The highest average concentrations of 33.2±14.62 μg $m^{-3}$, 28.2±14.19 μg $m^{-3}$ and 16.7±8.44 μg $m^{-3}$ for $PM_{10}$, $PM_{2.5}$, $PM_1$, respectively, were observed during winter. The lowest of 14.8±9. μg $m^{-3}$, 6.4±3.31 μg $m^{-3}$ and 5.5±2.47 μg $m^{-3}$ for $PM_{10}$, $PM_{2.5}$, $PM_1$, respectively, were registered during autumn. Average mass concentrations of anhydrosugars were the highest during the winter season followed by spring, autumn and summer. The highest average winter value for levoglucosan in $PM_{10}$ was 1.45±0.807 μg $m^{-3}$, for mannosan of 0.15±0.068 μg $m^{-3}$ and for galactosan of 0.06±0.036 μg $m^{-3}$. In every particle fraction, levoglucosan levels were the highest compared to mannosan and galactosan. Linear regression revealed that levoglucosan was mostly present in particles with smaller aerodynamic diameters, $PM_{2.5}$ and $PM_1$. Results indicated that $PM_{2.5}$ constituted approximately 84% of $PM_{10}$, while about 55% of $PM_{2.5}$ consisted of the $PM_1$ fraction.*

**Keywords:** *levoglucosan, biomass burning, HPAEC-PAD, fraction distribution*

## INTRODUCTION

The presence of levoglucosan and its isomers in air pollution and particulate matter in southeastern Europe has so far been rarely studied. They are known as tracers for biomass burning and are quite reliable markers since they only form by cellulose and hemicellulose pyrolysis (Simoneit et al., 1999). The current EU directive on ambient air quality has still not been regulated with regard to the monitoring of levoglucosan as a biomass burning tracer, which could explain the lack of information in terms of annual levels, seasonal variations, meteorological condition dependence, etc. Besides the annual levels and seasonal variations, which are expected due to the different origins of anhydrosugars throughout the year, it is important to get a better insight into the presence of such compounds in different particle fractions. Although there is no evidence of anhydrosugar toxicity, information regarding the distribution of anhydrosugars between particle size fractions and their composition is in general vital for health since it is known that the smaller the particle is, the deeper its penetration into the respiratory system (Pope et al., 2002). Previous studies showed that anhydrosugars were mostly present in the fine fraction (Bhattarai et al., 2019), however, most of these studies were performed in coarse and fine factions (Caseiro and Oliveira, 2012; Janoszka and Czaplicka, 2019). The aim of this study was to determine the mass concentrations of levoglucosan, mannosan, and galactosan in $PM_{10}$, $PM_{2.5}$, $PM_1$ fractions collected simultaneously at an urban background site in order to examine their seasonal pattern and find their relationship between different fractions.

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## MATERIALS AND METHODS

Three different fractions of particulate matter ($PM_{10}$, $PM_{2.5}$, $PM_1$) were simultaneously sampled at an urban background area of Zagreb, Croatia. Daily, 24-hour samples were collected during 2022 on 47 mm quartz fiber filters (Whatman® QM-A, or pre-treated (850°C, 3 h) Pallflex Tissue Quartz 2500QAT-UP) using low-volume air samplers (Sven Leckel 47/50) with an air flow rate of about 55 $m^3$/day. The mass of the collected samples was determined gravimetrically according to the EN 12341:2014 standard using precise microbalances (Mettler Toledo MX5 and XP6/M, Giessen, Germany, with 1 µg sensitivity) combined with an electrostatic discharge control system. After sample preparation, which included ultrasonic extraction in ultrapure water and centrifugation, the samples were analyzed by high-performance anion-exchange chromatography with pulsed amperometric detection (ICS-6000, Thermo Fischer Scientific, USA). Anhydrosugars were analysed using two methods detailed in Sopčić et al. (2024).

## RESULTS

Figure 1 presents the average mass concentrations of particulate matter for different fractions across the four seasons. Figure 2 illustrates the linear regression relationships between the fractions: a) the relationship between $PM_{2.5}$ and $PM_{10}$, and b) the relationship between $PM_1$ and $PM_{2.5}$. Figure 3 displays the average mass concentrations of levoglucosan, mannosan and galactosan measured in each fraction during spring, summer, autumn, and winter.

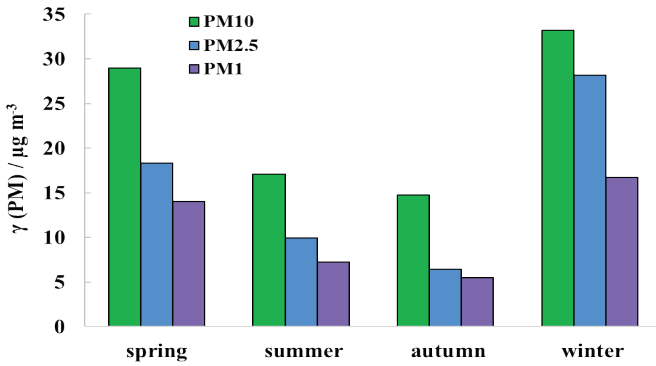


**Figure 1.** Average mass concentration (µg $m^{-3}$) of $PM_{10}$, $PM_{2.5}$, $PM_1$ during different seasons

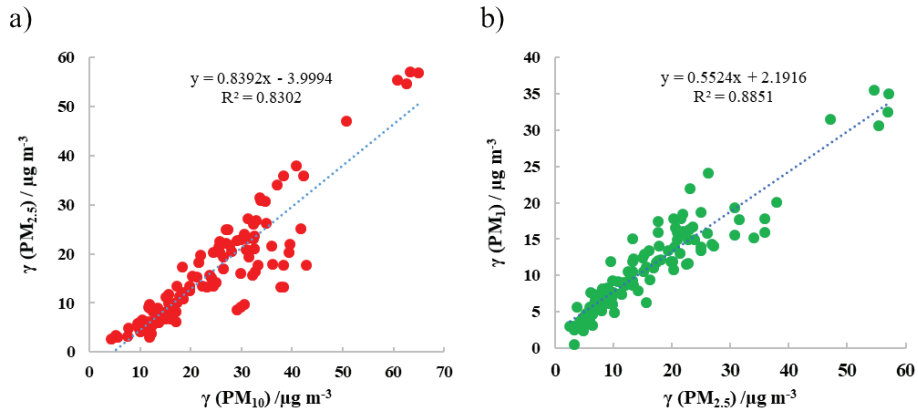


**Figure 2.** Linear regression between a) $PM_{2.5}$ and $PM_{10}$, and b) $PM_1$ vs. $PM_{2.5}$

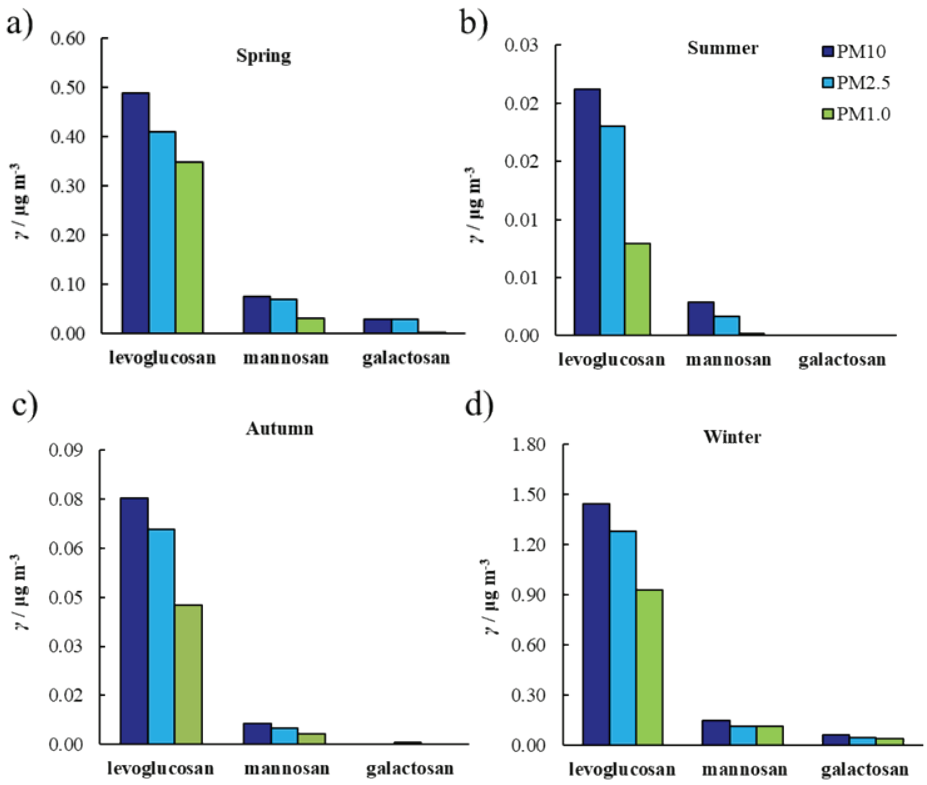


**Figure 3.** Average mass concentrations (µg $m^{-3}$) of levoglucosan, mannosan and galactosan in a) spring, b) summer, c) autumn and d) winter


**Figure 4.** Distribution of levoglucosan between fractions in different seasons

## DISCUSSION

The seasonal variation of PM mass concentrations was the same for $PM_{10}$, $PM_{2.5}$, and $PM_1$ fraction decreasing from winter, spring, summer and autumn (Figure 1). Such a pattern aligned with the usual increase of PM during winter due to higher emissions from heating, increased traffic and meteorological conditions (Perrino et al., 2019). The highest average $PM_{10}$ concentration of 33.2±14.62 μg $m^{-3}$ was observed during winter, and lowest of 14.8±9.21μg $m^{-3}$ during autumn. For $PM_{2.5}$ concentrations, the highest average value was 28.2±14.19 μg $m^{-3}$, and lowest 6.4±3.31 μg $m^{-3}$. The highest average $PM_1$ concentration was 16.7±8.44 μg $m^{-3}$, while the lowest was 5.5±2.47 μg $m^{-3}$. Maximum 24-hour levels of $PM_{10}$, $PM_{2.5}$, and $PM_1$ were 65 μg $m^{-3}$, 57 μg $m^{-3}$ and 36 μg $m^{-3}$, respectively. Linear regression indicated that $PM_{2.5}$ constituted approximately 84% of $PM_{10}$, while about 55% of $PM_{2.5}$ consisted of the $PM_1$ fraction (Figure 2). Anhydrosugar concentrations exhibited a similar seasonal pattern in all of the studied fractions, with the highest average levels in winter, followed by spring, autumn and summer (Figure 3). Levoglucosan consistently showed the highest levels among the anhydrosugars, significantly exceeding those of mannosan and galactosan, which were frequently below detection limits in summer and autumn. Levoglucosan was predominantly found in smaller particle sizes, indicating its association with fine particulate matter ($PM_{2.5}$, and $PM_1$). Results showed over 66% of levoglucosan was found in the $PM_1$ fraction compared to $PM_{10}$, and over 75% was detected in $PM_1$ when compared to $PM_1$ and $PM_{2.5}$. The distribution of levoglucosan in fraction ($PM_{10}$– $PM_{2.5}$), ($PM_{2.5}$– $PM_1$) and fractions smaller than $PM_1$ shown in Figure 4 indicated strong seasonal dependence. In most of the seasons (spring, autumn and winter) it was consistent in fractions smaller than $PM_1$, including the ultrafine fraction (< $PM_{0.1}$) with a contribution of 57 to 71%, while during summer it was more related to fraction ($PM_{2.5}$– $PM_1$) with a contribution of 48%. In the colder part of the year, increased heating activities and specific meteorological conditions such as lower temperatures and higher humidity favored the formation and retention of levoglucosan in finer particles (like $PM_{2.5}$ and $PM_1$). Conversely, in warmer seasons, different sources of biomass burning, changes in atmospheric stability, and increased photochemical activity influenced how levoglucosan distributes across particle sizes, often leading to higher proportions in the coarse fraction. Also, such results could suggest that levoglucosan is more likely to remain airborne and travel longer distances, potentially impacting air quality in distant regions.

## CONCLUSIONS

Most of the PM particles (approx. 83%) collected at the urban background site were of smaller size (< $PM_{2.5}$) and exhibited significant seasonal variation decreasing in the order winter, spring, summer, and autumn. The anhydrosugar levels determined in all three fractions were the highest during winter and spring season which can be associated with the increased use of biomass for residential heating and/or agricultural activities, while during autumn and summer seasons the levels were lower for one order of magnitude. Levoglucosan was consistently the most dominant anhydrosugar across all seasons and in every fraction. Generally, it was more associated with fractions ($PM_{2.5}$ and $PM_1$). The seasonal distribution of levoglucosan in coarse, fine fractions smaller than $PM_1$ showed variability, suggesting influence of levoglucosan and particulate matter sources as well as the influence of atmospheric conditions. Our results highlight the complex nature of biomass burning emissions and their interaction with meteorological conditions, causing changes in the distribution of levoglucosan between particle size fractions throughout the year.

## ACKNOWLEDGEMENT

This study was performed using the facilities and equipment funded by the European Regional Development Fund project KK.01.1.1.02.0007 "Research and Education Centre of Environmental Health and Radiation Protection – Reconstruction and Expansion of the Institute for Medical Research and Occupational Health".

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Poster presentation

**Magdalena Vincetić, Silva Žužul, Jasmina Rinkovec**

# TOTAL DEPOSITED MATTER AND ITS METAL CONTENT – A COMPARISON OF RESULTS OBTAINED IN RURAL AND URBAN SITES IN CENTRAL CROATIA

## Abstract

*Routine air quality monitoring required by EU and Croatian legislation includes monitoring of total deposited matter (TDM) levels and the concentrations of nickel, arsenic, cadmium, lead and thallium in TDM. The aim of this work was to compare the levels of TDM and its metal content at one rural background station located within the Šumbar Research Area in Karlovac County and two urban locations in the city of Zagreb. Twelve samples of total deposited matter at each sampling site were collected during 2022 from January to December, using the Bergerhoff method. Collected total deposited matter was determined gravimetrically, while metal concentrations in TDM were determined by inductively coupled plasma mass spectrometry. Results showed that the annual average value of TDM at the other two sites was lower than at Šumbar Research area with no statistically significant difference. In contrast to TDM, a statistically significant difference was found for nickel concentrations between all sampling sites. Metal concentrations and levels of TDM did not exceed the annual limit values set by the Regulation on the level of pollutants in the air passed by the Government of the Republic of Croatia (Official Gazette 77/2020).*

**Keywords:** *air monitoring, Bergerhoff method, heavy metals*

## INTRODUCTION

Trace metals, which are toxic substances, can be emitted into the atmosphere from both natural and anthropogenic sources. The impact of certain trace metals on human health, through the food chain or the broader environment, occurs via their concentrations in ambient air and subsequent deposition. Atmospheric deposition is the primary pathway for these metals to enter the surface environment (Puente et al., 2013). Total deposited matter (TDM) refers to the cumulative mass of all pollutants transferred from the air to soil, vegetation, water, and buildings over time, serving as a measure of visible air pollution that affects air quality. TDM is transported in the environment through both dry and wet deposition mechanisms. Dry deposition, occurring near the emission source, primarily involves the transport of coarse particles via Brownian motion, gravitational settling, impaction, or wind influence. In contrast, wet deposition, which includes precipitation (rain, hail, snow, dew, fog, etc.), mainly transports gases and fine suspended particles (Gluščić et al., 2021). Studies of urban total deposited matter at measuring stations in various countries have demonstrated that the quantity and composition of TDM depend on the type and intensity of the emission sources, their spatial and temporal distribution, meteorological conditions, and the deposition mechanisms themselves (Yatkin et al., 2016; Li et al. 2020; Kara et al., 2014). Therefore, long-term monitoring of the chemical composition of TDM can provide deeper insights into the interactions and origins of pollutants in a given area, as well as assess their environmental impact.

The Šumbar Research Area is a unique ecosystem monitored and managed by the Institute for Medical Research and Occupational Health which performs activities of safeguarding, improvement and control of habitat stability. The air quality monitoring station located

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within the area is classified as a rural background station and it is adequate for assessing a long-range air pollution transport. This paper presents a comparison of a one-year measurement of total deposited matter and its metal content at three different monitoring stations in central Croatia (urban traffic, urban industrial and rural background).

## MATERIALS AND METHODS

Samples of total deposited matter were collected with a Bergerhoff collector at the three research stations for air monitoring with the various sources of pollution. Two urban stations were located in the city of Zagreb, one with high traffic density (urban T) and the other classified as urban industrial station (urban I). The third station was located within the Šumbar Research Area in the Karlovac County and classified as rural background station. Twelve samples of TDM at each sampling station were collected during 2022 from January to December. Samples were collected over a period of 30 ± 2 days. Total deposited matter was determined gravimetrically (Mettler Toledo, AX 205/A). Mass concentrations of nickel, arsenic, cadmium, thallium and lead in TDM were determined by inductively coupled plasma mass spectrometry (ICP-MS 8900, Agilent Technologies) after microwave digestion in nitric acid under high pressure and temperature (UltraCLAVE, Milestone). Statistical data analysis was performed using MS Excel.

## RESULTS AND DISCUSSION

Results showed that monthly levels of total deposited matter varied between 9 mg/m$^2$d to 323 mg/m$^2$d at the rural background station and 17 mg/m$^2$d to 134 mg/m$^2$d at urban stations (Figure 1). Two maximum peaks were found for the levels of TDM, for all sampling stations simultaneously, one in April and the other one in June. The highest value of TDM at rural background station observed in June was five times higher than the annual average. If this extreme event is excluded, the annual mean values of TDM were 67 mg/m$^2$d (rural), 64 mg/m$^2$d (urban T) and 67 mg/m$^2$d (urban I) respectively, and did not differ significantly among the measuring stations despite their distance.

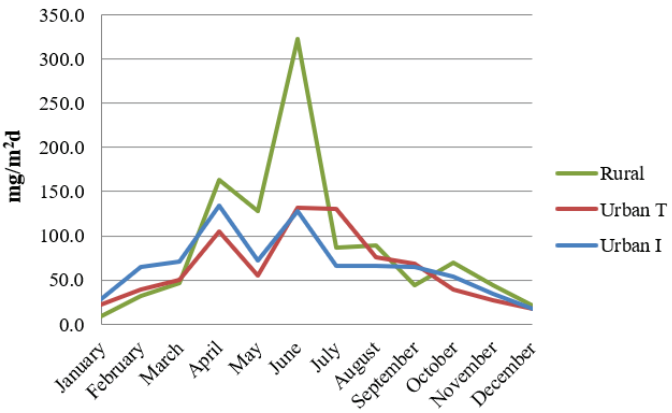


**Figure 1**. The monthly levels of TDM in central Croatia measured in 2022.

These results are in accordance with the previously published data for the city of Zagreb where slowly decreasing trend was found for the period from 2000 to 2016 (Žužul, 2017). The elevated values of TDM in April are often related to the pollination period while elevated values in the summer are often the result of Saharan dust intrusion which can reach the central Croatia (Penezić et al., 2021; Mifka et al. 2023).

The differences in the annual mean concentrations of some metals in TDM between sampling stations were more pronounced and are presented in Figure 2 while the minimum and maximum values of monthly results are presented in Table 1.

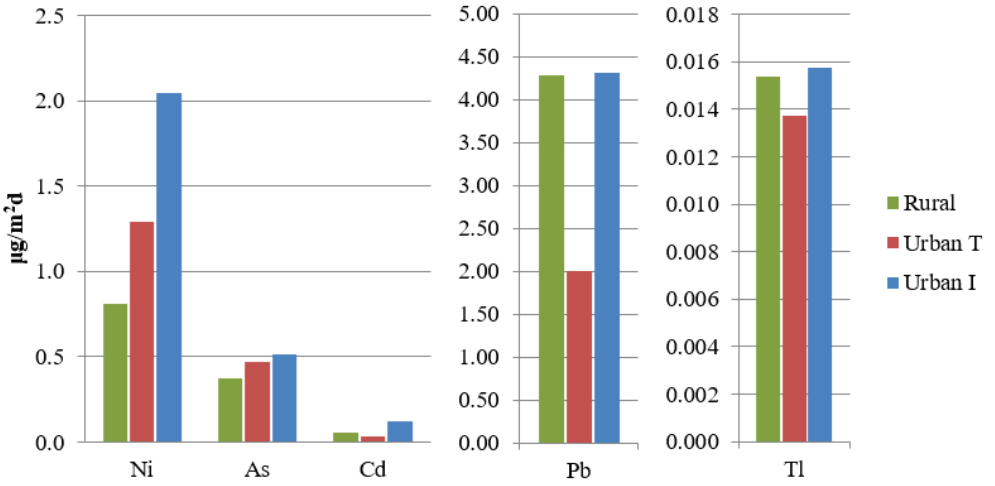


**Figure 2**. Annual average concentrations of metals in TDM measured in 2022.

**Table 1**. Minimum ($C_{min}$) and maximum ($C_{max}$) values for the monthly metal content in TDM.

| | $C_{min} – C_{max}$ / µg/m²d | | | | |
|---|---|---|---|---|---|
| | Nickel | Arsenic | Cadmium | Lead | Thallium |
| Rural | 0.1 – 2.1 | 0.19 – 0.50 | 0.02 – 0.22 | 0.53 – 13.51 | 0.004 – 0.028 |
| Urban T | 0.6 – 2.4 | 0.29 – 0.72 | 0.02 – 0.07 | 0.87 – 3.41 | 0.004 – 0.025 |
| Urban I | 0.9 – 3.3 | 0.31 – 0.75 | 0.04 – 0.29 | 0.21 – 7.29 | 0.006 – 0.030 |

Metal levels in TDM in all of the samples were low and the annual means did not exceed the limit values stated by the Croatian Regulation on Levels of Pollutants in Ambient Air (Official Gazette 77/2020). The highest annual means for all of the measured elements were found at the urban industrial station. A significant difference between sampling stations was found only for nickel and cadmium, indicating that sources around the industrial station are contributing to their increase in air levels. Levels of arsenic, cadmium and lead were very similar to the previously reported for these metals in TDM, while the nickel

levels were almost twice lower than for the period from 2007 to 2016 (Žužul, 2017). Fernández-Olmo et al. (2015) compared the results of trace elements in bulk atmospheric deposition at industrial, urban, traffic and rural sites worldwide. The results presented in this study are in accordance with some rural or less polluted areas in Europe.

## CONCLUSIONS

Atmospheric deposition is an important component of air pollution and requires a regular monitoring. The levels of TDM measured in this study were low during the whole sampling period and did not differ significantly between stations. The maximum values of TDM were found in April and June. The highest concentrations of arsenic, nickel, cadmium, lead and thallium were found at the urban industrial site. A statistically significant difference was found for nickel and cadmium concentrations between all of the sampling stations in contrast to thallium concentrations, where no statistically significant difference was found. Metal concentrations in TDM, as well as levels of TDM at all three stations were below limit values set by Croatian legislation.

## ACKNOWLEDGEMENT

This work was performed using the facilities and equipment funded within the European Regional Development Fund project KK.01.1.1.02.0007 "Research and Education Centre of Environmental Health and Radiation Protection – Reconstruction and Expansion of the Institute for Medical Research and Occupational Health".

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Poster presentation

**Silva Žužul[1], Zorana Kljaković-Gašpić[1], Gordana Pehnec[1], Jasmina Rinkovec[1], Ivana Jakovljević[1], Ivan Bešlić[1], Marinko Pleština[2], Marijan Sudić[2], Sandy Lovković[2], Jasna Jurasović[1]**

# ANALYSIS OF MICROPLASTIC IN INDOOR AIR WITHIN THE "JamINNO+" PROJECT

## Abstract

*Contaminants present in indoor air are directly and continuously inhaled, posing a potential risk to human health. The widespread occurrence of microplastics in the environment has driven the need for their study and analysis. Although various methods have been applied for microplastic identification, standardized approaches are still lacking. As part of the "JamINNO+" project, we aimed to develop a method for the detection and identification of microplastics in indoor air. Therefore, a test indoor air sample was collected from a multipurpose room, and preliminary results of active sampling and microplastic identification directly on filters, using quantum cascade laser based IR microscopy, are presented. The influence of blank levels and sampling duration was also examined. The results showed that the majority of the particles in the test sample were polyamides (47%) and chitin (16%), along with rubber (7%), carbonates (5%), polyethylene terephthalate (2%), and other particles composed of various materials (8%). In an automated analysis workflow, 15% of particles remained unidentified. Most particles (83%) were smaller than 30 µm, 11% were within the 30 to 50 µm range, and the rest were between 50 µm and 500 µm.*

**Keywords:** *air sampling, LDIR imaging, microplastics analysis*

## INTRODUCTION

Microplastics (MP) represent a class of emerging contaminants widely distributed in the environment. While the presence and distribution of MP in aquatic and soil ecosystems have been extensively investigated over the past decade (Ahmed et al., 2023; Anderson et al., 2016; Chaukura et al., 2021), interest in airborne MP has only recently attracted significant attention from researchers and the general public. Some of the earliest papers on airborne MP focused primarily on atmospheric fallout (Dris et al., 2016) and atmospheric deposition (Wright et al., 2019). However, investigations into the presence of MP in outdoor air remain limited (O'Brienet al., 2023), with even fewer studies addressing indoor air sampling and analysis.

Currently, there are no standard operation protocols for MP analysis in environmental samples. The diversity of sample types and chemical properties of MP present challenges during sampling, sample preparation, and analysis, often necessitating a combination of analytical methods, mainly vibrational spectroscopy and chromatography, for both qualitative and quantitative analysis. Different methods used for the characterisation of MP require also some pre-treatment procedures which usually separate MP particles and remove unwanted organic and inorganic material that may interfere during the analysis.

Sampling strategies for indoor air analysis involve either active sampling of indoor air with sampling pumps or passive sampling and analysis of dust collected either with vacuum pumps or by deposition into suitable containers (Torres-Agullo et al., 2021).

An additional analytical challenge in MP analysis and data interpretation involves minimizing potential contamination during the sample preparation and analysis, as well as characterising background levels of contaminants that may be introduced to the samples

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throughout the analytical process. A review of control and blank data correction methods (Dawson et al., 2023) indicated that, whenever applicable, LOD/LOQ methods are the most reliable for interpretation of microplastics data.

Within the project "Development of functional beverage in sustainable packaging – JamINNO+" funded by the European Regional Development Fund (KK.01.2.1.02.0305), the aim was to implement suitable methods for the analysis of MP in bottled water and indoor air. This study presents the preliminary results of the method development for the active sampling of indoor air directly onto filters suitable for MP analysis using a quantum cascade laser (QCL) based IR microscopy technique (commercialized by Agilent as 'Laser Direct Infrared Imaging', LDIR) without the need for additional sample pre-treatment.

## MATERIALS AND METHODS

Indoor air was sampled from a multipurpose room located at the Institute for Medical Research and Occupational Health. The room sized at 47 $m^2$ comprises an office area, a storage section, and a section used as a repair shop with a rubberized workbench. A MiniVS-C (Sven Leckel Ingenieurbüro GmbH, Germany) mini volume sampler was positioned in the centre of the room, with the air inlet located 1.4 m above the floor. Sampling was conducted at an air flow rate of 200 L/h for 30 minutes, to avoid saturation of the filter media. A polycarbonate gold-coated filter (25 mm diameter 0.8 µm pore size; SPI Structure Probe, Inc., PA, USA) was placed in the sampler just before the start of sampling and removed from the air inlet immediately after the sampling process was completed. A pre-cleaned glass petri dish was used for filter storage and transport. The filter was also analysed prior to the sampling to determine the background level of contamination. The analysis of MP was performed using an Agilent 8700 LDIR system (Agilent Technologies Inc, USA). The built-in Agilent Clarity software with the microplastic library comprising previously recorded spectra was used in automated workflow. The diameter, width and height of each particle were measured within the size range of 10 to 500 µm.

## RESULTS AND DISCUSSION

The 30-minute indoor air sampling period was sufficient to collect detectable particles for the MP analysis. However, the number of particles on the sample filter compared to a blank filter suggested that extending the sampling duration may yield more accurate results. The blank filter, analysed before sampling, contained a total of 479 particles. To account for this relatively high background level of MP in our laboratory conditions, the particle count from the blank filter was subtracted from the sample filter data, resulting in 372 particles attributed to indoor air. This corresponded to a total concentration of 3720 MP particles/$m^3$ in the investigated room. The results confirmed the importance of checking and analysing filters before sampling to improve the reliability of MP analysis, particularly when low particle counts are expected or when sample handling and analysis cannot be performed in clean laboratory conditions.

The chemical composition of particles from the blank and the sample filter is shown in Figure 1.

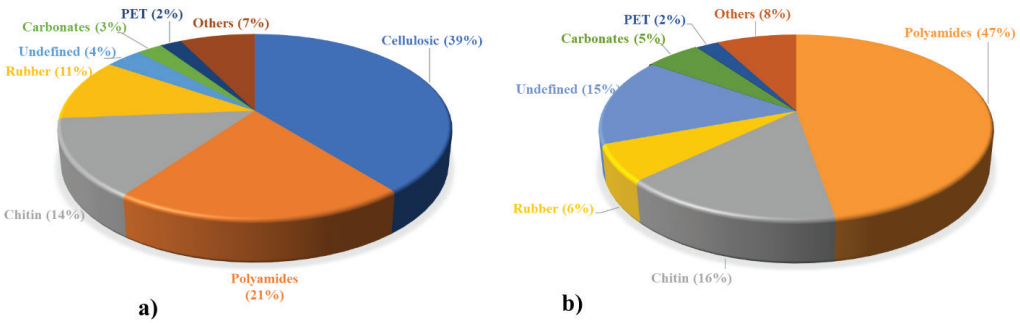


**Figure 1.** Chemical composition of particles collected on a polycarbonate gold-coated filter: a) blank sample and b) filter after the active sampling of indoor air (blank corrected).

Particle characterization showed that polyamide was the predominant polymer in the indoor air of the multipurpose test room, with rubber as the second most prevalent polymer. Compared to other polymer particles, polyethylene terephthalate (PET) was detected with high accuracy in both the blank and sample filters. Cellulosic particles were not identified in the sample, as their levels were comparable to those found on the filter blank. The recorded spectra of selected polymer particles from the filter analysed using the LDIR instrument and matching library spectra are shown in Figure 2.

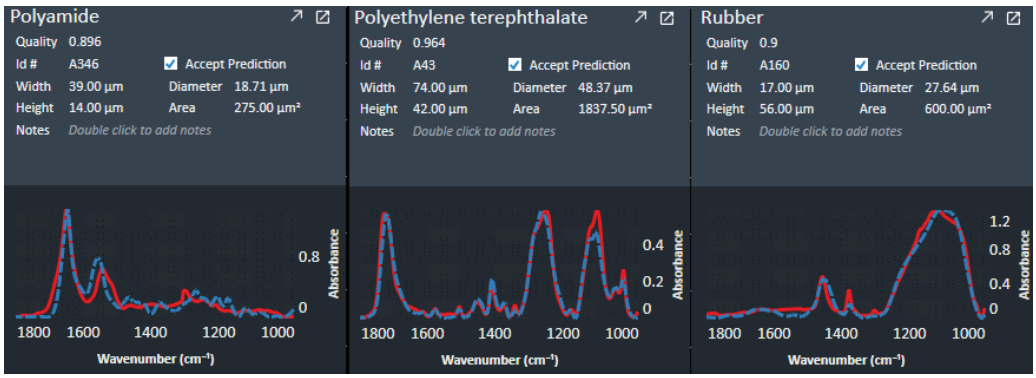


**Figure 2.** Characterization of polymer particles on the LDIR 8700 (blue lines are the reference spectra and red lines are the measured spectra).

The size distribution of the analysed particles in the sample (Figure 3) indicates that the majority of the identified particles (83%) had a diameter smaller than 30 µm. Smaller particles presented challenges for identification in both the automated and manual mode of analysis, leaving 15% of the total particles unidentified. Among the unidentified particles, 85% had diameters ranging between 10 and 20 µm, while 12% were between 20 and 30 µm. There were attempts to analyse airborne microplastic particles smaller than 10 µm using µFT-IR or µRaman spectroscopy. However, these preliminary data show that, in automatic mode, the LDIR system was not capable to reliably detect and characterise particles below this size threshold.

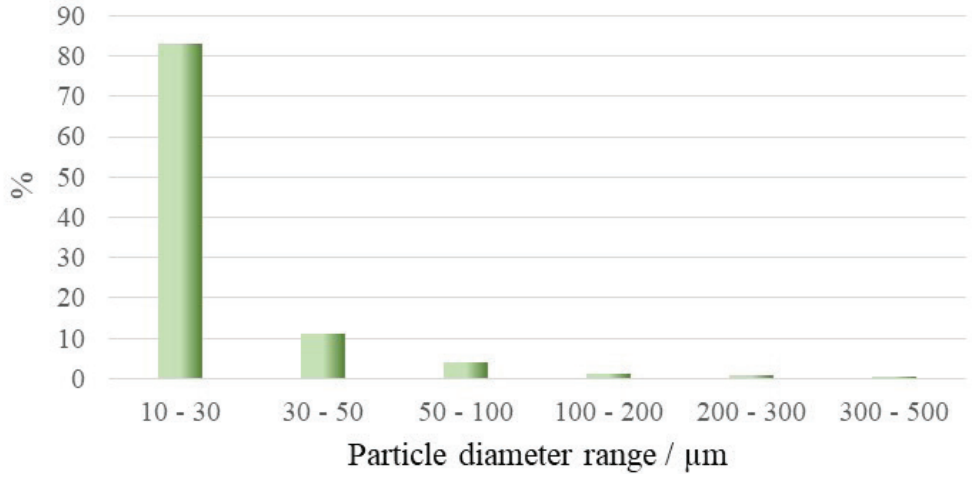


**Figure 3.** The size distribution of analysed particles.

Literature data show that the concentration and frequency of various polymer types in indoor environments fluctuate with the time of day, human activity and the type of ventilation system in the room (Maurizi et al., 2024). The results of this study are in good agreement with previously published data on indoor air (Maurizi et al., 2024, Torres-Agullo et al., 2021), although any comparison of these results with others is challenging due to the heterogeneity in result presentation, as well as differences in sampling strategies and MP extraction methods.

## CONCLUSION

The preliminary results of the active sampling of indoor air and detection and characterization of particles using the LDIR system are presented. An automated analysis workflow, set to measure particle diameters between 10 and 500 µm, successfully identified 85% of particles. However, a large number of particles were found on the blank filter, predominantly consisting of natural polymers – cellulosic material, polyamides and chitin. Particles of PET in the air were identified with high accuracy in both the blank filter and the air sample. The examination of blank filters should be included in each batch of samples as part of the quality control of the analytical method in order to determine potential contamination sources and correct the results of the analysis. Given the ubiquitous presence of MP in indoor air, careful manipulation, increased precautions and continuous control of all areas are required to minimize the contamination during sampling and analysis.

## ACKNOWLEDGMENT

This work was financially supported by the project *Development of functional beverage in sustainable packaging* – JamINNO+ (KK.01.2.1.02.0305) funded by the European Regional Development Fund within the Operational Programme Competitiveness and Cohesion 2014-2020.

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# PRESENTATIONS

# ULTRAFINE PARTICLES (UFP) – RECENT TRENDS & REGULATORY ACTIVITIES

Lucia Bustin[1], Torsten Tritscher[1], Sebastian H. Schmitt[1], Jürgen Spielvogel[1] and Oliver F. Bischof[1]

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AIR PROTECTION 2023"
20th - 23th September 2023 Mlini,
Dubrovnik, Croatia

## 21st century: Anthropogenic sources …<1 µm

UFP (Ultra Fine Particle) is are particulate matter of nanoscale size (less than 100 nm in diameter)

**PM10** 100xUFP
**PM2.5** 25xUFP
**PM1** 10xUFP

# A world needing air quality regulations

- Beijing air in 2005 after rain (left) and a smoggy day (right)

Source: https://en.wikipedia.org/wiki/Air_pollution



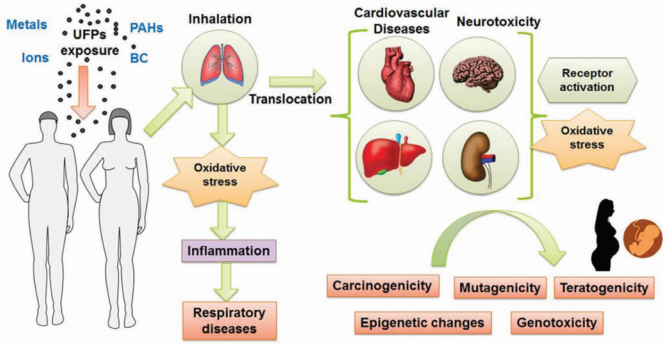

# Relevance of Ultrafine Particles (UFP) (< 100 nm)

- UFP reach deeper into the lungs and stay there longer
- Toxicity gets larger with decreasing particles size

Schraufnagel (2020) The health effects of ultrafine particles. Experimental & Molecular Medicine (2020) 52:311–317

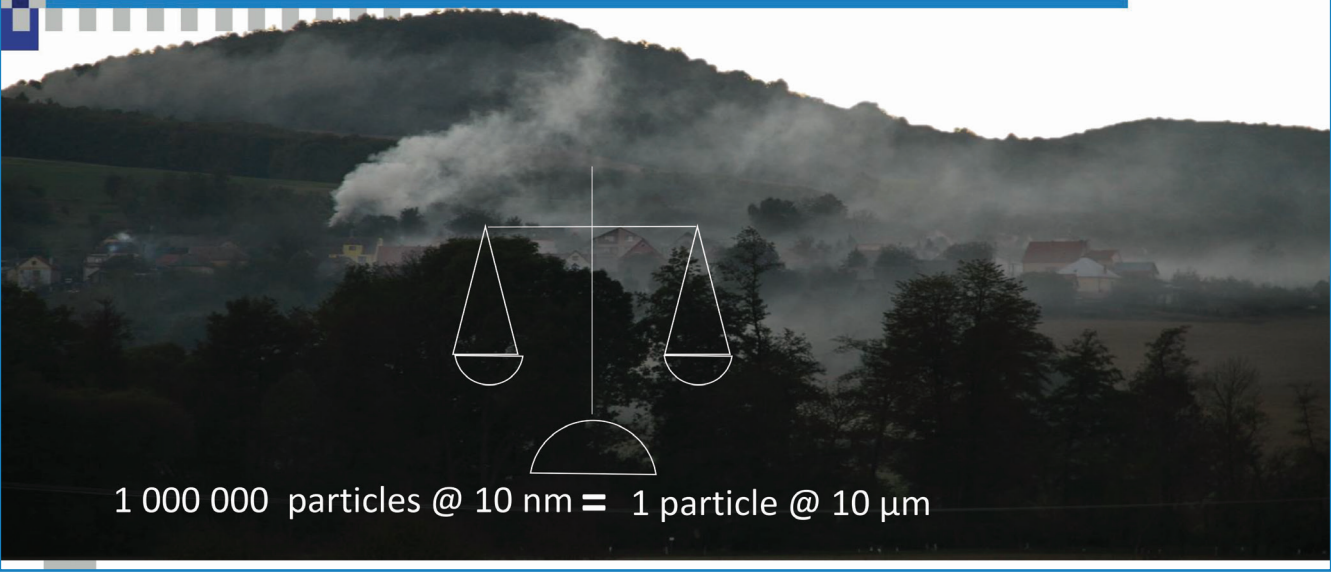
- WHO demands
  - Quantification of UFP in the ambient environment
  - Inclusion of real-time, size-dependent UFP measurements at selected air monitoring stations in addition to and concurrent with other air pollutants and characteristics of PM.

WHO global air quality guidelines. Particulate matter (PM2.5 and PM10), ozone, nitrogen dioxide, sulfur dioxide and carbon monoxide. Executive summary. Geneva: World Health Organization; 2021. Licence: CC BY-NC-SA 3.0 IGO.



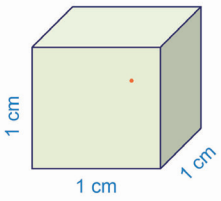

A. L. Moreno-Rios et al. (2021) Sources, characteristics, toxicity, and control of ultrafine particles: An overview. Geoscience Frontiers 13 (2022) 101147

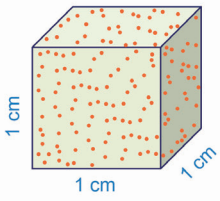
# How to measure small particles? Only by number concentration…..



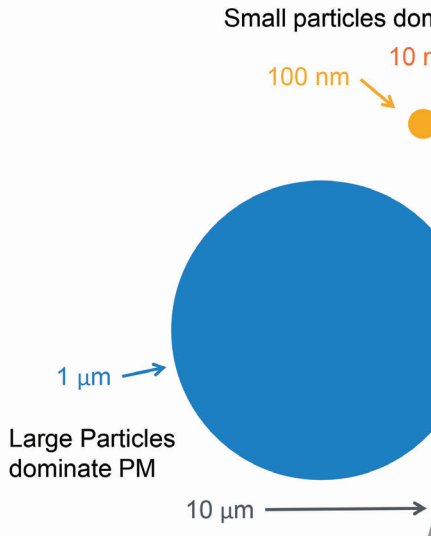

# Particle number concentration

1 Particle/cm³ ⟷ 1*10⁷ Particle/cm³

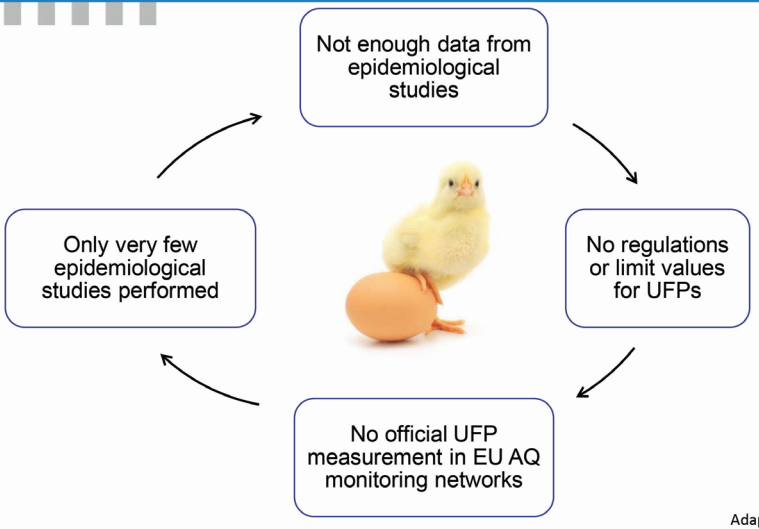



# Particle size



# The (Chicken and Egg) Problem




Adapted from Dr. J. Cyrys




# Regulating Particle Number?

- Proposal for **DIRECTIVE OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL** on ambient air quality and cleaner air for Europe (COM/2022/542 final)
  - Article 10 (Monitoring at supersites)
    1. Each Member State shall establish at least one monitoring supersite per 10 million inhabitants at an urban background location
    5. Measurements at all monitoring supersites at urban background locations shall include fixed or indicative measurements of size distribution of ultrafine particles …
    6. Measurements at all monitoring supersites at urban background locations and rural background locations shall include ultrafine particles (UFP)
  - Annex VII introduces UFP monitoring at locations where high concentrations are likely, such as at or close to airports, ports, roads & industrial sites


COMMISSIONE EUROPEA

Bruxelles, 26.10.2022

ALLEGATI

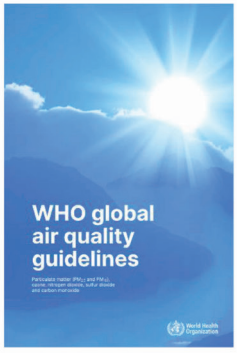
alla

proposta di direttiva del Parlamento europeo e del Consiglio

IT IT

# Regulating Particle Number?

- World Health Organization published **WHO global air quality guidelines** in 2021
  - Not yet sufficient evidence to formulate an AQG level
  - However, Guideline Development Group formulated four good practice statements on UFP "to guide national and regional authorities and research to reduce ambient UFP concentrations"
    1) Quantify ambient UFP as particle number concentration from > 10 nm (no upper limit*)
    2) Monitoring strategy: Integrate UFP monitoring into existing air quality monitoring
       - Incl. size-segregated real-time PNC measurements at selected air monitoring stations simultaneously with regulated PM fractions and other airborne pollutants
    3) Distinguish between low and high PNC for UFP source emission control
       - Low PNC: 10,000 particles/cm$^3$ (24-hour mean) or 20,000 particles/cm$^3$ (1-hour)
    4) Utilize emerging **→ science and technology** for assessment of exposure to UFP for epidemiological studies and UFP management




WHO new guidelines including UFPs: Link
Executive Summary: Link

* Upper limit defind by CPC technology




# European Standardization CEN/TS 16976 → DIN EN 16976

- DIN EN 16976 „Ambient air – Determination of the particle number concentration of atmospheric aerosol" now published as draft at (https://www.beuth.de/de/norm-entwurf/din-en-16976/366659847)
- Defines requirements for the CPC to be used in UFP monitoring
  - Performance criteria and test procedures for CPC
  - Performance criteria and test procedures for sampling system
  - Quality assurance and Quality control procedures
- Important changes to CEN/TS 16976:2016:
  - The lower limit of the measured particle size range is set to be 10 nm and thus identical to MPSS (Mobility Particle Size Spectrometers) measurements (see CEN/TS 17434). In air quality monitoring networks where MPSS will be used for determining the particle size distribution a CPC may be used for QA purposes for the MPSS data.
  - The parameter "calibration factor" was introduced and defined.
  - Aerosol diffusion dryer based on silica is excluded, because diffusion losses are too high with this type of dryer.
  - The test "Determination of low size cut-off" was removed, the "Number concentration check" was substantially revised. The term "transfer standard" is introduced.
  - Annex H: The new Annex "Coincidence correction" was added.
  - Annex I: The new Annex "Results of an experimental comparison of different CPCs" was added.

# European Standardization CEN/TS 17434

- CEN/TS 17434 „Ambient air - Determination of the particle size spectra of atmospheric aerosol using a Mobility Particle Size Spectrometer (MPSS)"
- Aims to harmonize measurements of the particle size distribution of UFPs
  - Provide general information about the properties of the aerosol and the method
  - Define **performance criteria** and **test procedures** for the measurement instruments (MPSS aka **SMPS**), and the **sampling system**
  - List requirements for the installation, initial checks and calibrations, and operation of a MPSS with sampling system at a monitoring site
    - Routine maintenance,
    - Data processing (with QA/QC data),
    - Standardized data reporting format
  - Describe Quality Assurance and Quality Control procedures

➔ Comparable measurements between monitoring stations




# The Science to Regulate Particle Number

- **ACTRIS**
  - Stands for "Aerosol, Clouds and Trace Gases Research Infrastructure"
    - Pan-European RI for short-lived atmospheric constituents
      - Supported by 22 countries
      - Currently >110 "research platforms"
    - Introduced standardized and harmonized measurements
    - Aerosol in-situ variables for observatories include
      - Particle number concentration >10 nm
      - Particle number size distribution 10 to 800 nm (mobility diameter)
    - World Calibration Center for Aerosol Physics (WCCAP)
      - Conducts calibrations of instruments and site audits of stations
      - Ensures high-quality data are produced

ACTRiS

Aerosols
Clouds
and
Trace gases
Research
Infra
structure

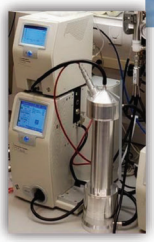
# ACTRIS Guidelines (excerpt from V-3.0)

- Go beyond requirements of DIN EN 16976 & CEN/TS 17434
  - All instruments must undergo regular calibration workshops
  - Obligatory measurements: **particle number concentration >10 nm** & **particle number size distribution 10 to 800 nm**
  - Other interests: **Nano-PNC & PSD <10 nm**
    **Particle number size distribution – aerodynamic diameter 0.8 to 10 µm**
  - Use of a PM10 inlet with a special low flow PM2.5 impactor or cyclone is recommended
  - Nano-particle measurements should preferable be done at a separate inlet with minimum 50% penetration at lowest size
  - Recommended use of a single tube Nafion dryer
  - No heating of the sampling pipe except for moderate heating to avoid freezing
  - Relative humidity and temperature should be determined with a high time resolution
  - **PNC measurements with a separate CPC should be done alongside SMPS measurements in order to be able to perform Near-Real-Time QC checks for all National Facilities.**
  - **A „pulse output" port on the CPC is obligatory**
  - The SMPS should employ an aerosol to sheath flow ratio for the DMA between 1:10 and 1:4
  - **A positive HV for the DMA is preferred to optimize the comparability**



https://www.actris-ecac.eu/pluginAppObj/pluginAppObj_235_191/V-3.0-Preliminary-ACTRIS-recommendations-for-aerosol-in-situ-measurements.pdf

# Harmonizing Measurement Solutions for Aerosol in-situ PNC and Size Distributions

Particle Number Concentration (PN) based on DIN EN 16976

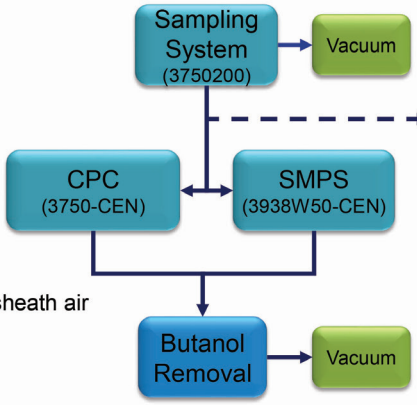
Particle Size Distribution (PSD) based on CEN/TS 17434

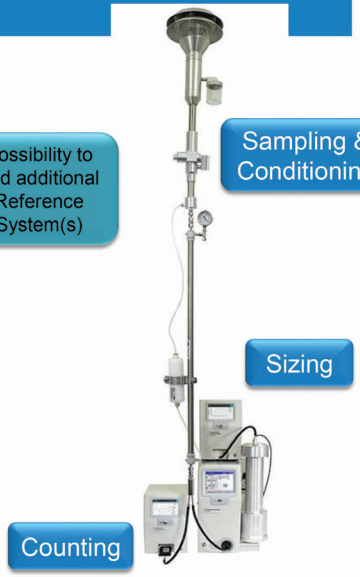
Additional technical specifications (ACTRIS, GAW, ...)

# Setup of TSI's Ambient Monitoring Solution

## Key Specifications

- DIN EN 16976
- CEN/TS 17434
- Size range: 10-800 nm
- Vienna type DMA (Winklmayr et al. 1991) based on TROPOS
- RH control for aerosol and sheath air
- Full system auto recovery
- Auto data export




Visit TSI.com for additional info:

*„CEN" versions of SMPS and CPC are calibrated at WCCAP*



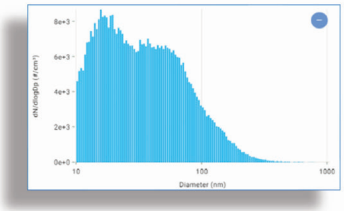

# Challenge: SMPS Measurement near Sourc

THEORY

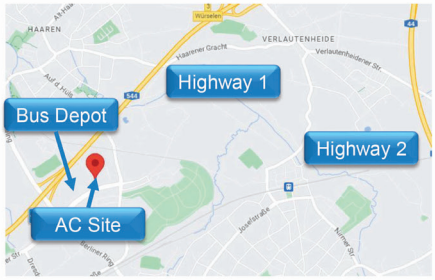
stable and representative aerosol population

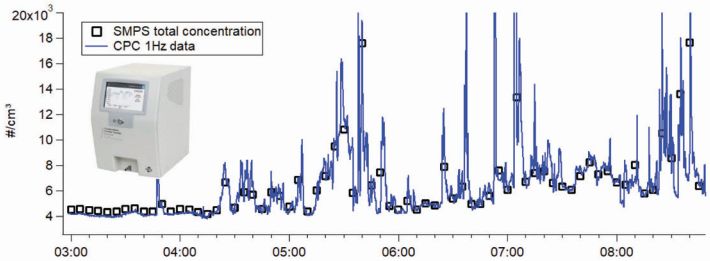
Scan time

Purge



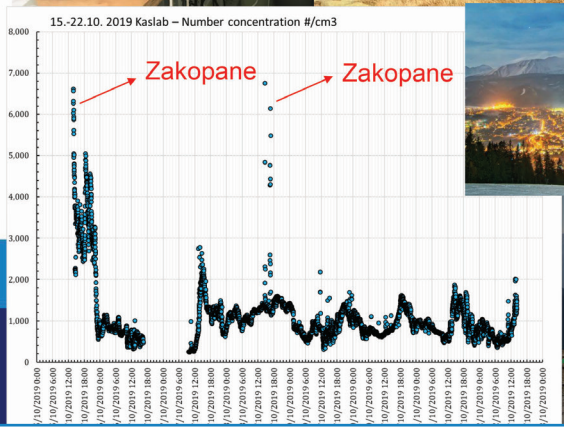

REALITY




Data from Aachen measurement (AC) site – 3 major sources!

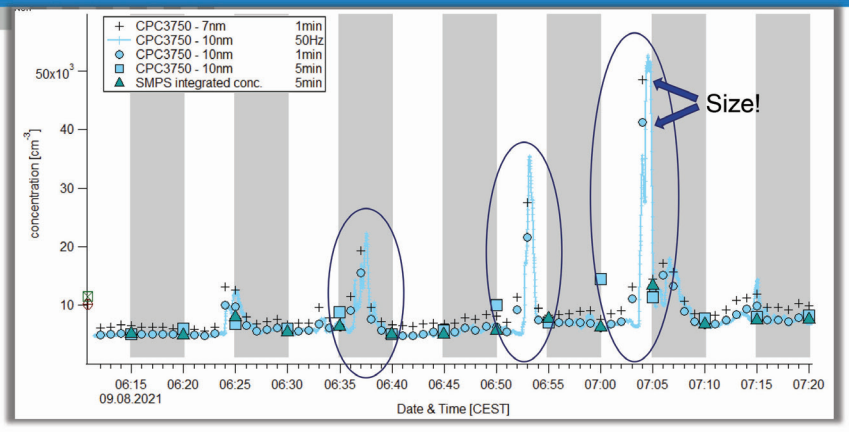
## KASPROWY VRCH a.s.l. 1 987 m (WCPC 3789), 15.-22.10.2019





TSI GmbH
AGH University
@Lucia Bustin

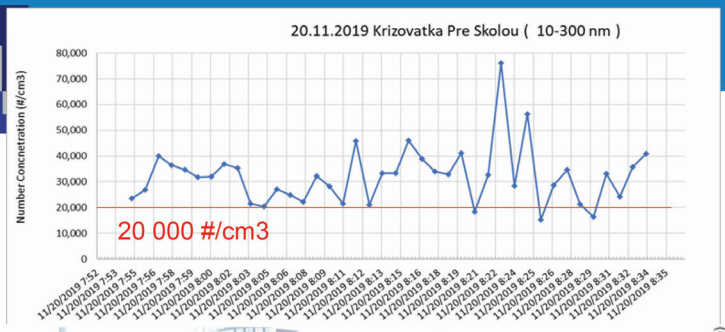
# Ambient Aerosol Close to Sources

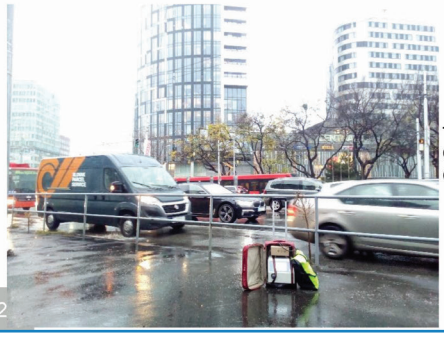



TSI GmbH
@Sebastian Schmitt

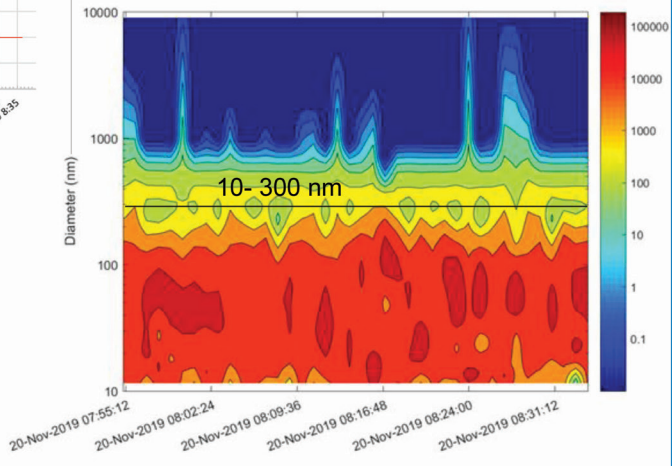
→ Instabilities in the aerosol population can explaind scatter when comparing SMPS and CPC
→ Besides using the CPC only as total number concentration validation it can act as a stability indicator to flag uncertainty of size distributions

# Mobile UFP Measurements in Bratislava



TSI GmbH
Cyklo Koalicia
@Lucia Bustin



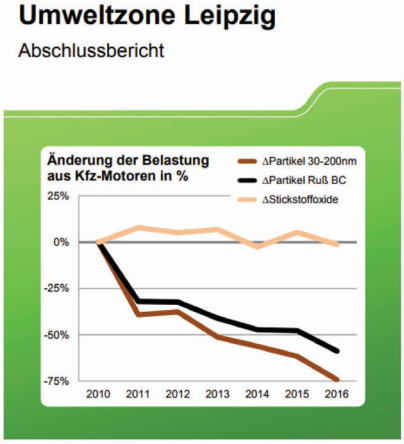



# Low Emission Zone Leipzig Germany

LANDESAMT FÜR UMWELT, LANDWIRTSCHAFT UND GEOLOGIE | Freistaat SACHSEN

Report of local EPA on reduction of Ultrafine Particles due to Low Emission Zone:

https://publikationen.sachsen.de/bdb/artikel/29757




This is one of the best example I know on how UFP measurement shows success of Low Emission Zones as they measured continuously for 10 years or so.

They used UFP monitor, SMPS systems and CPCs. This is on collaboration with Prof. Wiedersohler -> Actris / TROPOS

# TU Wroclaw – Actris Station inside



# Thank you!

lucia.bustin@tsi.com

# POSTERS

NACIONALNI LABORATORIJ ZA ZDRAVJE, OKOLJE IN HRANO
CENTER ZA OKOLJE IN ZDRAVJE

ZAŠTITA ZRAKA 2023
MEĐUNARODNA KONFERENCIJA I 13. HRVATSKI ZNANSTVENO-STRUČNI SKUP
20. – 23. rujna 2023

# Continuous 10-year air quality measurement in Maribor starting in 2013 with PMinter project

Nataša BELŠAK ŠEL, Uroš LEŠNIK

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## Introduction

The dominant air pollutants in middle Europe with a major negative impact on health are currently particulate matter (fine dust, PM10, PM2.5), NO2 (nitrogen dioxide), O3 (ozone) and B(a)P (benzo(a) pyrene).

Non-compliance of the European limit values for PM10 (40 µg/m³ annual average, 35 days maximum beyond 50 µg/m³ 24-hour average, Ambient Air Quality Directive EC/50/2008) in Maribor (Slovenia), Klagenfurt and Leibnitz (Austria) has led to curiosity of exploring the influences of possible dominant sources (traffic, domestic heating, industry) and their contribution rates. Because of that during 2010 – 2013 NLZOH has been a partner of PMinter project (Operational Programme Slovenia-Austria 2007-2013, Interreg Project). The main objective of PMinter project has been the development of methods and air pollution control plans that facilitate a sustainable improvement of the air quality as well as a reduction of health hazards (because of polluted air) for the people of Klagenfurt in Lower Carinthia, Leibnitz in Southern Styria (Austria) and Maribor in Northern Slovenia.

Along with other research, air quality was measured by means of 10 mobile and stationary measurement stations in the regions of Klagenfurt, Leibnitz and Maribor. In Maribor has been established stationary measurement station on which air quality has been continuously monitored to this date (Maribor Krekova/Tyrševa).

Outdoor air quality plans, which helped to reduce ambient concentrations levels (along renewal of car fleet, modernisation of heat devices, implementation of energy efficiency policy – thermal insulation of buildings etc) have been proven to be successful. A trend of dropping concentrations of PM10 has been seen in measuring location Maribor Krekova/Tyrševa, annual limit value in period 2013-2021 has been never exceeded, number of exceedances of daily limit value was over prescribed in years 2014, 2015 and 2016. In the 10-year monitoring of air quality, there is a noticeable trend of air quality improvement.

**Key words:** PM10, Maribor, PMinter project, air quality

## Measurements

Fig. 1: Measurement container with measurement devices at the location Maribor Krekova/Tyrševa.

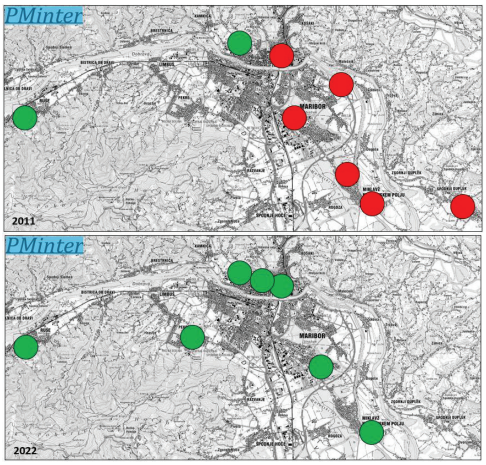



Fig. 2: Exceedances of PM10 daily limit value (50 µg/m³) in 2011 and 2022 at different measurement points in Maribor and surroundings. Green dots mean less or equal 35, red dots mean more than 35.

## Future

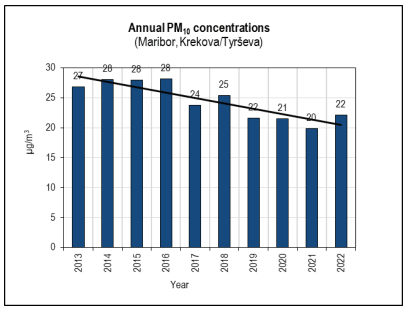
The European Commission has proposed stronger rules on ambient air quality. The proposed revision of the Ambient Air Quality Directives will set 'interim' 2030 EU air quality standards, aligned more closely with World Health Organization guidelines, while putting the EU on a trajectory to achieve zero pollution for air at the latest by 2050, in synergy with climate-neutrality efforts.

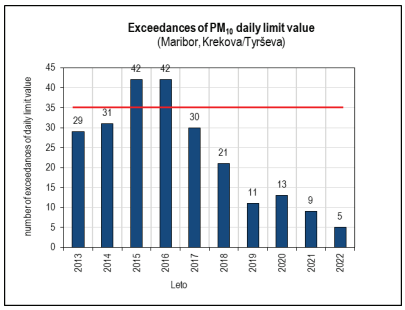
Tab. 1: Current and proposed (2030) EU air quality standards compared with WHO guidelines.

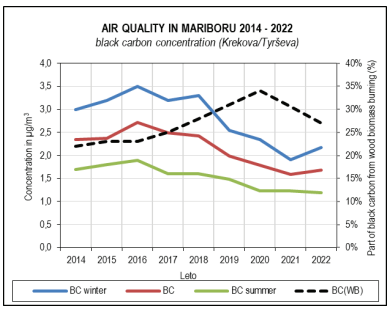
| Pollutant | Averaging time | EU current | EU 2030 | WHO 2005 | WHO 2021 |
|---|---|---|---|---|---|
| $PM_{10}$, µg/m³ | Annual | 40 | 20 | 20 | 15 |
| | 24 hour | 50 | 45 | 50 | 45 |

People suffering health damages from air pollution will have the right to be compensated in the case of a violation of EU air quality rules, and will have the right to be represented by non-governmental organization through collective actions for damage compensation. The new legislation will also support local authorities by strengthening the provisions on air quality monitoring, modeling, and improved air quality plans.

## Results




## Conclusion

The results show air quality improvement and the limit values for PM10 particles are no longer exceeded. It can be seen from the concentrations of black carbon that from 2014 to 2020 the share of black carbon from the burning of wood biomass increased, after 2020 this share began to decline. At the same time, the total concentrations of black carbon also decreased - in Center the roads have been closed and the traffic by the measuring site changed (increased).

Acknowledgement
The project " The interregional effect of ambient air protective measures concerning traffic and wood combustion related PM background levels in the border region Slovenia-Austria - PMinter " has been partly financed by the Operational Program Slovenia – Austria 2007-2013.

# RADON IN THE REPUBLIC OF CROATIA: AN OVERVIEW OF THE CURRENT STATE AND A NEED FOR AN ACCREDITED MEASUREMENT METHOD

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- Naturally occurring radioactive gas that is produced by the radioactive decay of radium ($^{226}Ra$) within the uranium ($^{238}U$) decay chain
- Its largest concentrations are usually found in the ground floor and in cellars, as well as in other places which are in a direct contact with soil
- Significant affect on air quality, especially in closed spaces

Exposure to high radon concent rations is, after smoking, the second most frequent cause of lung cancer. Hence elevated concentrations of radon in air may affect the air quality and have adverse effects on human health

- It was decided by Euratom Directive by the European Commission that the activity concentration in dwellings and workplaces should not exceed **300** $Bqm^{-3}$.
- The first systematic measurements of radon activity concentrations in households was carried out in 2003-2005, using 6000 detectors in 8 counties. It has been found that the activity concentrations were in the range 10-1600 $Bqm^{-3}$, that is, there are microlocations within some counties where the activity concentration exceeds the reference level several times.
- The current problem in the RC is the absence of a laboratory accredited for long-term measurements of radon concentrations.

- The **Institute for Medical Research and Occupational Health** (IMROH) is accredited according to the **HRN EN ISO/IEC 17025** standard, which permits measurements by means of high-resolution gamma-ray spectrometry for exposures of up to 3 days
- This is currently being supplemented by the method of measuring nuclear traces according to **ISO 11665-4** (Measurement of radioactivity in the environment — Air: radon-222 — Part 4: **Integrated measurement method for determining average activity concentration using passive sampling and delayed analysis**).

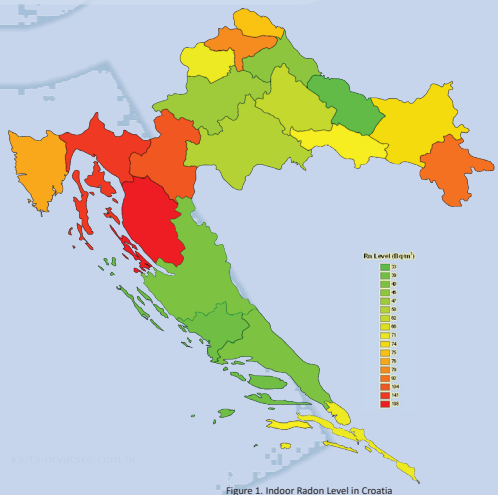


Figure 1. Indoor Radon Level in Croatia

Figure 2. RadoSys- Radon measurement system

Solid-state nuclear trace detectors are exposed for 1 to 3 months

# Fate of polycyclic aromatic hydrocarbons in indoor and outdoor environment: prediction of benzo[a]pyrene and benzo[b]fluoranthene levels


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Among **polycyclic aromatic hydrocarbons (PAHs)**, benzo[a]pyrene (B[a]P) has been recognized as a marker of carcinogenic potency of the air pollutant mixture, but environmental behavior of other individual health-relevant PAHs, as benzo[b]fluoranthene (B[b]F) are of scientific interest, as well. People spend more than 80% of their time indoors which results in elevated exposure to poor air quality. Indoor air quality depends on outdoor pollutants intrusion, emission from building materials, cooking, heating, individual activities. Advanced **machine learning (ML)** and **explainable artificial intelligence (XAI)** methodologies **(eXtreme Gradient Boosting – XGBoost and SHapley Additive exPlanations –SHAP)** were present for studying complex, heterogeneous, and non-linear interactions between indoor and outdoor B[a]P, B[b]F levels and $PM_{2.5}$, PAHs, inorganic gaseous pollutants, trace elements, ions, radon, 31 meteorological parameters, the number of people in the amphitheater, and the time they spent indoor. XGBoost, SHAP attribution method, and SHAP value fuzzy clustering applied to identify and characterize governing environmental conditions responsible for shaping pollutant levels. SHAP, an additive feature attribution method, provides a post-hoc explanation of the XGBoost model. For the purpose of source apportionment, the Unmix receptor model was applied.

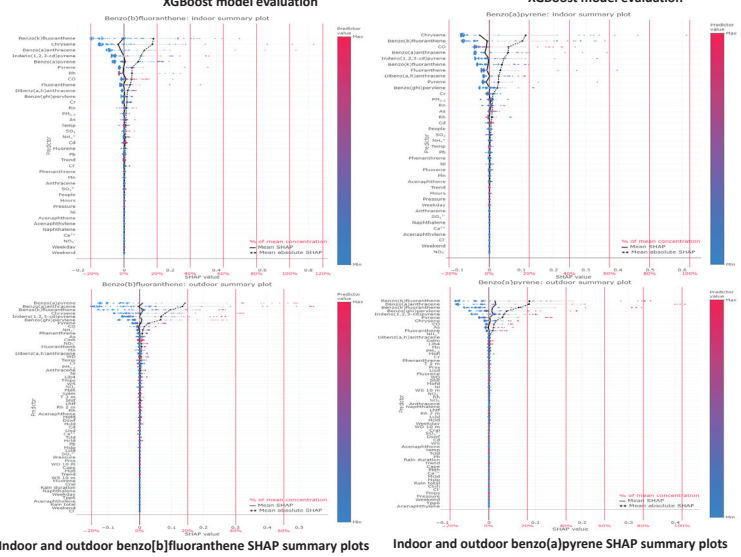
The **measurements** (inorganic gaseous pollutants, radon, $PM_{2.5}$ and particle constituents including metals (As, Cd, Cr, Mn, Ni, and Pb), ions ($Cl^-$, $Na^+$, $Mg^{2+}$, $Ca^{2+}$, $K^+$, $NO_3^-$, $SO_4^{2-}$, and $NH_4^+$) and 16 US EPA PAH were performed from March 1st – May 31st (N=74) simultaneously at indoor and outdoor sampling sites in a building of Singidunum University (44◦45'33.8'' N, 20◦29'47.6'' E), situated in the urban area of Belgrade, Serbia.
**PM2.5:** European Standard EN 12341:2014.
**Ion concentration measurements**: Dionex DX500 IC System, MDL 064 Standard operating procedure; **As, Cd, Cr, Ni, and Pb as $PM_{2.5}$ constituents**: European Standards (EN) 14902:2005; ICP-MS (Agilent 7500ce with Octopole Reaction System); **PAHs:** naphthalene (Nap), acenaphthylene (Ace), acenaphthene (Ane), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benz[a]anthracene (B[a]A), chrysene (Chy), benzo[b]fluoranthene (B[b]F), benzo[k]fluoranthene (B[k]F), benzo[a]pyrene (B[a]P), dibenz[a,h]anthracene (Db[ah]A), benzo[g,h,i]perylene (B[ghi]P), and indeno[1,2,3-cd]pyrene (In[cd]P): SRPS ISO 12884:2010 Standard (Ambient air —Determination of total (gas and particle-phase) polycyclic aromatic hydrocarbons — Collection on sorbent-backed filters with gas chromatographic/mass spectrometric analyses, 2010)
**Inorganic gaseous pollutants:** Horiba 370 series devices (APMA, APSA, APNA, APOA) European Standards EN 14211:2012, EN 14212:2012, EN 14625:2012 and EN 14626:2012; **radon**-SN1029 radon monitor.
**Meteorological data:** Vaisala weather station (Weather Transmitter WXT530 Series), GDAS1

**Descriptive statistics**
*Abbreviations: standard deviation (SD), limit of detection (LOD)
** prefix: i – indoor, o – outdoor

| Variable | Mean | SD | Median | Min | Max | LOD |
|---|---|---|---|---|---|---|
| iAcenaphthylene [ng m-3] | 0.015 | 0.022 | 0.005 | 0.005 | 0.120 | 0.01 |
| oAcenaphthylene [ng m-3] | 0.020 | 0.038 | 0.005 | 0.005 | 0.262 | 0.01 |
| iAcenaphthene [ng m-3] | 0.025 | 0.039 | 0.005 | 0.005 | 0.232 | 0.01 |
| oAcenaphthene [ng m-3] | 0.015 | 0.020 | 0.005 | 0.005 | 0.086 | 0.01 |
| iAnthracene [ng m-3] | 0.029 | 0.043 | 0.010 | 0.005 | 0.286 | 0.01 |
| oAnthracene [ng m-3] | 0.033 | 0.034 | 0.023 | 0.005 | 0.141 | 0.01 |
| iAs [ng m-3] | 0.705 | 0.396 | 0.659 | 0.200 | 1.865 | 0.4 |
| oAs [ng m-3] | 0.863 | 0.527 | 0.696 | 0.200 | 3.187 | 0.4 |
| iBenzo(a)anthracene [ng m-3] | 0.326 | 0.901 | 0.093 | 0.020 | 7.249 | 0.01 |
| oBenzo(a)anthracene [ng m-3] | 0.359 | 0.534 | 0.164 | 0.028 | 2.419 | 0.01 |
| iBenzo(a)pyrene [ng m-3] | 0.504 | 0.918 | 0.220 | 0.033 | 6.844 | 0.01 |
| oBenzo(a)pyrene [ng m-3] | 0.484 | 0.606 | 0.302 | 0.040 | 2.869 | 0.01 |
| iBenzo(b)fluoranthene [ng m-3] | 0.699 | 1.040 | 0.331 | 0.084 | 7.106 | 0.01 |
| oBenzo(b)fluoranthene [ng m-3] | 0.888 | 0.892 | 0.592 | 0.104 | 3.842 | 0.01 |
| iBenzo(ghi)perylene [ng m-3] | 0.571 | 0.727 | 0.347 | 0.005 | 4.896 | 0.01 |
| oBenzo(ghi)perylene [ng m-3] | 0.680 | 0.639 | 0.471 | 0.025 | 2.702 | 0.01 |
| iBenzo(k)fluoranthene [ng m-3] | 0.595 | 0.927 | 0.293 | 0.061 | 6.472 | 0.01 |
| oBenzo(k)fluoranthene [ng m-3] | 0.737 | 0.759 | 0.479 | 0.074 | 3.395 | 0.01 |
| iCa2+ [µg m-3] | 14.073 | 19.278 | 4.000 | 4.000 | 71.580 | 8 |
| oCa2+ [µg m-3] | 13.773 | 17.502 | 4.000 | 4.000 | 82.931 | 8 |
| oCape [J kg-1] | 51.783 | 82.647 | 12.956 | 0 | 376.429 | / |
| iCd [ng m-3] | 0.206 | 0.094 | 0.223 | 0.025 | 0.370 | 0.05 |
| oCd [ng m-3] | 0.236 | 0.118 | 0.236 | 0.025 | 0.610 | 0.05 |
| iChrysene [ng m-3] | 0.527 | 1.214 | 0.214 | 0.021 | 9.406 | 0.01 |
| oChrysene [ng m-3] | 0.645 | 0.806 | 0.357 | 0.025 | 3.781 | 0.01 |
| oCinh [J kg-1] | -11.663 | 17.941 | -4.383 | -103.941 | 0 | / |
| iCl- [µg m-3] | 1.716 | 3.191 | 1.000 | 1.000 | 23.696 | 2 |
| oCl- [µg m-3] | 1.312 | 1.048 | 1.000 | 1.000 | 7.484 | 2 |
| iCO [mg m-3] | 0.300 | 0.089 | 0.277 | 0.163 | 0.552 | 0.1 |
| oCO [mg m-3] | 0.287 | 0.093 | 0.259 | 0.154 | 0.549 | 0.1 |
| oCrai | 0.318 | 0.342 | 0.250 | 0 | 1.000 | / |
| iCr [ng m-3] | 11.878 | 5.985 | 11.564 | 3.298 | 42.497 | 2 |
| oCr [ng m-3] | 11.518 | 6.309 | 10.554 | 3.148 | 43.886 | 2 |
| iDibenz[a,h]anthracene [ng m-3] | 0.083 | 0.092 | 0.049 | 0.010 | 0.459 | 0.01 |
| oDibenz[a,h]anthracene [ng m-3] | 0.097 | 0.095 | 0.076 | 0.010 | 0.526 | 0.01 |
| oDswf [W m-2] | 213.026 | 83.677 | 233.059 | 31.203 | 340.581 | / |
| iFluoranthene [ng m-3] | 0.278 | 0.318 | 0.186 | 0.005 | 1.590 | 0.01 |
| oFluoranthene [ng m-3] | 0.303 | 0.289 | 0.200 | 0.005 | 1.339 | 0.01 |
| iFluorene [ng m-3] | 0.047 | 0.087 | 0.005 | 0.005 | 0.483 | 0.01 |
| oFluorene [ng m-3] | 0.044 | 0.090 | 0.005 | 0.005 | 0.565 | 0.01 |
| oHcld [%] | 44.152 | 30.992 | 44.324 | 0 | 97.779 | / |
| iHours [h] | 4.050 | 3.328 | 5.075 | 0 | 9.917 | 0.02 |
| iIndeno(1,2,3-cd)pyrene [ng m-3] | 0.468 | 0.579 | 0.266 | 0.030 | 3.600 | 0.01 |
| oIndeno(1,2,3-cd)pyrene [ng m-3] | 0.544 | 0.533 | 0.378 | 0.011 | 2.287 | 0.01 |
| oLcld [%] | 29.195 | 29.453 | 20.919 | 0 | 95.328 | / |
| oLhtf [W m-2] | 78.533 | 37.242 | 76.203 | 13.514 | 165.274 | / |
| oLibd [K] | 3.491 | 3.261 | 2.958 | -2.279 | 10.531 | / |
| oLisd K] | 278.311 | 3.819 | 278.185 | 271.856 | 286.141 | / |
| oMcld [%] | 30.270 | 28.819 | 21.181 | 0 | 92.883 | / |
| iMn [ng m-3] | 3.415 | 2.021 | 3.043 | 1.000 | 11.816 | 2 |
| oMn [ng m-3] | 3.525 | 1.479 | 3.102 | 1.000 | 9.188 | 2 |
| oMofd [°] | 159.516 | 102.558 | 146.173 | 1.458 | 360.091 | / |
| oMofi [N m-2] | 0.100 | 0.081 | 0.080 | 0.007 | 0.392 | / |
| oMslp [hPa] | 1012.724 | 5.565 | 1013.741 | 1000.900 | 1023.753 | / |
| iNaphthalene [ng m-3] | 0.028 | 0.043 | 0.005 | 0.005 | 0.224 | 0.01 |
| oNaphthalene [ng m-3] | 0.041 | 0.090 | 0.005 | 0.005 | 0.644 | 0.01 |
| iNH4+ [µg m-3] | 1.513 | 1.319 | 1.213 | 0.100 | 7.277 | 0.2 |
| oNH4+ [µg m-3] | 2.486 | 2.311 | 1.955 | 0.100 | 12.042 | 0.2 |
| iNi [ng m-3] | 7.926 | 8.198 | 5.118 | 1.000 | 45.963 | 2 |
| oNi [ng m-3] | 7.951 | 5.867 | 6.455 | 1.000 | 31.617 | 2 |
| iNO3- [µg m-3] | 1.279 | 1.198 | 1.000 | 1.000 | 10.142 | 2 |
| oNO3- [µg m-3] | 4.423 | 3.898 | 3.325 | 1.000 | 16.987 | 2 |
| iPb [ng m-3] | 4.079 | 2.924 | 3.621 | 1.000 | 23.951 | 2 |
| oPblh [m] | 512.239 | 152.702 | 517.356 | 194.949 | 1070.878 | / |
| oPb [ng m-3] | 4.605 | 2.796 | 4.145 | 1.000 | 22.494 | 2 |
| iPeople | 185.973 | 208.428 | 167.500 | 0 | 1226.000 | 1 |
| iPhenanthrene [ng m-3] | 0.166 | 0.266 | 0.083 | 0.005 | 1.478 | 0.01 |
| oPhenanthrene [ng m-3] | 0.170 | 0.226 | 0.116 | 0.005 | 1.215 | 0.01 |
| iPressure [mbar] | 992.676 | 5.536 | 993.555 | 980.996 | 1003.425 | 1 |
| iPM1 [µg m-3] | 16.196 | 7.340 | 14.729 | 4.182 | 45.266 | 1 |
| iPM2.5 [µg m-3] | 17.469 | 8.003 | 15.862 | 5.785 | 50.718 | 1 |
| oPressure [mbar] | 992.732 | 5.548 | 993.813 | 981.037 | 1003.086 | 1 |
| oPrss [hPa] | 988.226 | 5.417 | 989.418 | 976.491 | 998.371 | / |
| iPyrene [ng m-3] | 0.320 | 0.396 | 0.193 | 0.010 | 2.451 | 0.01 |
| oPyrene [ng m-3] | 0.338 | 0.313 | 0.216 | 0.011 | 1.426 | 0.01 |
| oRain duration [h] | 1.536 | 2.707 | 0.025 | 0 | 12.233 | 0.02 |
| oRain total [h] | 181.989 | 394.929 | 0.200 | 0 | 1897.600 | 0.02 |
| oRh 2 m [%] | 67.950 | 13.061 | 70.443 | 42.081 | 89.196 | / |
| iRh [%] | 36.783 | 7.795 | 36.081 | 20.200 | 56.985 | 0.1 |
| oRh [%] | 61.534 | 15.717 | 59.228 | 31.208 | 89.668 | 0.1 |
| iRn Bq m-3] | 74.525 | 24.616 | 67.884 | 40.802 | 141.425 | 0.1 |
| oShif [W m-2] | 25.551 | 19.374 | 26.026 | -23.071 | 80.690 | / |
| iSO2 [µg m-3] | 1.849 | 1.453 | 1.204 | 0.573 | 6.913 | 1 |
| oSO2 [µg m-3] | 3.155 | 2.638 | 2.269 | 0.590 | 12.225 | 1 |
| iSO4 2- [µg m-3] | 5.319 | 3.961 | 4.466 | 0.500 | 19.170 | 1 |
| oSO4 2- [µg m-3] | 7.051 | 4.498 | 6.594 | 0.500 | 23.972 | 1 |
| oSolm [frac.] | 0.299 | 0.017 | 0.299 | 0.260 | 0.330 | / |
| oT 2 m [°C] | 12.766 | 4.421 | 13.353 | 4.220 | 20.853 | / |
| oTcld [%] | 58.645 | 31.046 | 67.126 | 1.370 | 99.905 | / |
| iTemp [°C] | 23.407 | 1.525 | 23.371 | 20.290 | 27.921 | 0.1 |
| oTmps [°C] | 13.020 | 4.231 | 13.439 | 5.015 | 20.795 | / |
| oTemp [°C] | 13.843 | 4.953 | 14.148 | 4.785 | 22.977 | 0.1 |
| oTpp6 [m] | 0 | 0.001 | 0 | 0 | 0.003 | / |
| oWD 10 m [°] | 210.976 | 60.974 | 208.671 | 88.849 | 325.800 | / |
| oWD [°] | 220.327 | 74.935 | 225.833 | 23.289 | 359.233 | 1 |
| oWS 10 m [m s-1] | 3.136 | 1.103 | 2.963 | 1.550 | 6.111 | / |
| oWS [m s-1] | 1.467 | 0.478 | 1.328 | 0.730 | 2.759 | 0.1 |

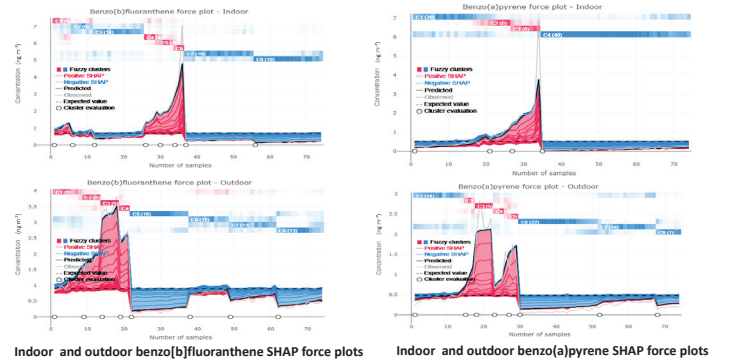

XGBoost model evaluation

XGBoost model evaluation




Indoor and outdoor benzo[b]fluoranthene SHAP summary plots

Indoor and outdoor benzo(a)pyrene SHAP summary plots




Indoor and outdoor benzo[b]fluoranthene SHAP force plots

Indoor and outdoor benzo(a)pyrene SHAP force plots


Details in:
1) S. Stanišić, M. Perišić, G. Jovanović, T. Milićević, S. Herceg Romanić, A. Jovanović, A. Šoštarić, V. Udovičić, A. Stojić. The PM2.5-bound polycyclic aromatic hydrocarbon behavior in indoor and outdoor environments, part I: Emission sources. Environmental Research 193 (2021) 110520.
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3) S.Stanišić, G.Jovanović, M.Perišić, S.Herceg Romanić, T.Milićević, A.Stojić. Explaining the Environmental Fate of PAHs in Indoor and Outdoor Environments by the Use of Artificial Intelligence. Polycyclic Aromatic Hydrocarbons: Sources, Exposure and Health Effects Warren L. Gregoire (Editor) Nova Science Publishers, Inc., 2022. ISBN: 978-1-68507-626-9.

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**The correlation showed relationships between 5- and 6-ring high molecular weight PAHs and CO. Unmix resolved four source profiles for both the indoor and outdoor environments. The major contributor to PAH emission was combustion of low-calorie lignite of poor quality and high moisture content. The PAHs associated with B[a]P specific behavior and fate were Chry and B[b]F as main factors, followed by B[a]A, I[cd]P, B[k]F, Fla, D[ah]A, Pyr, and B[ghi]P. Less important associations were attributed to CO, As, Cr, $PM_{2.5}$, and soil moisture. Dominantly related with B[b]F were B[a]P, B[k]F, B[ghi]P, I[cd]P, D[ah]A, Chry, B[a]A, Fla and Pyr; and minor: CO, Rn, As, Cr, $SO_4^{2-}$, $NH_4^+$ and $NO_3^-$, indicating aerosol formation and oxidative degradation.**

# EVALUATION OF GENOTOXICITY BIOMARKERS BASED ON THE EXPOSURE TO AIR POLLUTANTS IN COLDER AND WARMER PERIODS IN GENERAL POPULATION IN ZAGREB (Croatia)

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"AIR PROTECTION 2023"

International Conference and 13th Croatian Scientific and Professional Meeting, 19-23 September 2023, Dubrovnik, Croatia

The growing demand for energy, the use of fossil fuels, the increase in traffic, as well as the increase in industrial production greatly contribute to air pollution in cities. It affects the environment and human health. The air in urban areas is a complex and variable mixture of various chemical compounds whose mechanism of action is not fully understood.

Human biomonitoring provides very important information about environmental exposure and helps identify potential health risks. The aim of this study was to evaluate the alkaline comet assay descriptor (% of tail DNA) and the frequency of micronuclei (MNi) in the human population living in Zagreb (Croatia) and relate them to air quality measurements.

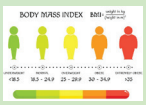
**Zagreb, Croatia 2021/2022**

Cold season

Warm season

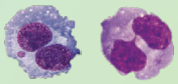
60 persons
age: 36±7 years


**BMI < 30 kg/m²**




**Whole blood**

**Cytome MN assay**



Microphotographs of binucleated lymphocyte with a micronucleus, and binucleated lymphocyte with nucleoplasmic bridge.

**Alkaline comet assay (% DNA)**

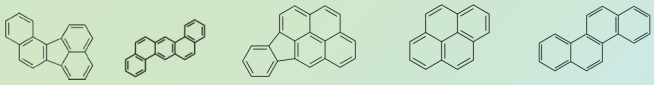
Cell with undetectable degree of DNA fragmentation, resulting in the cellular, DNA remaining in nucleus.

The comet of damaged cell. Tail represents DNA migrating out of the nucleus due to the fragmentation and loss of structure.

**BTEX**
**Benzo[a]pyrene**

**Outdoor air pollution**

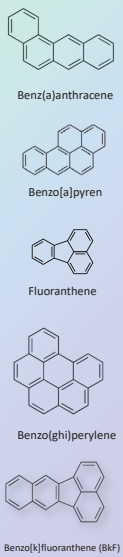
**Air quality data**



Benzo(j)fluoranthene | Dibenz(a,h)anthracene | Indeno(1,2,3-cd)pyrene | Pyrene | Chrysene

| | COLD SEASON | WARM SEASON | |
|---|---|---|---|
| | Observed outdoor air pollution parameters | Observed outdoor air pollution parameters | Regulatory limits / Reference limits |
| $O_3$ | 20.57 [μg/m³] | 65.82 [μg/m³] | 120 [μg/m³] (max.) |
| Benzo[a]pyren BaP * | **2.57 [ng/m³]** | 0.14 [ng/m³] | 1 [ng/m³] (an.avr.) |
| $PM_{10}$ | 31.33 [μg/m³] | 16.45 [μg/m³] | 40 [μg/m³] (an.avr.) |
| $NO_2$ | 17.61 [μg/m³] | 12.00 [μg/m³] | 40 [μg/m³] (an.avr.) |
| o-Xylene | 1.93 [μg/m³] | 0.73 [μg/m³] | 200 [mg/m³] (max.) |
| Toluene | 8.11 [μg/m³] | 0.70 [μg/m³] | 200 [μg/m³] (max.) |
| Benzene | 2.11 [μg/m³] | 0.94 [μg/m³] | 5 [μg/m³] (an.avr.) |
| Ethylbenzene | 0.64 [μg/m³] | 0.81 [μg/m³] | 2 [μg/m³] (an.avr.) |
| % Tail DNA | 1.22 % | 1.78 % | < 11 % |
| MNi | 4.42 | 4.86 | < 13 |
| NBs | 4.45 | 4.46 | - |
| NPBs | 0.32 | 0.06 | - |

*for PAHs there are no regulatory values except for BaP which is a known group 1 carcinogen, instead values for $PM_{10}$ particles have been added



Benz(a)anthracene | Benzo[a]pyren | Fluoranthene | Benzo(ghi)perylene | Benzo[k]fluoranthene (BkF)

## CONCLUSIONS

Results for alkaline comet assay and MN frequencies were in agreement with our previous results for the general population.

All measured outdoor air pollution parameters were bellow the regulatory limit except for **benzo[a]pyrene bound to PM10 particle fraction** (particles with an aerodynamic diameter less than 10 μm), which exceeded the regulatory annual limit level.

*Supported by the Croatian Science Foundation (HUMNap and Young researchers career development project -training of doctoral student KM)*

# Atmospheric deposition of nitrogen and phosphorus to the Central Adriatic area and biogeochemical implications

Andrea Milinković[1], Abra Penezić[1], Valentina Gluščić[2], Silva Žužul[2], Ranka Godec[2], Gordana Pehnec[2], Sanja Frka[1]

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

## Introduction:

The atmosphere is not only a significant, but in some cases the dominant pathway by which natural and anthropogenic material is transported from the continents to the coastal areas and open seas [1, 2]. Once deposited through dry and wet processing, atmospheric particles provide the aqueous ecosystems with an external source of macronutrients (N and P) [3]. This, in turn, influences the quality and quantity of organic matter produced by the phytoplankton within the photic zone, changes $CO_2$ uptake and indirectly affects the climate. The input of atmospheric deposition (AD) can be of particular importance in oligotrophic regions such as the Mediterranean Sea which continuously receives anthropogenic aerosols from European regions. The impacts of human activities, including open-field biomass burning (BB) from wildfires and agricultural practices, are thought to be stronger in the Mediterranean Sea than in any other sea in the world. The effect of the AD inputs to oligotrophic surface waters of Adriatic Sea is generally unknown.

In order to assess the impact of atmospheric deposition of nutrient salts on the change of biological and chemical properties of the sea surface of the oligotrophic coastal area, a field campaign was conducted from February to July 2019 at the coastal zone of the Šibenik archipelago in the central part of the north-east coast of the Adriatic Sea.

## Experimental:


**Fig. 1a. Sampling site**

- 07 February–10 July 2019
- coastal oligotrophic zone
- extensive tourism and mariculture; low industrial activities; high to very high fire risks

**b. $PM_{10}$ samples**

- collected for 48h
- low-volume automatic sampler
- 77 samples total
- $PM_{10}$ mass
- $NH_4^+$, $NO_3^-$, $PO_4^{3-}$

**c. Rainwater samples**

- automatic wet-only collector
- 10 samples total
- $NH_4^+$, $NO_3^-$, $PO_4^{3-}$

- **Meteorological parameters:** temperature, pressure, relative humidity, wind velocity and direction
- **Methods:** gravimetry ($PM_{10}$ mass), ion chromatography ($NH_4^+$, $NO_3^-$, $PO_4^{3-}$ concentrations)
- **Dry flux ($F_d$) calculations:** $F_d = C_d \times V_d$

  $C_d$ - $PM_{10}$ concentrations
  $V_d$ - deposition velocity

  $V_d(NO_3^-) = 1.2$ cm s$^{-1}$
  $V_d(NH_4^+) = 0.6$ cm s$^{-1}$
  $V_d(PO_4^{3-}) = 2.0$ cm s$^{-1}$

## Results:

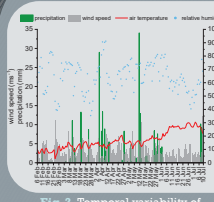


**Fig. 2.** Temporal variability of meteorological parameters during the studied period.

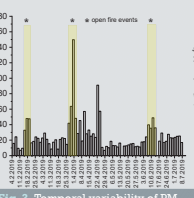


**Fig. 3.** Temporal variability of $PM_{10}$ mass concentrations. Periods with intensive regional open fires are marked in yellow (*).

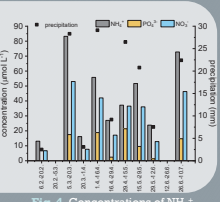


**Fig. 4.** Concentrations of $NH_4^+$, $NO_3^-$ and $PO_4^{3-}$ in rainwater samples. Black squares show the 2-week average precipitation levels.

**Table 2.** Mean dry, wet, and total inorganic N and P deposition fluxes (μmol m$^{-2}$ d$^{-1}$), and the contribution of each species deposition to respective total inorganic N and P deposition (in brackets). DIN = $NH_4^+$ + $NO_3^-$.

| | Dry deposition | Wet deposition | Total deposition |
|---|---|---|---|
| $NH_4^+$ | 17.08±15.07 (13%) | 58.97±33.39 (41%) | 65.33± (54%) |
| $NO_3^-$ | 25.44±18.94 (19%) | 39.68±23.35 (27%) | 57.91± (46%) |
| $PO_4^{3-}$ | 1.43±0.32 (88%) | 0.19±0.11 (12%) | 1.51± 0.28 |
| DIN | 42.53±32.48 (32%) | 98.65±56.19 (68%) | 123.24±53.21 |
| DIN/$PO_4^{3-}$ | 29.4±21.1 | 647.5±213.4 | 80.2±31.6 |

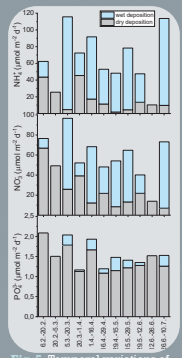


**Fig. 5.** Temporal variations of dry and wet deposition fluxes for $NH_4^+$, $NO_3^-$ and $PO_4^{3-}$.

**Table 1.** Distribution of average (median) $PO_4^{3-}$, $NO_3^-$ and $NH_4^+$ concentrations (nmol m$^{-3}$) in aerosol samples as a function of month, season and special biomass burning (BB) events collected at the central Adriatic coastal site.

| Overall | February – July 2019 | | | | | |
|---|---|---|---|---|---|---|
| $PO_4^{3-}$ | 0.8 ± 0.5 (0.9) | | | | | |
| $NO_3^-$ | 24.3 ± 42.5 (10.2) | | | | | |
| $NH_4^+$ | 32.5 ± 84.7 (14.7) | | | | | |
| DIN/$PO_4^{3-}$ | 81.4±137.2 (46.0) | | | | | |
| **Month** | **February** | **March** | **April** | **May** | **June** | **July** |
| $PO_4^{3-}$ | 1.1±1.1 (0.9) | 0.9±0.4 (0.9) | 0.8±0.4 (0.9) | 0.6±0.3 (0.8) | 0.8±0.2 (0.9) | 0.9±0.1 (0.9) |
| $NO_3^-$ | 61.5±92.0 (13.8) | 29.9±28.3 (17.0) | 15.1±11.8 (13.8) | 9.8±5.5 (7.6) | 16.8±17.2 (7.4) | 7.1 ± 1.6 (7.2) |
| $NH_4^+$ | 76.1±109.8 (22.3) | 40.7±53.9 (16.9) | 26.6±24.3 (24.8) | 6.2±6.1 (3.8) | 26.0±14.0 (24.6) | 14.1±13.8 (10.2) |
| DIN/$PO_4^{3-}$ | 186.1±217.1 (46.9) | 132.7±216.0 (52.8) | 63.9±49.8 (50.7) | 28.1±15.0 (23.5) | 54.6±24.3 (48.7) | 24.5±15.0 (20.5) |
| **Seasonal background** | **Winter (Feb-Mar)** | | **Spring (Apr-May)** | | **Summer (Jun-Jul)** | |
| $PO_4^{3-}$ | 1.0 ± 0.9 (0.9) | | 0.7 ± 0.3 (0.8) | | 0.8 ± 0.2 (0.9) | |
| $NO_3^-$ | 20.2 ± 18.9 (11.5) | | 12.4 ± 9.8 (8.2) | | 6.7 ± 1.8 (6.1) | |
| $NH_4^+$ | 25.7 ± 30.9 (16.9) | | 15.8 ± 20.1 (5.4) | | 24.6 ± 15.8 (27.5) | |
| DIN/$PO_4^{3-}$ | 68.8 ± 96.2 (45.7) | | 43.0 ± 34.6 (33.7) | | 42.1 ± 21.7 (46.0) | |
| **BB events** | **BB winter** | | **BB spring** | | **BB summer** | |
| $PO_4^{3-}$ | 0.91 ± 0.01 (0.9) | | 0.4 ± 0.0 (0.4) | | 0.88 ± 0.03 (0.9) | |
| $NO_3^-$ | 204.3 ± 73.7 (231.7) | | 61.8 ± 67.6 (61.5) | | 35.2 ± 17.1 (30.2) | |
| $NH_4^+$ | 280.0 ± 72.7 (250.8) | | 114.1 ± 96.3 (114.1) | | 20.2 ± 11.1 (18.1) | |
| DIN/$PO_4^{3-}$ | 497.2 ± 185.7 (538.2) | | 476.6 ± 444.6 (776.6) | | 63.1 ± 31.4 (51.5) | |

## Conclusions:

- Aerosol inorganic P levels were less likely to be affected by the open fire inputs than N species.
- The occasional but intensive open fire emissions dominantly changed the $NH_4^+$ and $NO_3^-$ ratio and their contribution to DIN, as well as the DIN/$PO_4^{3-}$ ratio of aerosols at the central Adriatic area.
- $NH_4^+$ is a more important N species supplied by the wet deposition at the coastal central Adriatic area.
- Soluble nutrients are efficiently washed out with the rain .
- Wet deposition may particularly play an important role in the supply of atmospheric inorganic N to the central Adriatic area.
- Dry deposition has an important role for the $PO_4^{3-}$ loss processing at the central Adriatic coastal area.
- Open fire events could significantly enhance already imbalanced atmospheric N and P deposition at the central Adriatic coastal area.
- Inorganic N and P deposited from the atmosphere to the central Adriatic coastal area can support up to 8% of new primary production (impact of open fire events - up to 12 % of new primary production

## References:

[1] A. Milinković, A. Penezić, et al. *Sci. Tot. Environ.* **838** (2022) 156440, 14.
[2] K. R. M. Mackey, K. N. Buck, J. R. Casey, A. Cid, M. W. Lomas, Y. Sohrin, *Front. Microbiol.* **3** (2012a) 359.
[3] C. Ridame, C. Guieu, S. l'Helguen, *Biogeosciences* **10** (2013) 7333–7346.

## Acknowledgments:

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# MONTHLY ACTIVITY CONCENTRATIONS OF $^{7}$Be IN THE AIR OF ZAGREB

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## INTRODUCTION

One of the most important gamma emitters in the air is cosmogenic $^{7}$Be, which is produced in the upper Earth's atmosphere as a result of interactions between cosmic rays and airborne atoms. It has a relatively short half-life of 53.3 days. Being naturally occurring, $^{7}$Be is always present in the air and is regularly monitored because changes in its concentration might signal unusual disturbances in the atmosphere.

## METHOD

Samples were collected by pumping the air through Petiran filters (FPP-15-1.5) positioned 1.5 m above the ground and connected to an ASS-500 HVS (high volume sampler) pump. High-resolution gamma-ray spectrometry is used to determine activity concentrations of anthropogenic and naturally occurring radionuclides, which are either of terrestrial or cosmogenic origin.
Gamma-ray spectrometry system used in this research is based on a GAMMA-X HPGe ORTEC detector with a resolution of 2.2 keV and a relative efficiency of 74%, all at 1.33. MeV $^{60}$Co, coupled with an electronic system and a computer.

## THE RESULTS

Monthly values of the activity concentration of airborne $^{7}$Be in Zagreb in 2022 averaged at 3.81 mBq/m$^{3}$. The maximum was recorded in May (5.79 mBq/m$^{3}$) and minimum values were measured in December (1.54 mBq/m$^{3}$).

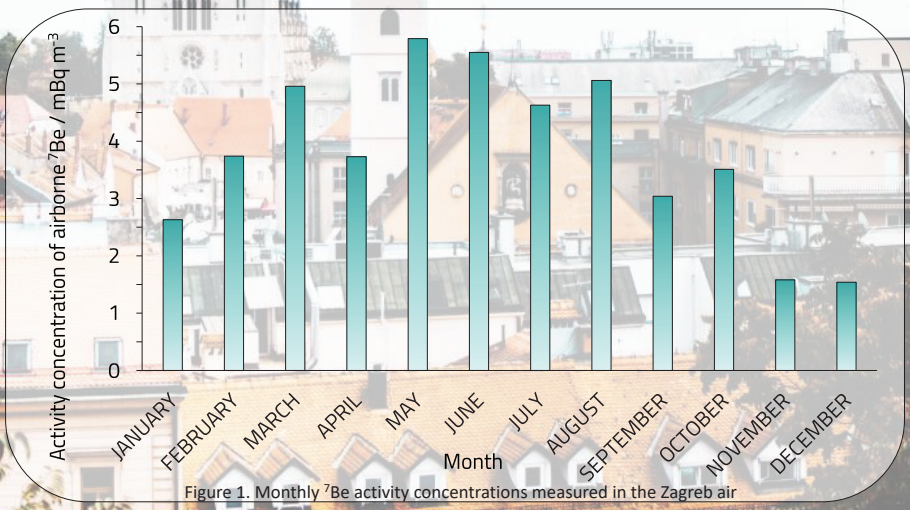


Figure 1. Monthly $^{7}$Be activity concentrations measured in the Zagreb air

## CONCLUSION

According to UNSCEAR 2000, the average value for troposphere is 12.5 mBq/m$^{3}$, which exceeds the values measured in Zagreb.

*International Conference and 13th Croatian Scientific-Professional Assembly*
*Dubrovnik, Croatia, 20 - 23 September, 2023.*

# Photochemistry of marine lipids at the air-water interface: Abiotic production of volatile organic compounds and new particle formation

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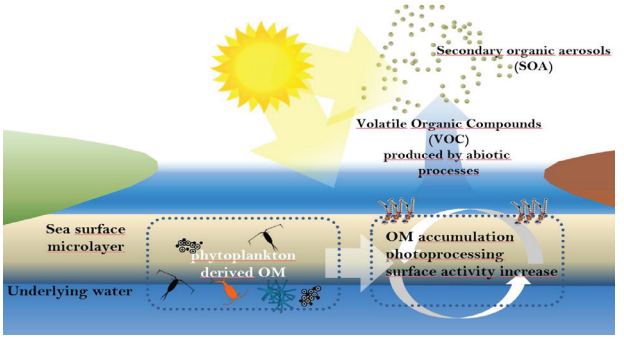
## INTRODUCTION

Abiotic production and the global relevance of volatile organic compounds (VOCs) from marine sources still hold a high level of uncertainty related to secondary organic aerosol (SOA) formation. Especially relevant is the understanding of the abiotic processes at the atmosphere-ocean interface, which covers > 70% of the Earth's surface. Naturally-occurring surface-active organic material (OM) accumulates at the air-water interface and forms surface films. This work presents an investigation of photochemical VOCs production at the air-water interface containing organic material (OM), incuding its lipid fraction, from authentic culture of marine diatom *Chaetoceros pseudocurvisetus*, as well as their potential for the aerosol particle formation and growth. Arial




## SAMPLES PREPARATION

**Marine diatom *Chaetoceros pseudocurvisetus*** was cultivated in a medium with lowered nitrogen content relevant oligotrophic waters representing 60% of the global ocean. Growth was terminated at the onset of stationary phase.

Three samples were prepared:

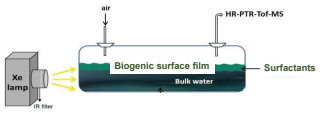
**TS** –original, non-filtered phytoplankton solution

**DS** - phytoplankton dissolved organic matter sample

**LS** – lipid material extracted from the dissolved sample.

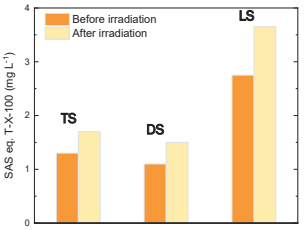
All samples contained only non-living material, and direct biological mechanisms can be assumed to have no effect on the VOCs production.

## PHOTOCHEMICAL REACTOR EXPERIMENTS




Samples were irradiated with a Xenon lamp mimicking solar irradiation on the Earth's surface.

The VOCs were quantified by PTR-ToF-MS




Quantification of **surface active substances (SAS)** before and after irradiation by alternating current voltammetry

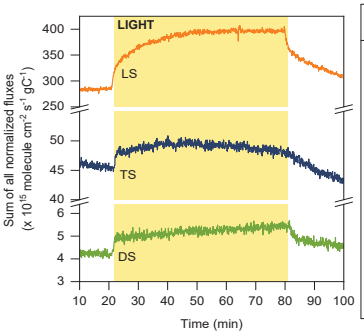
The observed **increase in surface activity upon irradiation** indicates OM (photo)transformation.

## VOCs FLUXES FROM PHYTOPLANKTON DERIVED OM

Rapid release of saturated oxygenated VOCs, such as aldehydes and ketones, as well as unsaturated and functionalized VOCs (e.g., alkenes, dienes, unsaturated aldehydes or ketones) was detected following irradiation of different phytoplankton culture samples.

**LS** sample showed the highest normalized VOC flux, implying that **biogenic lipid material** at the air-water interface is primarily responsible for the photochemical reactions leading to the production of VOCs from diatom OM during irradiation.

### NORMALIZED VOC FLUXES




### DETECTED VOC COMPOUNDS

| Assigned molecular formula | TS | DS | LS | Assigned molecular formula | TS | DS | LS |
|---|---|---|---|---|---|---|---|
| | pptv | | | | ppbv | | |
| CH2O | – | – | 0.3 | C4H8 | – | 0.9 | 5.8 |
| CH2O2 | – | – | – | C4H8O | – | – | 0.9 |
| CH3NO | – | – | – | C5H10 | 0.3 | – | 1.9 |
| CH4O | – | – | 2.4 | C5H10O | – | – | 0.8 |
| C2H2O | – | – | 1.7 | C5H8 | 0.7 | 0.3 | 1.0 |
| C2H3N | – | – | – | C5H8O | 0.4 | – | 1.6 |
| C2H3O | – | – | – | C5H8O2 | 0.3 | – | – |
| C2H4O | 5.1 | 7.1 | 8.4 | C6H8 | 0.6 | – | 0.5 |
| C2H4O2 | – | – | 1.1 | C6H10 | 0.4 | – | 0.6 |
| C2H5NO | – | – | 2.1 | C6H12 | – | – | 1.4 |
| C2H6O2 | – | – | 0.2 | C6H8O | – | – | 0.1 |
| C3H4 | 1.0 | 0.6 | 2.2 | C6H10O | 0.4 | – | 0.5 |
| C3H4O | – | – | 0.4 | C6H12O | – | – | 0.3 |
| C3H4O2 | – | – | 0.2 | C7H12 | – | – | 0.6 |
| C3H6 | 1.7 | 0.9 | 4.3 | C7H8O | 0.2 | – | – |
| C3H6O | 125.9 | – | 60.9 | C7H10O | – | – | 0.1 |
| C3H6O2 | – | – | – | C8H14 | – | – | 0.4 |
| C3H7N | – | – | 0.4 | C8H14O | – | – | 0.2 |
| C4H4O3 | – | – | – | C9H16O | – | – | 0.5 |
| C4H6 | 0.7 | – | – | C10H16 | – | – | 0.3 |
| C4H6O | 0.3 | – | 0.5 | C10H14O | 0.2 | – | – |
| C4H6O2 | – | – | 0.2 | C10H18O | – | – | 0.5 |

## ATMOSPHERIC SIMULATION CHAMBER - PARTICLE PRODUCTION BY OZONOLYSIS

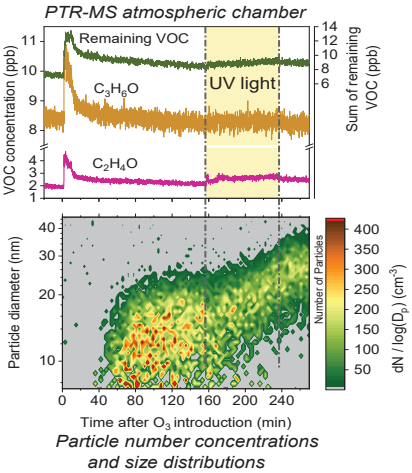
**LS** sample exhibited the highest concentration and number of produced VOCs, which lead to further investigation of the impact of biogenic lipids on the atmosphere's oxidation potential, aerosol particle formation and growth.

**LS** sample was irradiated within the photochemical reactor cell for a period of **48 h**, during which the **produced VOCs were directly introduced into a dark atmospheric simulation chamber**.

Following introduction of ozone, a sharp increase of several VOCs was observed, most pronounced for **C2H4O** and **C3H6O**, attributable to acetaldehyde and acetone, respectively, likely due to ozonolysis of organic unsaturated compounds.

Significant particle formation was observed within approximately 40 min after a maximum $O_3$ concentration of cca 300 ppb was reached. After an initial growth phase when small sized particles with diameter around **10 nm** were observed, larger particles began to form reaching average diameters of around 25 nm.

The UV light, used to study SOA aging, facilitated the oxidation of the yet unreacted VOCs as well as further low-volatile compound formations, which condensed on the already existing particles, causing particles to increase in size.




*Particle number concentrations and size distributions*

## CONCLUSIONS

- For the first time, photochemical processing at the air-water interface containing organic material from marine diatom *Chaetoceros pseudocurvisetus* was studied.
- Irradiation caused an increase of surface activity of OM facilitating accumulation of the transformed OM at the air-water interface
- Particulate material from the dead cells may play a role in facilitating the accumulation of biogenic surfactants at the air-water interface.
- Biogenic lipids are primarily responsible for the photochemical reactions leading to the production of VOCs from diatom OM exposed to irradiation.
- The emitted VOCs can significantly affect the oxidation potential of the atmosphere and promote the aerosol formation and growth
- Marine lipids are natural surfactants ubiquitous at air-water interfaces, such as on rivers, lakes, oceans, aerosols, and cloud droplets, and photo-induced abiotic VOCs production can be expected to occur globally, influencing ocean-atmosphere exchange processes

This research was financed by the European Union's Horizon 2020 research and innovation programme - EUROCHAMP-2020 Infrastructure Activity under grant agreement No 730997, COGITO project and Croatian Science Foundation project BiREADI IP-2018-01-3105.

# $^{137}$Cs IN THE ZAGREB AIR IN 2022

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## INTRODUCTION

The Radiation Protection Unit of the Institute for Medical Research and Occupational Health has been monitoring and analysing airborne radioactive matter since 1962, which has been carried out as part of the monitoring or environmental radioactivity in the Republic of Croatia. In the wake of the Chernobyl disaster, a significant amount of anthropogenic $^{137}$Cs leaked out into the environment, which has called for monthly checks of its presence in the air.

## METHOD

Air is sampled by pumping it through Petiran filters (FPP-15-1.5) positioned 1.5 m above the ground and connected to an ASS-500 HVS (high volume sampler) pump. These samples are subsequently analysed by means of a high-resolution gamma-ray spectrometry. The used gamma-ray spectrometry system is based on a GAMMA-X HPGe ORTEC detector with a resolution of 2.2 keV and a relative efficiency of 74%, all at 1.33. MeV $^{60}$Co, coupled with an electronic system and a computer.

## THE RESULTS

We show monthly values of the activity concentration of airborne $^{137}$Cs in Zagreb in 2022. They averaged at 0.57 Bq/m$^3$, whereas the maximum and minimum values were recorded in December (1.32 Bq/m$^3$) and August (0.23 Bq/m$^3$), respectively.

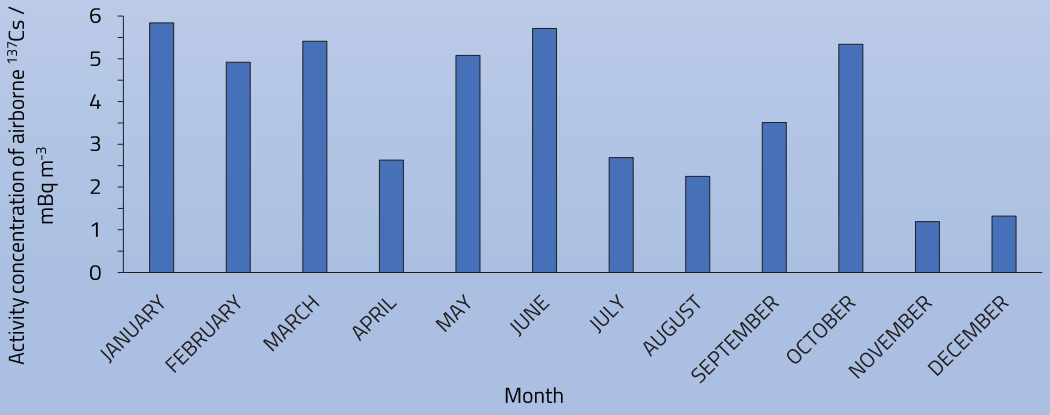


Figure 1. Monthly $^{137}$Cs activity concentrations measured in the Zagreb air

## CONCLUSION

Besides $^{137}$Cs, we have also monitored $^{134}$Cs, a radionuclide that is produced only in nuclear reactors. No $^{134}$Cs was found in the air during 2022, which implied that there were no accidents in nuclear power plants during this year.

*International Conference and 13th Croatian Scientific-Professional Assembly*
*Dubrovnik, Croatia, 20 - 23 September, 2023.*

# SAMPLING AND QUALITATIVE DETERMINATION OF ASBESTOS IN SOLID MATERIALS (AIR QUALITY ISO 22262-1:)

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Institute for Medical Research and Occupational Health
Ksaverska c. 2, Zagreb, Croatia,
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**In the past, asbestos was used in a wide range of products. Three types of asbestos have found wide commercial use. Chrysotile was used in construction and industry for fire protection, heat insulation and sound insulation, in asbestos-cement products, as well as in woven, spun, felt and paper products.**
**Amosite and crocidolite account for almost all remaining asbestos use. Amosite was used as fire protection and in thermal insulation products. Crocidolite was used as fire protection and in thermal insulation and chemical insulation products, and was particularly important for the production of high-pressure asbestos-cement pipes for the delivery of potable water.**

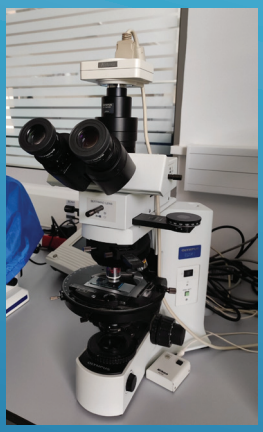
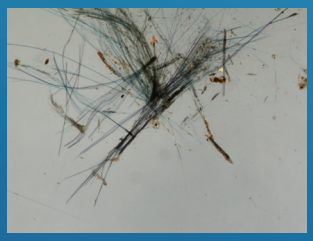


Figure 1. Olympus/Evident polarized light microscope



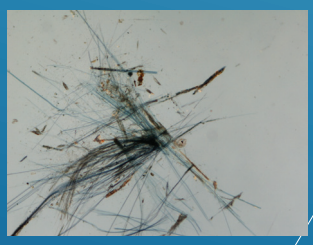


Figure 2. Chrysotile asbestos under bright field polarized light microscopy

Figure 2. Chrysotile asbestos under dark field polarized light microscopy

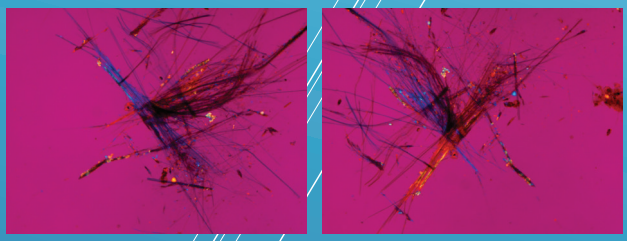


Figure 3. Chrysotile asbestos under gypsum retardation plate polarized light microscopy

**Materials containing anthophyllite are rare, but are also used as a filler and reinforcing fiber in composite materials, and as a filter media. Tremolite asbestos and actinolite asbestos have not been used commercially to any great extent. Other minerals may also occur as asbestos. For example, richterite asbestos and winchite asbestos occur in mass fractions between 0.1% and 6% associated with vermiculite, which was formerly mined in Libby, Montana, USA. Vermiculite from this source was widely distributed and is often found as loose insulation and as an integral part of a range of building materials and fire protection materials.The mass fraction of asbestos in products can be from 100% to 0.1%. The standard specifies the procedures for collecting samples and qualitative analysis of solid materials for the presence of asbestos. The primary method used to identify asbestos is polarized light microscopy (PLM). Although the norm specifies the possibility of visual assessment of the mass fraction of asbestos within very wide ranges, the accuracy and repeatability of such an assessment is very limited. The need to quantify asbestos in the material depends on the maximum mass fraction that defines the material containing asbestos. The definition of asbestos material goes from "any asbestos" to 0.1%, 0.5% or 1%.**

# *TRADESCANTIA ANDERSONIANA*: A NEW PLANT SPECIES FOR *IN SITU* BIOMONITORING OF AIR QUALITY

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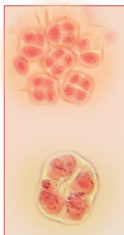
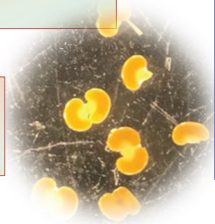
The *Tradescantia* micronucleus assay is the most widely used bioassay to detect genotoxins in the environment. Several species of the genus *Tradescantia* can be used but here we wanted to compare two species of plants belonging to the genus, in particular, *Tradescantia clone #4430*, and *Tradescantia andersoniana* which has never been used before for these types of studies. In the first part of this work, we wanted to better understand the interspecies differences in the spontaneous mutation rate and the reaction of a single species to two known mutagens. In the second part of this work, we used these two species to conduct an *in situ* biomonitoring study in the area of Borgo Val di Taro, Italy, to assess the air quality.

## MATERIALS AND METHODS



TRAD-MCN assay: after treatment with known mutagens, cuttings were subjected to a 24h recovery time to allow the formation of MN in tetrads. Following recovery, inflorescences were fixed in Carnoy solution for 24h and after that, they were stored in 70% ethanol until the time of slide preparation. To prepare slides, inflorescences were dissected with the aid of a surgical probe under a stereo microscope in order to isolate flower buds. After that, buds were arranged on the glass slide and dissected to expose the anthers. Anthers were crushed and then, two or three drops of acetocarmine (2%) were added and in the end a coverslip were placed on the top of the preparation.

Cytogenetic analysis to estimate the number of micronuclei is performed under an optical microscope (400X), must include counting 300 tetrads per slide and five slides must be prepared from individual inflorescences for each exposure, thus scoring 1,500 tetrads per treatment.



*Tradescantia andersoniana*

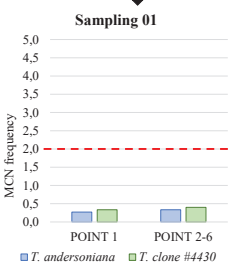
*Tradescantia clone #4430*

## SECOND PART RESULTS

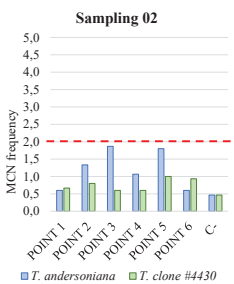

During May, June and July 2022 *T. andersoniana* and *T. clone #4430* were used as bioindicators to investigate the quality of air in Borgo Val di Taro, Italy. Plants were distributed in six different points in the city in supports at 2 meters above the ground.

**T. Andersoniana was never used before for an *in situ* study!**

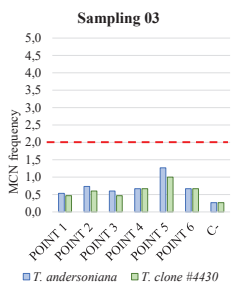
The first sampling was conducted on plants maintained in a greenhouse to assess the spontaneous frequency of micronuclei.




20 days

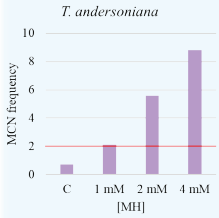


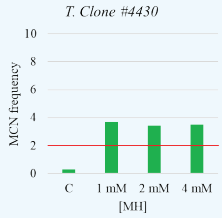

30 days

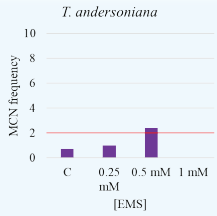


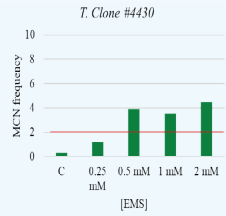

## FIRST PART RESULTS

In the case of maleic hydrazide (MH), we noted an increase in micronuclei directly proportional to the increase in mutagen concentration in both plants.



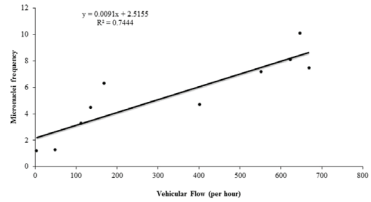




In the case of ethyl methane sulfonate (EMS), we noted a toxic effect and inhibition of tetrads production at 1 mM for *T. andersioniana* and a decrease production of tetrads at 2 mM for *T. clone #4430*.

It was seen, in a previous study, a direct correlation between vehicular flow and miconuclei frequency in Tradescantia.




The two *Tradescantia* species have a comparable micronuclei frequency, always below 2 micronuclei per 100 tetrads analysed (MCN/100 tetrads), as can be seen from the analysis carried out on plants at the time of the planting of the first sample. The analysis of the inflorescences carried out in successive samples of the same plants has allowed to highlight a lack of induction of genotoxic events. Although small variations in the number of micronuclei are observed, they remain within a biological variability of the spontaneous frequency of mutation.

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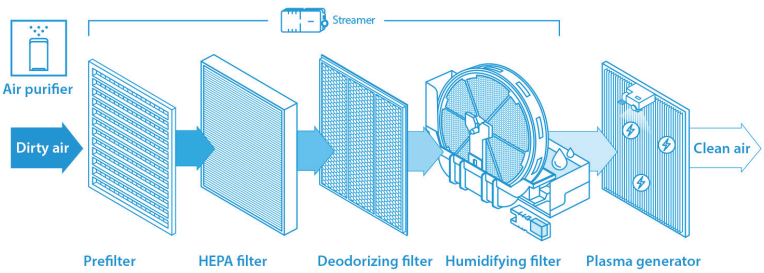


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| $SO_2$ | PM-2.5 | rh | *rain |
| NO | PM-10 | p | *noise |
| $NO_2$ | | | *EMF |
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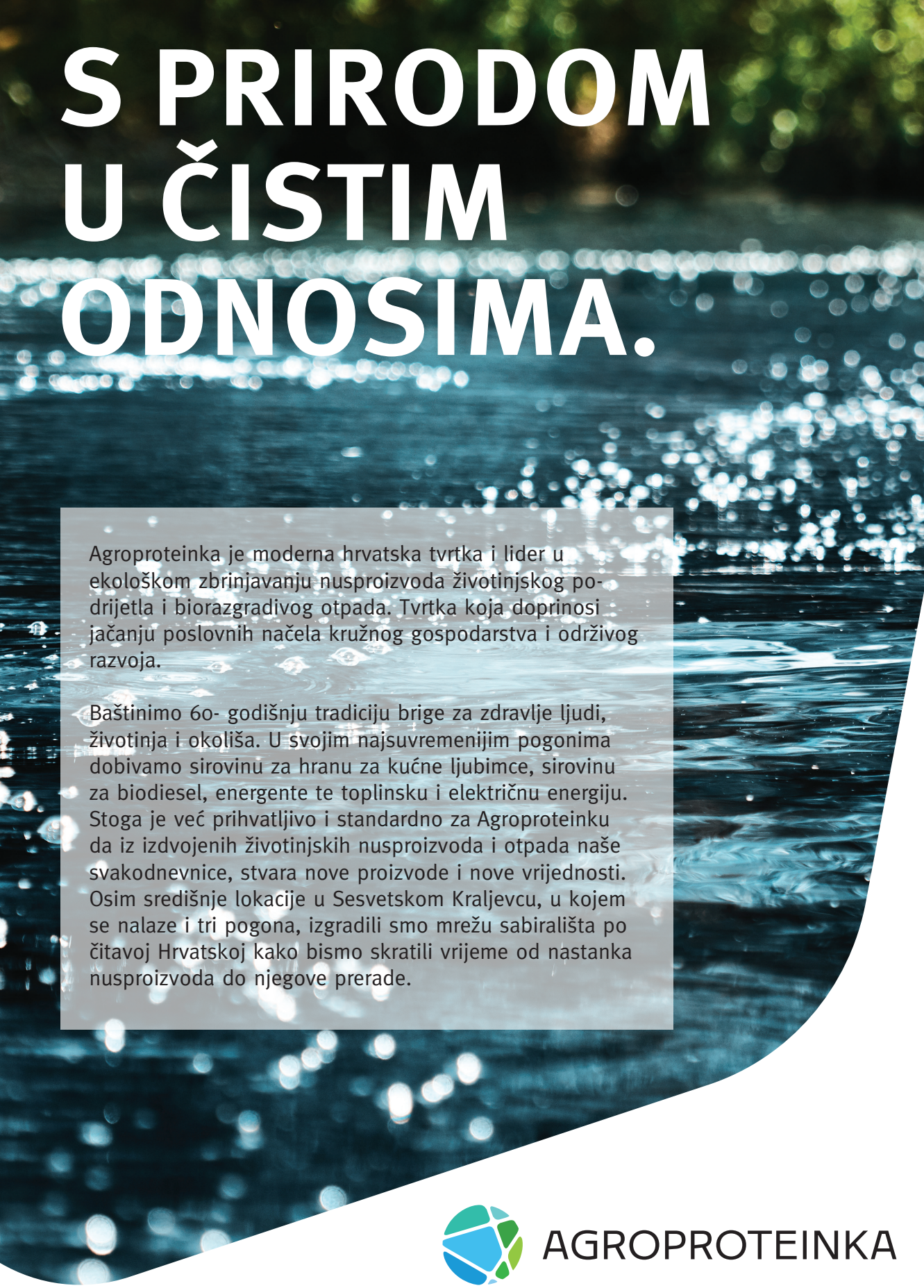

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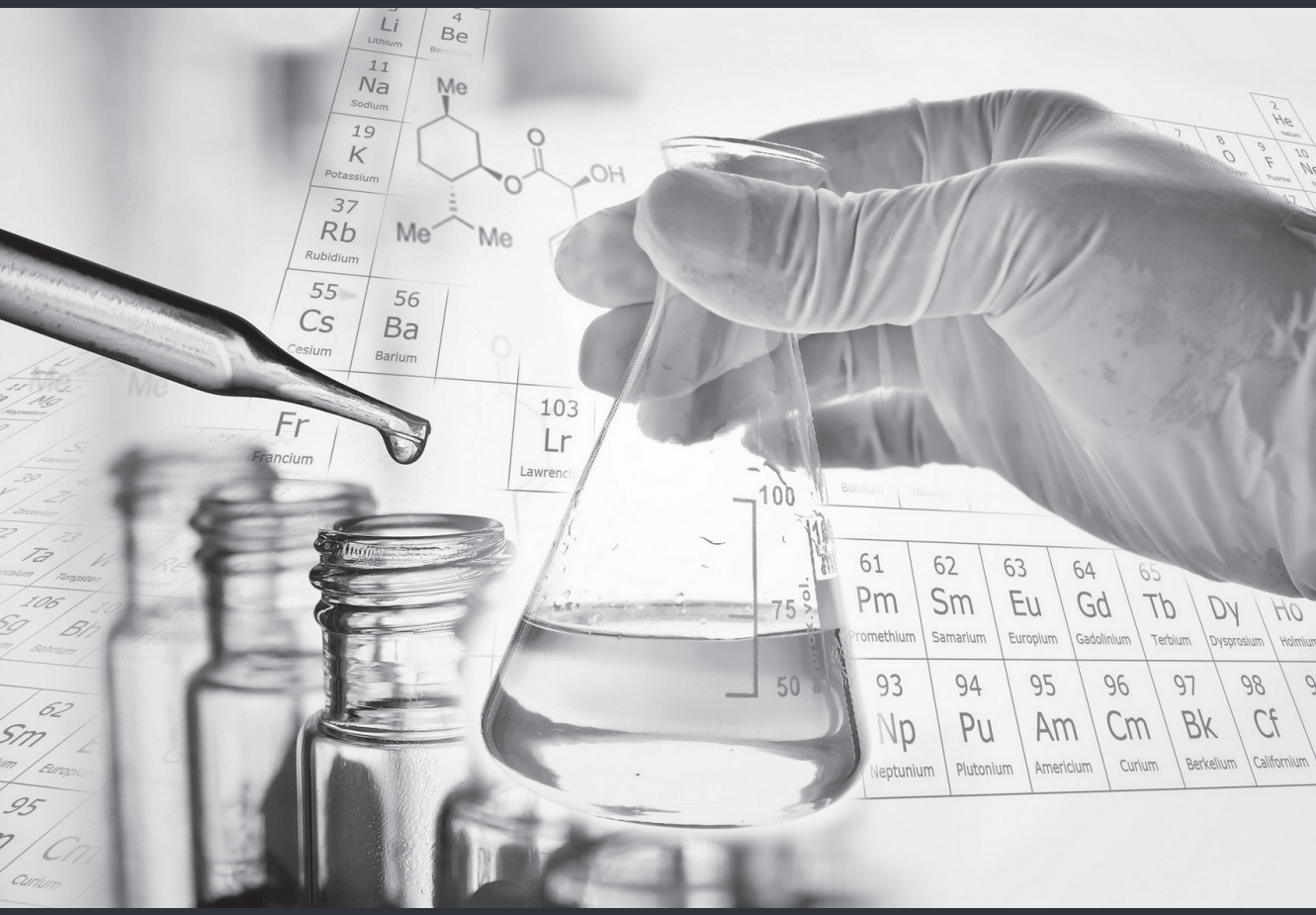


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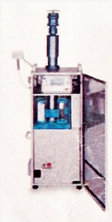

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