WeBIOPATR2017

THE SIXTH INTERNATIONAL WeBIOPATR WORKSHOP & CONFERENCE PARTICULATE MATTER: RESEARCH AND MANAGEMENT

ABSTRACTS OF KEYNOTE INVITED LECTURES AND CONTRIBUTED PAPERS

Editors Milena Jovašević-Stojanović and Alena Bartoňová

Public Health Institute of Belgrade

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The Sixth International WeBIOPATR Workshop & Conference Particulate Matter: Research and Management WeBIOPATR2017

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Editors Milena Jovašević-Stojanović Alena Bartoňová

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- sources and formation of particulate matter
- particulate matter composition and levels outdoors and indoors
- *environmental modeling*
- nanoparticles in the environment
- *exposure to particulate matter*
- health aspects of atmospheric particulate matter
- *full chain approach*

PARTICULATE MATTER AND REGULATORY ISSUES

- issues related to monitoring of particulate matter
- legislative aspects
- abatement strategies

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Ministry of Education, Science and Technological Development of Republic of Serbia

PREFACE

The International Workshop and Conference, Particulate Matter: Research and Management – WeBIOPATR is a biennial event held in Serbia since 2007. The conference addresses air quality in general and particulate matter specifically. Particulate matter, arising both from primary emissions and as a result of secondary formation in the atmosphere, is one of the least well understood local and regional air pollution issues, and at the same time, it is perhaps the one with the highest health relevance, and with many challenges in monitoring.

The 1st WeBIOPATR Workshop was held in Beograd, 20.-22. May 2007, associated with a project funded from the Research Council of Norway. The workshop was attended by more than 70 participants presenting 35 contributions, and received wide multi-media attention. This event has started the efforts to create a sustainable platform for knowledge exchange within the research community and between the research community and the responsible authorities (Ministry of Health, Ministry of Environment, and the Serbian Environmental Agency).

The 2nd WeBIOPATR workshop was held in Mecavnik, Serbia, 28.8.-1.9. 2009. The 40 participants discussed air quality issues, research needs and management tools, and strategies currently used in Serbia. For the first time, the workshop had a section on health issues related to particulate matter. Proceedings are available at http://www.nilu.no/index.cfm?ac=publications&folder_id=4309&publication_id=24659&view=rep. Selected extended contributions are published in CHEMICAL INDUSTRY & CHEMICAL ENGINEERING QUARTERLY Vol: 16 No 3 (2010).

WeBIOPATR2011 was held in Beograd 14.-17- November 2011. We included own student workshop. Forty three presentations were given (for book of abstracts see <u>http://www.vin.bg.ac.rs/webiopatr/3rd-workshop/</u>). Selected extended contributions are published in CHEMICAL INDUSTRY & CHEMICAL ENGINEERING Vol 18, No 4/II (2012).

WeBIOPATR2013 was held in Beograd 2.-4. October 2013. It covered the traditional PM research and management issues as well as topics that aim to encourage citizens to contribute to environmental governance. Ways to provide the citizens and authorities with a range of tools and services related to the environment including PMs, and developing participatory sensing methods and tools utilizing smaller and less expensive monitoring devices and advanced ITC technologies, were one of the foci. The book of abstracts can be downloaded at http://www.vin.bg.ac.rs/webiopatr/4th-workshop/. Selected extended contributions were published in CHEMICAL INDUSTRY & CHEMICAL ENGINEERING Vol 20, No 3/II (2014).

WeBIOPATR2015 workshop and conference was held in Belgrade 14th to 16th October, 2015, with 41 oral contributions and 18 posters. Own sessions were devoted to sensor technologies for air quality monitoring, utilizing information and input from the EU FP7 funded CITI-SENSE (<u>http://co.citi-sense.eu</u>) and the EU COST action EuNetAir (www.eunetair.it). The proceedings are available at <u>http://www.vin.bg.ac.rs/webiopatr/5th-workshop/#News</u>.

We have now the pleasure to welcome you to the 6th conference. We are excited to welcome old friends and new acquaintances, and we are pleased that more of our West Balkan colleagues are able to support us this time with their contributions and presence. We are hoping that their support will extend to the future, as the problems we face require a strong scientific community and commitment of all societal actors. We are grateful also to our unrelenting sponsors for their support.

Milena Jovašević-Stojanović and Alena Bartoňová

CONTENTS

1	PM C	OMPOSITION AND MODELING I 11
	1.1 and Gl	Black Carbon Measurements: Methodology, Sources, and Relevance on a Local, Regional obal Scale
	1.2 Vicinit	Source Analysis of Particule- Associated Polycyclic Aromatic Hydrocarbons (PAHs) in the y of a Steelmaking Industry Smederevo, Serbia
	1.3 Factori	Source Apportionment Study near Cooper Smelter Complex in Serbia Using Positive Matrix ization
	1.4	Spatial Distribution of Carbon Mass Concentrations in Croatia 15
	1.5 Serbia	Characterization of Suspended Particles in the University Classrooms and Offices in Bor, 16
2	ADVA	NCES IN PM CHARACTERIZATION I 17
	2.1	Electroanalytical Methods in Aerosols Particulate Matter Characterization
	2.2 Chrom	Determination of Low Molecular Weight Organic Acids in Atmospheric Aerosols by Ion atography
	2.3	Polycyclic Aromatic Hydrocarbons: The Importance of (Bio)Monitorization 20
	2.4 Polluti	Leaves Of Common Urban Tree Species as a Measure of Particle and Particle-Bound on: a Four-Year Study
	2.5	Node-to-Node Field Calibration of Wireless Distributed Air Pollution Sensor Network 22
3	HEAL	TH EFFECTS I
	3.1	Health Impacts of Air Pollution in Serbia
	3.2 Popula	Comparative Analysis of Air Pollution and the Incidence of Diseases in the Exposed tion in Serbia
	3.3	Exposure to Biomass Fuel Smoke and Use of Primary Health Care in Women
	3.4 Source	Cytotoxic and Genotoxic Effects of Combustion-Derived Particles from Different Emission s
4	SCIEN	NCE, POLICY & EDUCATION
	4.1 Policie	The Activities of WHO Regional Office for Europe in Supporting the Development of and Interventions in Improving Air Quality Related to PM
	4.2	Urban Particulate Matter: Technologies for Assessment and Need for Information
	4.3	A Dusty Road to Gardaland - An Insight into the School Science Project
5.	PM C	OMPOSITION AND MODELING II
	5.1	Atmospheric Mineral Dust as the Most Abundant Aerosol: Modelling and Impacts
	5.2 Northv	Analysis of Regional Atmospheric Conditions Associated with Higher Ozone Days in vest Anatolia of Turkey

	5.3	A Study Of a Dust Intrusion Event Over Belgrade, Serbia	36
	5.4 PM10	Relative Importance of Gaseous Pollutants and Aerosol Constituents for Identification Of sources of Variability	37
6.	POST	ER SESSION	39
	6.1	Multiscale Multifractal Analysis of Nonlinearity in Particulate Matter Time Series	40
	6.2	Modeling of PM10 Dispersion From Coal Thermal Power Plants Kostolac A and B	41
	6.3	PM ₁₀ and PM _{2.5} Emission During the Process of Preparing the Material for TIG Welding	42
	6.4 Biomo	Convergence Chromatography as an Emerging Technique for Determination of PAHs in nitors	43
	6.5 Air Qu	Presentation of Current Atmospheric Particulate Matter Levels Within National Network for ality Monitoring in Serbia	or 44
	6.6 Numbe	A Candidate Measurement System for the Standardized Routine Monitoring of Particle er Concentration in Ambient Air	45
	6.7 Belgra	Preliminary Characterization of Carbonaceous Aerosols collected Close to a Busy Tunnel i de, Serbia	n 46
	6.8 Institut	Scope of Ambient Air PM10 Monitoring Within the Network of Local Public Health tions in Serbia	47
	6.9 Concer	Evaluation of the Traffic Density and Meteorological Conditions Influence on PM2.5 ntration Levels in Ambient Air on Highway E75	48
	6.10 Tempe	Impact of Street Level Traffic Emissions (CO2, CO, NOx, PM And VOC) on Outdoor rature and Thermal Comfort in Complex Urban Environment	49
7.	HEAL	TH EFFECTS II	51
	7.1 Overvi	Health Effects of Short- and Long-Term Exposure to Air Pollution in Denmark: An ew of Epidemiological methods and Major Findings	52
	7.2	Particulate matter in Nis, Serbia: Levels, Sources and Major Health Effects	53
	7.3	The Development of Who Airq+ Tool to Assess the Impacts of Air Pollution on Health	54
8.	PM C	OMPOSITION AND MODELING III	55
	8.1 Matter	Concentration Weighted Boundary Layer Hybrid Receptor Model for Analyzing Particulat Altitude Distribution	e 56
	8.2	Estimation of PM Emissions from Cruise Ships in Kotor Bay	57
	8.3 Paper 1	Practical Application of Short-Range Calpuff Modelling for PM _{2.5} Assessment from Pulp a Mill in Canada	nd 58
	8.4	Efficient Tools for Creation and Validation of LUR Based Maps	59
9.	EXPO	SURE TO TOXIC AND INFECTIVE PM AGENTS	61
	9.1	Procedure of Microbiological Quality Control of Air in Medical Laboratories	62
	9.2	Development of an Evidence Base for Respirator Selection for Bioaerosols	63
	9.3	Aerosol Transmission of Infective Agents: Possible Impacts	64
1	0. ADV	ANCES IN PM CHARACTERIZATION II	65

10.1	Development of Real-time Reactive Oxygen Species Monitors	56
10.2 Envir	Comparison of Low-Cost and Conventional PM Sizers and Counters in Indoor Ambient onment	57
10.3 Senso	Artificial Intelligence Models with Multivariate Inputs for Calibration of Low Cost PM	58
10.4 on Ba	Analysis of Particulate Matter and Small Ion Concentrations in Indoor Environment Based lance Equation	59
10.5 Pollut	Current Status of Applicability of Low-Cost Particulate Matter Sensors for Ambient Air tion and Exposure Assessment	70
AUTHO	DR INDEX	71

1. PM COMPOSITION AND MODELING I

1.1 BLACK CARBON MEASUREMENTS: METHODOLOGY, SOURCES, AND RELEVANCE ON A LOCAL, REGIONAL AND GLOBAL SCALE

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Aerosolized Black Carbon (BC) is the second most important climate forcing agent (Bond et al., 2013) and a good indicator of undesired health effects caused by air pollution (Janssen et al., 2012). It is a primary pollutant, well suited to describe the behavior of the sources of particulate air pollution and its abatement.

We present robust and widely used instruments – filter absorption photometers, Aethalometers, and measurements using these instruments (Drinovec et al., 2015). Filter loading effects and their use, including techniques to examine the data are discussed. The non-linearities are shown to depend on the coating on the BC. This information is useful to discriminate between the fresh and aged BC aerosols, which separates the local and regional (transported) contributions to BC concentrations.

BC source apportionment is presented (Sandradewi et al., 2008), separating the contributions from traffic from the ones of biomass (wood) burning. The results help to determine the sources which should be the focus of the abatement, and the same methodology can be used to measure the efficiency of the actions to reduce air pollution.

The effects of BC emissions are felt on local (Titos et al., 2015), regional (Titos et al., 2017; Drinovec et al., 2017) and global scale (Močnik et al., 2017). Measurements relevant for all three types of consequences are presented. We show, how aggressive measures can effectively improve local air quality, and that wood combustion is an important air pollutant, regionally more important than traffic. Global airborne measurements show how distributed small sources influence regional climate.

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1.2 SOURCE ANALYSIS OF PARTICULE- ASSOCIATED POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) IN THE VICINITY OF A STEELMAKING INDUSTRY SMEDEREVO, SERBIA

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Particle-associated polycyclic aromatic hydrocarbons (PAHs) concentration were analyzed ambient air in residential region of Smederevo city, site with strong influence of industrial activities of steelmaking industry located nearby. PM10 were analyzed for a total of 16 PAHs by Gas Chromatography with Mass Selective Detector. In period November 2016 – July 2017 the total of 185 PM samples were collected. Campaigns were performed in cold periods where officially heating is used (H), October 15th to April 15th (116 samples) and warm periods where heating is not required (NH), April 15th to July 15th (69 samples).

The total PAHs concentration in performed campaigns was 59.38 ng/m3 in heating and 5.77 ng/m3 in nonheating that is similar as during campaigns performed in period 2012-2014 at Smederevo. By diagnostic ratio analysis, traffic emission and combustion (coal or wood) were identified as potential sources for PAHs. Ratio of InP/(Bpe +Inp) and Baa/Chr was 0.46 during both season and 0.91 and 0.67 during winter and summer season, while Ant/(Ant+Phe) was 0.19 and 0.15, respectively. For coal combustion BaP/Chr ratio was above 0.5 (0.8 in NH and 1.25 in H season). Finally, Positive Matrix Factorization (PMF) receptor model was used to identify potential sources of PAHs and to determine their mass contribution to total PAHs concentration. Three potential groups of sources were identified: (1) traffic-diesel and gasoline exhaust, (2) stationary sources, (3) wood and coal combustion (wood and coal) 18.8 and 13.1% during nonheating and heating season, respectively. PMF results confirm the major sources were vehicle emission, steel industry emission, and coal combustion for both heating and non-heating seasons, which agreed with the results from the diagnostic ratio analysis.

Moreover, ambient PAH profiles were studied and high molecular weight PAH (including 4–6 rings) species occurred in the high fractions. Toxic equivalent factors analysis gave the potential carcinogenic risks in residential area of ambient air in Smederevo. Health risk assessment (BaPeq value) showed that the most negative impact was found in H season-9.52 ng/m³ while in NH it was 1.00 ng/m³.

The highest value for cancer risk we obtained in H (0.00083) due to the increase emission of PAHs in ambient air and the proximity of mining industrial complex. All values for the lifetime cancer risk were above target individual lifetime risk, which is 10^{-6} (US EPA, 2012).

Keywords: Particulate matter, Polycyclic aromatic hydrocarbons, Source apportionment, Diagnostic ratio, Toxic equivalent factor, Health risk assessment

1.3 SOURCE APPORTIONMENT STUDY NEAR COOPER SMELTER COMPLEX IN SERBIA USING POSITIVE MATRIX FACTORIZATION

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The positive matrix factorization (model EPA PMF 5.0) was used for source apportionment and characterization of the collected PM_{10} collected during the period from September 2009 to July 2010 in the vicinity of copper smelter in Bor, Eastern Serbia. Sampling site (kindergarten) is located downwind of the copper smelter and of the dumped tailing soils of mining activities and related manufactures.

The total of 104 samples of ambient PM_{10} particulate matter were analyzed for 23 chemical elements and ionic species by atomic emission spectrometry with inductively coupled plasma (ICP AES) and ion chromatography (IC), respectively.

According to the results of PMF modeling, a total of seven factors were identified during the heating season (HS), period when the smelter does not works (SNW) and when it works (SW), and six factors during the non-heating season (NHS).

The major contributor of PM_{10} at the urban-industrial site in Bor during the heating and non-heating season was industrial dust with contribution of 53.8% and 36.5% respectively. Industrial dust was also identified as major air pollution source during the period when the smelter works (38.0%) while the major contributor of PM_{10} during the period when the smelter does not work was dust from tailings (30.5%). Among those sources the prominent one is the fuel combustion source with contribution from 10.2% (SNW) to 33.0% (SW). Sources, storage and preparation of raw materials and secondary nitrate, were also identified during the all observation period. The smelter source was not identified only during the period when the smelter does not work. The contribution of this source is approximately 10%. The source named cadmium was isolated as separate source only during the period when the smelter does not work. One more independent source, marked as Gold drive, was identified during the period of campaign of processing anode slimes (GS and SNW).

Findings indicate that the influence of RTB complex on the air quality in urban area of Bor is evident. Nine different sources were identified, of which the contribution to the total mass of the PM_{10} particles of 83.1% related to the metallurgical activity at the very smelter (frying, melting), as well as the consequences caused by these activities (industrial dust). During the period when the smelter does not work the contribution to the total mass of the PM10 particles emitted from pollution from the RTB complex is 2.3-fold lower (35.8%) compared to the period when the smelter works.

Overall action plan preparation will need to concentrate on local sources as priority, as reduction of these source strengths will give maximum benefit in terms of lower exposure from air pollution.

1.4 SPATIAL DISTRIBUTION OF CARBON MASS CONCENTRATIONS IN CROATIA

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The purpose of this study was to determine distribution of carbon mass concentrations in different types of environments in Croatia and to observe if carbon mass contributions to the overall PM_{10} mass, as well as elemental and organic mass concentrations change with the seasons of the year. The sampling sites were located at four different parts of Croatia and they were defined as:

- site A urban background site characterised with domestic heating and moderate traffic,
- site B semirural industrial site burdened with pollution which originated from wood used as fuel for cooking and space heating, as well as from the local wood pellet industry,
- site C- rural site characterised with pollution which originated from wood used as fuel for cooking and space heating,
- site D rural background site characterised with pollution which originated from agriculture.

Samples of PM_{10} particle fraction were collected from approximately 55 m³ of ambient air on quartzfiber filters (Pall flex Tissuequartz 2500QAT UP, Pall Life Sciences), pre-fired at 900 °C for three hours. Sven Leckel LVS3 and Sven Leckel Sequential Sampler SEQ47/50 (Sven Leck Inginierbüro, Berlin, Germany) reference samplers were used for sample collection and PM_{10} mass concentrations were determined gravimetrically according to the HRN EN 12341 standard. Organic carbon (OC) and elemental carbon (EC) in PM_{10} fraction were determined by the thermal-optical transmittance method (TOT), using a Carbon Aerosol Analyzer (Sunset Laboratory Inc.) with a FID flame ionization detector following the NIOSH-like protocol called Quartz (Birch and Cary, 1996, described by Godec et al., 2012 and Godec et al., 2016).

Significance of difference among EC and OC mass concentration between different sampling sites was tested with analysis of variance at significance level of 0.05. In the cold part of the year (winter and spring), the OC mass concentrations determined at the site A were statistically significantly lower than the concentrations determined at the site B, C and D. At sites B and D, OC mass contribution to the overall PM_{10} mass were higher in the winter than in the summer period of measurement, while at site C, OC mass contribution to the overall PM_{10} mass at sites C and D were the same.

The mass concentrations of EC and OC in the PM_{10} particle fraction at the rural sites were statistically significantly higher in the cold part of the year (winter and spring) than the concentrations measured in the warmer part of the year (summer). EC and OC mass contribution to the overall PM_{10} mass were also higher during a colder than warmer period of measurements.

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1.5 CHARACTERIZATION OF SUSPENDED PARTICLES IN THE UNIVERSITY CLASSROOMS AND OFFICES IN BOR, SERBIA

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Indoor air quality in educational buildings is of great importance since children and students spend a large part of their time in classrooms. Unfortunately, there are almost no systematic monitoring programs dealing with the indoor air quality in educational buildings in the Republic of Serbia. This work present result of an ongoing study on student's and teacher's exposure to suspended particles in the selected classrooms and offices at the Technical Faculty in Bor. The town of Bor is situated in the south-eastern part of the Republic of Serbia, it is assumed as representative of hot spot urban-industrial environment in the country. The main source of air pollution is the copper smelter within the RTB Bor Company (Copper Mining and Smelting Complex Bor).

The faculty buildings are located about 1 km NW from the copper smelter facilities. The mass concentrations of particulate matter (TSP, PM_{10} and $PM_{2.5}$) were measured in the selected classrooms and offices with the real-time air particulate monitor Turnkey OSIRIS (Model 2315). Several sampling campaigns were conducted in the no heating (April-September) and heating seasons (October-March) in the time interval from 2011 to 2016. In all places of interest, the measurement of PM was conducted for a period of 14 days in each season. In the first week of measurements, Sven/Leckel low-volume samplers LVS3 were collocated with the OSIRIS monitor to collect the PM_{10} and $PM_{2.5}$ gravimetric samples.

The indoor average daily concentrations of suspended particles in the no heating season were within the ranges from 19.9 to 59.3 μ g/m³ for TSP, 12.9 to 39.6 μ g/m³ for PM₁₀, and 4.6 to 13.4 for PM_{2.5}. Similarly, the outdoor average daily concentrations of suspended particles in the no heating season were within the ranges from 50.3 to 98.2 μ g/m³ for TSP, 35.9 to 75.2 μ g/m³ for PM₁₀, and 18.5 to 36.7 for PM_{2.5}. The indoor average daily concentrations of suspended particles in the heating season were within the ranges from 20.8 to 41.3 μ g/m³ for TSP, 13.3 to 24.2 μ g/m³ for PM₁₀, and 5.2 to 11.8 for PM_{2.5}. Similarly, the outdoor average daily concentrations of suspended particles in the heating season were within the ranges from 33.8 to 77.9 μ g/m³ for TSP, 21.1 to 55.6 $\mu g/m^3$ for PM₁₀, and 10.4 to 32.7 for PM_{2.5}. The average I/O ratios in the no heating season were within the ranges from 0.33 to 0.70 for TSP, 0.32 to 0.61 for PM_{10} , and 0.20 to 0.40 for $PM_{2.5}$. Similarly, the average I/O ratios in the heating season were within the ranges from 0.33 to 0.90 for TSP, 0.28 to 0.87 for PM₁₀, and 0.18 to 0.86 for PM_{2.5}. The exceeding of the daily limit of PM₁₀ in the ambient air was observed in 17% of days in the heating season and in 40% of days in the no heating season. The exceeding of the daily limit of $PM_{2.5}$ in the ambient air was observed in 21% of days in the heating season and in 48% of days in the no heating season. In contrast to that, exceeding of daily limits of PM in the indoor air was observed in the very few cases (exceeding of PM_{10} in one office in 5% of days during the no heating period) in the studied period. The lowest PM concentrations in the indoor air were detected during non-working days (weekends).

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2. ADVANCES IN PM CHARACTERIZATION I

2.1 ELECTROANALYTICAL METHODS IN AEROSOLS PARTICULATE MATTER CHARACTERIZATION

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In this work simple, direct, and nondestructive electrochemical methods, that are developed in our group, were applied for rough and rapid characterization of dissolved organic matter (DOM) with surface active properties (SAS) (Frka et al., 2012) in water soluble particulate matter fractions of marine aerosols (PM_{2.5}), and indoor and outdoor school air environments (PM_{2.5}, PM₁₀). In parallel in some samples presence of sulphur species (RSS) that accumulate at the Hg electrode (Krznarić et al. 2001) were determined as well. Carbonaceous aerosol (organic carbon-OC, and elemental carbon-EC) makes up a large fraction of air particular matter. Therefore, electrochemistry measurements were combined with measurements of total and dissolved organic carbon (TOC, DOC) by high temperature catalytic oxidation (HTCO). Mass concentrations of indoor and outdoor PM fractions were measured with low volume sampler Sven/Leckel LVS3 with size-selective inlets for PM₁₀ and PM_{2.5} fractions (2.3 m³/h, sampling time: 24 h) in the school Vožd Karađorđe in the city of Niš, Serbia (Kovačević et al. 2015). Quartz fiber filters (Whatman QMA, 47 mm diameter) were used for this ambient air sampling. The marine aerosol samples (PM_{2.5}) were collected seasonally on GF/F filters (47 mm diameter) by low volume sampler Sven/Leckel SEQ 47/50 (2.3 m³/h, sampling time: 24 h) in the central Dalmatia (Middle Adriatic). Concentrations of the marine aerosol mass fluctuated from around 2.5 to 50 μ g/m³, while average daily school outdoor PM_{2.5} concentration was 22 μ g/m³, and indoor 32 μ g/m³.

The water-soluble particulate fractions from both aerosol location was extracted by placing half of the filters in 0.13–0.2 dm³ of high purity deionised MilliQ water (Millipore Corp.) for 24 h. The extracts were then filtered through 0.7 μ m GF/F filters pre-combusted at 450 °C for 5 h and directly used for electrochemical measurements and water soluble organic carbon analysis.

Study on the SAS and DOC in water soluble fraction of PM provides an important insight in the content and type of the complex mixture of organic matter with mainly hydrophobic and hydrophilic characteristics. Characterization of sulfur fraction, based on measurements of inorganic and organic RSS, comprise a group of compounds that contain sulfur in nominally -II and 0 oxidation states (sulfide, organic thiols, inorganic and organic di- and polysulfides, polysulfanes, dissolved molecular S0) (Orlović et al. 2016, 2017). Preliminary results, as expected showed diference among marine and urban air PMs organic matter content, that will be compared and discussed.

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2.2 DETERMINATION OF LOW MOLECULAR WEIGHT ORGANIC ACIDS IN ATMOSPHERIC AEROSOLS BY ION CHROMATOGRAPHY

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Low molecular weight (LMW) organic acids constitute a significant fraction of atmospheric water-soluble organic aerosols. They are resulting from fossil fuel combustion and biomass burning, cooking, forest biosources, anthropogenic emissions and have important roles in climatic processes and human health (Kawamura and Bikkina, 2016; Tsai et al, 2008). Concentrations of seven LMW organic acids (formate, glyoxilate, glutarate, succinate, malate, malonate and oxalate) in atmospheric aerosol samples, collected in a suburb of Belgrade (Serbia), were determined by ion chromatography (IC).

A total of 94 daily samples of atmospheric aerosols were collected between September 2013 and June 2014 at the Mirijevo, outskirt of Belgrade. Aerosols were collected with the TCR Tecora (Echo Hi-Vol) filter sampler. The sampling was performed continuously for 24 hours at a flow rate of 225 L/min. The collected samples were stored at the temperature -18 °C, until the time of analysis. A portion of each loaded filter (1.0 cm² punch) were transferred to a clean 15 mL polystyrene tube and extracted with 10 mL of deionized water. All extracted filters were mechanically shaken for 20 minutes and after the filtration of samples through 0,22 µm syringe filters, the resulting extracts were analyzed on a Dionex IC system with AS11 analytical column and hydroxide eluent. Analysis of LMW organic acids in samples of atmospheric aerosols can be quite a challenging analytical task due to the presence of high concentrations of inorganic anions such as fluorides, chlorides, nitrates and sulfates which tend to overlap the peaks of LMW organic acids. Therefore, a complicated gradient program must be applied.

Oxalate was the most abundant organic species detected. Its concentration ranged from 15 to 280 ng/m³ with an average of 95 ng/m³. Malonate was the second most abundant species followed by succinate, with concentration ranged from 0.1 to 100 ng/m³ with an average of 19 ng/m³. Formate, glyoxylate, succinate and malate are present in similar concentration ranges. Glutarate is present in lowest concentration with mean value of 7 ng/m³. Vehicle emissions and biomass burning in the vicinity of the sampling site are primary sources of LMW organic acids. Photo-oxidation of volatile and semi-volatile organic compounds emitted to the atmosphere by industrial processes located in the vicinity of the sampling site is one of the main sources.

To examine the trends of the concentration changes over a ten-month period (fall 2013 to summer 2014), the concentrations of analyzed LMW organic acids for various emission sources were plotted by the moving averages for all samples. The time-trends of these variables were also fitted by quadratic curves. All of the analyzed organic acids, except glyoxylates, show a trend of increased concentrations in autumn and spring, with lower concentrations in the winter period. Succinate showed opposite trends over the same time-period. Time-series analysis strongly suggests that concentrations of LMW organic acids in aerosol samples are linked to the dominant contribution from anthropogenic sources.

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2.3 POLYCYCLIC AROMATIC HYDROCARBONS: THE IMPORTANCE OF (BIO)MONITORIZATION

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Polycyclic Aromatic Hydrocarbons (PAHs) are a large group of organic compounds formed during incomplete combustion of organic matter, known for their cytotoxic, mutagenic and carcinogenic properties (IARC 2010). PAHs are endocrine disrupting chemicals (WHO, 2013), with some compounds causing neuro-, immuno-, hemato-, cardio-, reproductive and developmental toxicities in humans and laboratory animals. As a consequence, sixteen PAHs are classified as priority pollutants (USEPA, 2005). The major anthropogenic sources include traffic, coal combustion processes, emissions from power plants and waste treatment, and from biomass and wood burning. Indoor PAHs result from activities such as smoking and cooking, from various fuels and candle burning, as well as from penetration of outdoor emissions (by ventilation systems, due to structural cracks, etc.).

Assessment of PAHs exposure is complicated due to the mixed aerosol/vapor composition of airborne compounds. In addition, exposure occurs through several routes, namely inhalation, food ingestion, and dermal contact. For these reasons, researchers have turned to biological monitoring to assess total exposure to PAHs. These compounds are absorbed into the blood stream and, following possible metabolism (biotransformation), are distributed within the body, especially to lipophilic tissues. Urine is the easiest, cheapest and less invasive matrix to determine human biomarkers of exposure. 1-hydroxypyrene is the most widely used biological indicator of internal dose while 3-hydroxibenzo[a]pyrene is the main metabolite of the known human carcinogenic PAH. Acenaphthene, fluorene, and phenanthrene are common PAHs in different matrices being 1hydroxylacenaphthene, 2-hydroxylfluorene, and 1-hydroxyphenanthrene their major urinary metabolites, respectively (Oliveira et al, 2017).1-hydroxynaphthalene and 2-hydroxynaphthalene are the most described metabolites of naphthalene which is one of the selected pollutants to indoor air quality (WHO, 2010). Thus, urinary monohydroxyl-PAHs (OH-PAHs) reflect a more accurate estimation of PAHs intake and should be combined with information reached by environmental monitoring since a more comprehensive assessment can be attained. However international guidelines or references values for urinary OH-PAHs are still inexistent, being only available some benchmarks (mainly for 1-hydroxypyrene) proposed for non-occupational and occupational exposed individuals.

Data from some case studies, namely schoolchildren environmental and firefighters' occupational exposures to PAHs will be reviewed, and the impact of indoor air emissions on the excretion of main urinary OH-PAHs will be summarized. Combined levels of 1-hydroxynaphthalene and 2-hydroxynaphthalene are frequently predominant among the detected urinary metabolites, while 1-hydroxypyrene and 3-hydroxibenzo[a]pyrene are usually the less abundant compounds; correlations have been reported among urinary OH-PAHs excretion and inhaled PAHs.

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2.4 LEAVES OF COMMON URBAN TREE SPECIES AS A MEASURE OF PARTICLE AND PARTICLE-BOUND POLLUTION: A FOUR-YEAR STUDY

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Magnetic biomonitoring has been proven as a reliable proxy for deposited airborne particles (PM) (Hofman et al, 2014). However, the leaf entrapment of PM is species-specific and it is of importance to study which tree species reliably reflect PM pollution (Aničić et al, 2011; Tomašević et al, 2011; Deljanin et al, 2014). In this study, four tree species common in urban areas of Europe and beyond (Acer platanoides, Aesculus hippocastanum, Betula pendula and Tilia cordata) were investigated to select the appropriate biomonitor that enables the most consistent 'signal' to particle, and particle-bound toxic elements. The tree leaves were sampled in the central urban and suburban parks in Belgrade (Serbia) in May and September from 2011 until 2014. The magnetic PM fraction in the leaf samples was quantified by Saturated Isothermal Remanent Magnetization (SIRM), and the concentrations of Al, Cr, Cu, Fe, Ni, Pb and Zn were determined by inductively coupled plasma optical emission spectrometry (ICP-OES). Magnetic and elemental measurements were considered in a relation to the regulatory PM₁₀ data. The median leaf SIRM values of T. cordata, A. hippocastanum and A. platanoides (174, 140, and $123 \times 10^{-5} \times A m^2$ kg⁻¹, respectively) implied the prominent capacity of these species for capturing magnetic particles contrary to B. pendula (68 \times 10⁻⁵ \times A m² kg⁻¹). However, *B. pendula* leaves showed statistically significant correlation of SIRM and PM₁₀ values (r = 0.75), SIRM and element concentrations (r > 0.50), and spatio-temporal differences in SIRM/element content between the studied parks/years. These results recommend B. pendula as a valuable biomonitor of particles and associated elements. Nevertheless, high SIRM values, significant correlation between SIRM and PM_{10} (r = 0.71), and literature findings (abundance, adaptability, PM removal efficiency), favour A. platanoides over B. pendula in magnetic biomonitoring of particles.

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2.5 NODE-TO-NODE FIELD CALIBRATION OF WIRELESS DISTRIBUTED AIR POLLUTION SENSOR NETWORK

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Low-cost air quality sensors offer high-resolution spatiotemporal measurements that can be used for air resources management and for exposure estimation. Yet, such sensors require frequent calibration to provide reliable data. Even after laboratory calibration the sensors may not report correct values when they are deployed in the field, due to interference with other pollutants and due to high sensitivity to environmental conditions. Hence, field calibration has been suggested as a means for overcoming this limitation, with the common strategy involving periodical collocations of the sensor nodes adjacent to an air quality monitoring station. However, the cost and complexity involved in transferring numerous sensor nodes back and forth, and the loss of data during the long and repeated calibration periods make this strategy inefficient. This work examines an alternative approach, a node-to-node (N2N) calibration, where only one sensor in each chain is directly calibrated against the reference measurements and the rest of the sensors are calibrated sequentially one against the other while they are collocated in pairs. This procedure minimizes the total number of transfers and enables calibration while simultaneously collecting data at the measurement sites. We studied N2N chain calibration and the propagation of the calibration error analytically, computationally and experimentally. N2N calibration will be shown to be generic and applicable for different pollutants, sensor technologies, sensor platforms, chain lengths, and node order. Although N2N calibration will be shown to be suitable for calibration of distributed sensor networks, we will also discuss its limitations.

3. HEALTH EFFECTS I

3.1 HEALTH IMPACTS OF AIR POLLUTION IN SERBIA

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Long-term exposure to air pollution leads a relevant percentage of the population to die prematurely, according to a comprehensive investigation on the impact of air quality on health in Serbia. The aim of the work is the assessment of air pollution impacts on health in the major Serbian cities with a detailed analysis of the situation of Belgrade. Long-term and short-term exposure to air pollution also increases mortality risk.

A thorough data collection of air pollution data has been associated with an extensive collection of population and health data covering the period 2010 and 2015. The application of the AirQ+ by WHO has allowed to process data from the main Serbian cities to calculate the attributable proportion of deaths due to air pollution.

Exceedance of WHO air quality targets, as well as EU air quality limit values, have been recorded in several Serbian cities. This work presents the results of monitoring PM10, SO2, NO2, and O3 in ambient air of major Serbian cities and examine likely impacts of air pollution on mortality.

The results indicate the importance of a serious monitoring of air pollution and the need of interventions to reduce the burden of air pollution in Serbia and in specific cities.

3.2 COMPARATIVE ANALYSIS OF AIR POLLUTION AND THE INCIDENCE OF DISEASES IN THE EXPOSED POPULATION IN SERBIA

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Using the health assessment methodology recommended by the US EPA, this paper assesses the probability of health risk in the exposed population in Serbian cities with an increased air pollution level. Comparative analysis of air quality in the cities of Bor, Pančevo, and Užice, in which air pollution is higher, and the City of Kikinda, which is in the first category of air quality, indicates a cause-effect relationship between the air pollution level and the incidence of respiratory and other diseases registered in the observed cities. The percentage of health risk probability monitored in terms of the hazard quotient (HQ) is almost identical to the percentage of actual registered respiratory diseases in Bor than in other analyzed cities, in which lower levels of air pollution were registered. The paper also analyzes the impact of air pollution due to PM_{10} particulate matter, which was used to determine individual risk and the probability of cancerous diseases in the exposed population. In the analyzed areas, the individual risk in the population aged over 18 is about 20%, whereas the risk in the younger population is about 17%.

Key words: air pollution, hazard quotient, probability of cancer risk, health risk

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3.3 EXPOSURE TO BIOMASS FUEL SMOKE AND USE OF PRIMARY HEALTH CARE IN WOMEN

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Background and Aims. Indoor air pollution is usually quite different from outdoor air pollution, as represented by the type of pollutants, as well as by their concentration. The way of heating, especially if it is based on the use of coal and wood, releases toxic and harmful gases, such as carbon monoxide, carbon dioxide, sulfur dioxide, particles, oxides of nitrogen and others. Inhaled pollutants reduce the movement of cilia in the trachea that do not perform their very important function of cleaning, which affects the increase in the risk of respiratory symptoms and diseases. The aim of the research was to determine how exposure to biomass fuel smoke impact on the prevalence of respiratory symptoms and the degree of use primary health care in female population.

Method. A survey was conducted of 411 women, aged 20-50 years, from two areas with different levels of common outdoor air pollutants (sulfur dioxide and black smoke). Control group (n=214) were women who used electricity for heating and exposed group (n=197) were women who used wood or coal for heating. Women in both groups were no smokers, they were not professionally exposed to air pollution, and they have lived in their current homes for at least five years. The survey was adapted from the American Thoracic Society and validated for Serbian language. The questionnaire includes questions about personal data of the subjects, prevalence of respiratory symptoms and respiratory illnesses in the last 12-month period of life. The survey was conducted by a physician, through interviews in the period from May to June 2014. Data on use of primary care and absence from work was collected on the basis of hospital registrations. In order to determine statistically significant differences we used Student T-test and $\chi 2$ –test.

Key results of the studies. The exposed group of subjects used most commonly wood for space heating (28.21%) and coal (17.11%). The average age of respondents in the exposed group was 35.33 ± 6.03 and the average age of the non-exposed subjects was 35.44 ± 3.12 . Between the two groups of women there was a statistically significant difference in the incidence of respiratory symptoms related to the upper and on the lower respiratory tract (p<0.01). The number of women who have used primary health care and were absent from work due to respiratory symptoms and disease is statistically significantly higher in the group that is exposed to biomass fuel smoke ($\chi 2=89.02$; p< 0.001). The number of days of absence from work is significantly longer in women who are exposed to biomass fuel smoke ($\chi 2=82.56$; p< 0.001).

Conclusion. The results show that biomass fuel smoke is a significant constituent of indoor air pollution and affects negatively the health of women, and also increases the cost of health care.

3.4 CYTOTOXIC AND GENOTOXIC EFFECTS OF COMBUSTION-DERIVED PARTICLES FROM DIFFERENT EMISSION SOURCES

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BACKGROUND AND AIMS

Diesel and Biomass combustion-derived particles (CDPs) largely contribute to air pollution and likely to the adverse health effects observable in the exposed populations. Anyway our knowledge on the different biological responses deriving from the particles emitted from different sources is still poor, as well as the comprehension of the modes of action of such particles with variable physico-chemical properties. This study aims at comparatively investigate the cytoxic and genotoxic properties of particles collected during the combustion of different diesel and biomass sources.

METHODS

Diesel Exhaust ultrafine Particles (DEP) were from two standard references (DEP 1650b and 2975) and directly sampled from a Euro4 vehicle run over a chassis dyno. Biomass-derived combustion particles were collected from the emission of heating systems operating with pellet, charcoal and wood. CDPs were morphologically and chemically characterized. Monocultures of human lung cells and a 3D *in vitro* model of the alveolar blood barrier (ABB) were used to study the CDP-induced biological effects. Cell viability, inflammatory response, antioxidant and xenobiotic metabolism activity, DNA damage were investigated.

KEY RESULTS OF THE STUDY

DEP exposure of lung cells did not cause significant cell death, but especially DEP Euro4, collected during a standard urban cycle driving, did induce oxidative stress and release of inflammatory cytokines, that were also able to activate endothelial cells. Pellet-derived particles decreased cell viability, inducing necrosis, while charcoal and wood CDPs mainly induced apoptosis. The strongest cytotoxic action was achieved after exposure to CDPs from not-certified pellet in respect to certified pellet and other biomass-derived CDPs. Significant increase of HO-1, the activation of the cytochrome P450 enzymes and DNA strand breaks were observed for all biomass-derived CDPs, confirming the oxidative-mediated genotoxicity as a shared mechanism of action.

3D coculture of alveolar and endothelial cells revealed the ability of subcytotoxic CDP concentrations to induce vascular endothelial dysfunction upon exposure of the alveolar epithelium.

CONCLUSIONS

These results suggest that CDPs from different emission sources may impact at different extent on the respiratory health and can activate different toxicological pathways, pointing out the importance of more specific strategies to lower the health hazard coming from the emission of diesel vehicles and biomass-propelled heating systems.

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4. SCIENCE, POLICY & EDUCATION

4.1 THE ACTIVITIES OF WHO REGIONAL OFFICE FOR EUROPE IN SUPPORTING THE DEVELOPMENT OF POLICIES AND INTERVENTIONS IN IMPROVING AIR QUALITY RELATED TO PM

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Ambient and household air pollution is the biggest environmental risk to health, responsible for the premature deaths of 6.5 million people every year globally and almost 600,000 in the WHO European Region, out of which 482 000 could be attributed to ambient air pollution. The economic cost of deaths and diseases from air pollution in the WHO European Region amounts to USD 1.6 trillion, according to a study by the WHO Regional Office for Europe and the Organization for Economic Cooperation and Development in 2015. This figure is the equivalent of one tenth of the gross domestic product of the European Union in 2013. Emissions of the main air pollutants in Europe have declined in recent decades, resulting in generally improved air quality across the region. However, a large proportion of European population remains exposed to PM2.5 levels exceeding the WHO AQGs in about 74% of stations in monitored countries of the European Region in 2014.

Of major health concern is fine particulate matter (PM2.5), associated with health effects, both for long-term and short-term exposure. PM2.5 shows the most consistent associations with mortality and morbidity, such as lung cancer, hospitalizations for stroke, ischaemic heart disease and respiratory diseases, acute and chronic bronchitis, and restrictions in daily activity.

WHO Regional Office for Europe reviews scientific evidence on the health effects of air pollution and provides evidence-based guidance to policy-makers on how to protect public health from air pollution. Air Quality Guidelines, first published in 1987, are regularly updated, and based on the new scientific evidence. The latest WHO Air Quality Guidelines, Global Update 2005, focus on classical air pollutants, including PM2.5, PM10, ozone, nitrogen dioxide and sulphur dioxide. Currently, the WHO Regional Office for Europe, in coordination with WHO Headquarters and other WHO Regions, is leading the update of the WHO air quality guidelines, considering the conclusions from technical reports such as the REVIHAAP (WHO review of evidence on the health aspects of air pollution2013) and responding to WHA resolution on "Health and the Environment: Addressing the health impact of air pollution" in 2015.

WHO Regional Office for Europe supports the development and implementation of international legal instruments. For almost 20 years, it has been chairing the Joint Task Force on the Health Aspects of Air Pollution, which provides advice to the UNECE Convention on Long Range Transboundary Air Pollution, a key legally binding instrument since 1979, whose ratification and implementation need to be promoted across the European Region. WHO Regional Office for Europe also contributes to developing comprehensive national and regional strategies and actions to reduce air pollution, and has been working with Member States to highlight the health aspects of air pollution and potential for public health benefits of improving air quality in the World Health Assembly resolution 68.8 (2015), Batumi Action for Cleaner Air (2016) and Declaration of Ostrava (2017).

WHO Regional Office for Europe develops quantification tools to assess health risks from air pollution. It launched the upgraded software tool AirQ+ to perform calculations that allow quantification of the health effects of exposure to air pollution and is developing tools to assess co-benefits of climate change and air pollution policies on health. AirQ+ has been used by several Member states to analyse health risks from air pollution, since its launch in 2016. By using these tools, WHO Regional Office for Europe helps countries build capacity to assess health risks from air pollution and develop sustainable policies on air quality.

WHO work on air quality and health is in line with the European Health 2020 policy: it also contributes to the achievement of the 2030 global Agenda for Sustainable Development. WHO also helps connecting air pollution to sustainable development by providing data for global reporting, and by helping refine the indicators (Indicator 3.9.1) to make them more health relevant. Scaling up and accelerating interventions that reduce air pollution in energy production, transport and other sectors is a way to help meeting the sustainable development goals on health (SDG3), energy (SDG7), and cities and communities (SDG11), as well as contributing to climate change mitigation.

4.2 URBAN PARTICULATE MATTER: TECHNOLOGIES FOR ASSESSMENT AND NEED FOR INFORMATION

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Particulate matter (PM) is a heterogeneous atmospheric entity with an adverse effect on human health. This adverse relationship constitutes the basis for e.g., the European legislation determining limit values of PM in the ambient air. This association has been shown for a number of different metricas and different health endpoints (e.g., Schwarze et al 2006). Suggestions for the metric by which the PM is to be characterized include PM mass in different size bins (the chosen metric for the current European legislation), PM optical properties, particle number, and PM composition, in addition to more specific properties of PM such as oxidative potential. This suggests a possibility for varying mechanisms of action of PM as a health determinant (e.g., Kelly and Fussel, 2015). The multitude of metricas and PM properties implies the use of different monitoring technologies, adding to the common challenges of varying temporal and spatial scale. Risk communication, and development of measures to reduce ambient particle concentrations, are seldom able to take the above fully into account.

In Europe, there are many sources of information from measurements of particulate matter. Most notably, a systematic approach to Europe-wide monitoring over almost five decades has led to development of a comprehensive system of ground-based monitoring stations for urban and background areas, applying quality systems that ensure comparability of results across the region, and make it possible to detect relatively subtle changes. In addition, there are a number of assessment systems in place including satellite observations, specialized observation networks and atmospheric modeling. They allow investigating with high precision long-term development in concentrations of PM in relation to a number of factors including changes in emissions of atmospheric constitutents affecting the PM concentrations.

With the advent of new miniaturized sensor technologies for assessmet of PM (e.g., Jovasevic-Stojanovic et al. 2015), there open new opportunities as well as challenges to complement the existing systems, and to provide useful public information.

Today, scientists and legislators alike recognize the need to involve the public in tackling air pollution – we wish the public to take measures to reduce their exposure and to reduce activities leading to emissions. On their side, the public shows interest in air pollution and 56% recognizes it as the most important environmental issue – despite the improvements of the last decades, yet, over 25% of people asked says they lack information (Eurobarometer, 2014). Bringing the knowledge to the public to enable making scientifically sound decisions seems thus a priority.

We will address some of the issues of measurement quality related to different technologies. We will show that quality systems exist or are under development for the new technologies, and that information systems for the public are available (see, e.g., luftkvalitet-nbv.info, luftkvalitet.info) even if we suspect that both are generally underused. We will show the perceived public information needs as reported in our surveys, and demonstrate that public perception of air quality is more dependent on the level of perceived problematisation of the issue than on objective pollution level. These results have implications for legislators and managers alike – public acceptance of measures will depend on how successful the dialogue with the public is. The results are based on the data and methods collected by the CITI-SENSE project (http://co.citi-sense.eu).

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4.3 A DUSTY ROAD TO GARDALAND – AN INSIGHT INTO THE SCHOOL SCIENCE PROJECT

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In the last decade a lot of progress was made in the field of environmental sensing and associated information and communication technologies. Among others, advantages of new technological solutions enable establishment of online environmental monitoring systems in real-time, and even more important, active involvement of citizens in the overall process. In turn, public participation can lead to and support community-based environmental governance (Liu et al., 2014).

This contribution summarises the lessons learned in Ljubljana, Slovenia, regarding the engagement and empowerment of citizens on issues related to the air quality within the recently finished CITI-SENSE project. Overall objective of the CITI-SENSE was to develop technology enabled "Citizens' Observatories" to empower citizens and various citizens' groups to (i) contribute to and participate in environmental governance, to (ii) support and influence community and policy priorities and the associated decision making, and to (iii) contribute to European and global monitoring initiatives (CITI-SENSE, 2016a).

More specifically, this contribution will focus on student activities carried out in schools participating in the project and where low-cost air quality sensors and other means were used for the engagement and empowerment purposes. Level of involvement of pupils and other stakeholders in schools depended on their specific interest and ability, and ranged from traditional science projects, inclusion of air quality related topics in the curriculum, to organisation of various awareness raising activities. Involvement of schools in the project resulted in numerous win-win situations, including increased awareness regarding the indoor and outdoor air quality, more pro-environmental behaviour of the people involved and enhanced cooperation and interaction of various local stakeholders (CITI-SENSE, 2016b). This will be demonstrated based on a specific case study where elementary school pupils used low-cost air quality monitoring devices to investigate characteristics and behaviour of dust in their classroom. They presented their research work at a national school competition and were rewarded with a trip to Gardaland.

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5. PM COMPOSITION AND MODELING II

5.1 ATMOSPHERIC MINERAL DUST AS THE MOST ABUNDANT AEROSOL: MODELLING AND IMPACTS

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Mineral dust is the most abundant aerosol in the atmosphere (e.g. Rosenfeld et al., 2001). A large amount of dust, up to 1500×10^6 tons/year (Tegen and Fung, 1994) is mobilized over arid regions and injected into the atmosphere under favorable weather conditions. Once in the atmosphere, dust particles are elevated into the free atmosphere by turbulent processes and then transported hundreds and thousands kilometers away from sources, and finally deposited to the Earth surface through wet and dry deposition.

Dust models are typically driven by atmospheric models as an online component in which dust concentration is calculated by solving the Euler-type partial differential nonlinear continuity equation for mass. In such integrated model systems, dust processes are computed utilizing the prognostic wind, turbulent mixing and precipitation of the atmospheric model. One of the most critical dust component is computation of dust emission fluxes, depending on both surface properties and surface wind speeds, and which cannot be prescribed externally as, for example, anthropogenic emissions. Over the last decade, numerical prediction of dust aerosol concentration has become important at several research and operational weather centres due to growing interest from diverse stakeholders, such as solar energy plant managers, health professionals, aviation authorities and policymakers.

Atmospheric dust interacts with the Earth system. Dust influences the Earth's radiative budget by affecting the processes of absorption and scattering. Indirect effects include strong changes in e.g. the number of cloud ice nuclei, which in turn affect the optical properties, lifetime of clouds and precipitation. Dust deposition at the surface causes changes in the biogeochemical processes of terrestrial and marine ecosystems through delivery of primary nutrients (Jickells et al., 2005). Human exposure to airborne mineral dust may adversely affect human health, causing allergies, respiratory diseases and eyes infections (e.g. Sprigg et al, 2014). Desert dust outbreaks over southern Europe frequently exceed daily and annual safety thresholds of particulate matter set by the European Union directives on ambient air quality and cleaner air. High dust concentrations may affect aircraft operations and ground transportation. They also can reduce turbine performances of aircraft engines. In addition, dust is a serious problem for solar energy power plants.

In this study the Dust Regional Atmospheric Model - DREAM (Nickovic et al. 2001), a widely used dust model in the community, will be described in more details: DREAM modelling methods, impact studies performed with it and its validation against observations.

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5.2 ANALYSIS OF REGIONAL ATMOSPHERIC CONDITIONS ASSOCIATED WITH HIGHER OZONE DAYS IN NORTHWEST ANATOLIA OF TURKEY

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This study focuses on an analysis on the role of meteorological conditions associated with higher ozone in the Biga Peninsula of NW Turkey.

The surface ozone data over a 3-year period (2013-2015) are derived from total ten passive samplers and two continuous air quality stations while the meteorological data came from the meteorological stations in the region. Surface ozone concentrations in the study region tend to a seasonal cycle; generally reach the maximum levels in spring-summer especially during July–August and minimum values in October–December periods. The mountainous areas have higher cumulative exposure to ozone than the rural and suburban locations in the study region. The annual average of surface ozone concentrations were found in the range of 48–117 μ g/m³ while monthly average ozone concentrations were between 78 and 187 μ g/m³ for summer periods (June, July and August). Moreover, the maximum O₃ concentration appears at around 16:00–17:00 in rural; 15:00–16:00 in suburban sites respectively while the minimum ozone concentration appears during the morning hours (07:00–08:00 LST in rural; 04:00–05:00 LST in suburban site), respectively (Sarı et al., 2016). Days with daily maximum 8-h ozone concentrations; reaching 120 μ g/m³ or above (which is the 8-h European standard threshold) are considered for episode identification; five different ozone episodes were selected for further analysis.

In the presented study, the ability of the WRF model to simulate the meteorological conditions leading to high ozone conditions was analyzed. The WRF simulations for these five episodes are run using a set of 9, 3 and 1 km one-way nested grids that have 30 vertical sigma layers from the surface to the top pressure of 100hPa.

Model predicitions are compared observatons and subjected statistcal analysis. According to results, ozone episodes were developed under specific atmospheric conditions. High ozone days were shown to be mainly associated with sufficient sunshine duration, high temperature and pressure, and low wind speed.

In the present study, the trajectory analysis by The Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model was also performed to follow the long-range transport sources contributing to the high ozone levels in the region. The WRF fields served as input for HYSPLIT to analyze the ozone episodes. This analysis was completed with 3-day backward air mass trajectories to assess the contribution of long-range transport of away contributors, resulting in the following main routes: İstanbul, Eastern Europe, and Western Russia. Most episodes were caused by local photochemical production and pollutant accumulation, and transport of pollutants from the highly polluted regions could significantly influence the air quality in the site, especially from İstanbul.

Keywords: Biga Peninsula, HYSPLIT, WRF, Surface ozone

5.3 A STUDY OF A DUST INTRUSION EVENT OVER BELGRADE, SERBIA

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Mineral dust is one of the most abundant components of the global aerosol burden (Kinne et al., 2006), and Sahara is the world's largest dust source region. Saharan dust is transported over long distances (Prospero et al., 1999; Ansmann et al., 2003) and it mixes with other aerosol types along the transport path, affecting their microphysical, optical and radiative properties. It affects the Earth's radiative budget twofold: by scattering and absorbing solar and terrestrial radiation (direct effect), and by modifying cloud properties due to their role in cloud formation (indirect effect). Furthermore, dust impacts air quality even at locations distant from its source region (Prospero, 1999). To improve understanding of these effects, it is important to characterize dust properties and their vertical distribution. A case study of long-range transport of Saharan dust to Balkans, that took part on July 5-6, 2014, will be presented. For analysis of dust layer spatial and temporal evolution, we used a synergy of ground-based measurements in Belgrade, satellite observations and dust transport model.

Temporal evolution of dust layer vertical distribution during the July 2014 dust episode was analyzed based on lidar measurements in Belgrade. The lidar system performs elastic backscatter and Raman measurements at the wavelengths of 355 and 387 nm, respectively, with high temporal (1 min) and spatial (7.5 m) resolution. The elastic backscatter measurements were analyzed to obtain vertical profiles of aerosol backscatter coefficient and Saharan dust layer was identified as a distinct elevated layer in the profile (Papayannis et al., 2008). The presence of dust was then confirmed using airmass backtrajectory analysis and dust forecast using Dust Regional Atmospheric Model - DREAM (Ničković et al. 2001). We analyzed temporal evolution of vertical extent and optical properties of dust layer. Furthermore, analysis of PM_{10} and $PM_{2.5}$ temporal evolution in Belgrade was performed to assess the impact of dust on air quality.

In order to examine dust layer spatial distribution and properties during transport, the analysis was complemented with MODIS (Moderate Resolution Imaging Spectroradiometer) and CALIPSO (Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observations) data. In addition, DREAM model was used to simulate dust transport over the study area.

The study demonstrates the use of satellite measurements combined with DREAM model simulations to provide insight into distribution and properties of dust layer during transport and to clarify results of ground-based measurements.

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5.4 RELATIVE IMPORTANCE OF GASEOUS POLLUTANTS AND AEROSOL CONSTITUENTS FOR IDENTIFICATION OF PM10 SOURCES OF VARIABILITY

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Due to adverse effects on human health and the increased risk of morbidity and mortality, particulate matter (PM) is one of the most studied atmospheric pollutants and perhaps the most pressing issue in air quality regulation worldwide (Fuzzi et al, 2015). During the last decade, poor air quality in Belgrade(Serbia), with a large number of PM_{10} limit value exceedances (Directive 2008/50/EC), is identified as an important environmental risk factor (Perišić et al, 2017). Therefore, identification of factors affecting PM_{10} variability could provide a better insight into the aerosol spatio-temporal distribution and source composition, revealing their dominant sources in an urban area (Stojić et al, 2016).

This study discusses the relative importance of PM_{10} constituents and the gaseous pollutants, as well as the effect of specific time series additive components (trend, seasonality and the remainder) for the prediction of aerosol mass concentrations. Feature selection was implemented by the use of guided regularized random forest method (Deng and Runger, 2013), while time series decomposition was obtained by the use of loess smoothing decomposition model (Li et al., 2014). The analyzed dataset comprised of daily concentrations of PM_{10} and its constituents (As, Cd, Cr, Mn, Ni, Pb, BaP, Cl⁻, NO₃⁻, NH₄⁺, SO₄²⁻, Na⁺, K⁺, Mg²⁺ and Ca²⁺) and hourly concentrations of PM_{10} and gaseous pollutants (CO, SO₂, NO, NO₂, NO_x, benzene, toluene, o- and m, p-xylene) obtained from urban locations in Belgrade during the period 2011-16.

According to the results, the highest relative importance of As, Cd, BaP, CO and benzene for the prediction of PM_{10} indicate that the environmental burden is mainly associated with fossil fuel combustion, particularly pronounced during the colder part of the year. This finding is in compliance with the large variance of the remainder component of the decomposed PM_{10} times series, that occurs as a result of short-term air pollution episodes.

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6. POSTER SESSION

6.1 MULTISCALE MULTIFRACTAL ANALYSIS OF NONLINEARITY IN PARTICULATE MATTER TIME SERIES

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Considerable scientific evidence suggests that exposure to even modest levels of particulate matter (PM) has detrimental effects on the environment and human health (Lelieveld et al., 2015). Besides the fact that PM levels in Serbia are higher than in most of the European countries, with a significant number of air quality standard exceedances, our studies have shown that suspended particles contain also high concentrations of carcinogenic contaminants, such as arsenic and benzo(a)pyrene (Stojić et al., 2015a; Stojić et al., 2015b; Stojić et al., 2016). In this study, we use multiscale multifractal analysis (MMA) to investigate the presence of fractal behaviour in the complex time series of PM_{10} and $PM_{2.5}$ concentrations, obtained from almost three-year (2012-2014) regular pollutant monitoring in Belgrade (Serbia). Multifractal methods reveal variable fluctuation properties, i.e. to what extent and on which time scale changes in concentration levels can be considered random or persistent. MMA is a generalization of the standard multifractal detrended fluctuation analysis, which adds the dependence on scale, providing a broader analysis of the fluctuation properties, as well as more general and stable results (Gierałtowski et al., 2012).

According to the results, multiscale multifractal derived Hurst surfaces confirmed the non-linear behavior of PM time series. Namely, for most of the scale and multifractal parameter values, local Hurst exponent remains in the interval between 1 and 1.5 indicating persistency of the PM_{2.5} time series, slightly affected by the concentrations occurring randomly. Random concentration values occur only at the level of small fluctuations for scales below 44, which corresponds to a period of about 2 days. Clear crossover, the result of different correlation properties, denoting significant impact of random events, emerges at this scale. Occurrence of concentrations in narrow bands (Hurst exponent equals 2) were not recorded, which is expected, since the sampling site is not exposed to the direct impact of the major $PM_{2.5}$ sources. PM_{10} Hurst surface reveals similar features, except that in the area of small variance and scales below 90, its growth to the maximum around 1.9 is steeper, almost reaching black noise area values of local Hurst exponent. Compared to PM2.5, PM10 Hurst structure around its maximum corresponds to clearly visible more pronounced peeks in the time series. However, unlike PM_{2.5}, PM₁₀ Hurst surface shows no crossover. In addition, generalized distance coefficient between PM fraction Hurst surfaces higher than the threshold value implies that PM_{2.5} and PM₁₀ time series have to be considered statistically different. The difference is particularly pronounced in the area of small fluctuations and medium scales. Furthermore, it is shown that the source of multifractality, examined by PM time series randomization, originates from both nonlinear correlations and a fat-tailed probability distribution. As can be concluded, the multifractal analysis can be used to capture important features of the air pollution data and recognize the laws that are governing pollutant concentrations, which is important for better understanding of underlying atmospheric processes.

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6.2 MODELING OF PM10 DISPERSION FROM COAL THERMAL POWER PLANTS KOSTOLAC A AND B

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Serbian electricity production is predominantly based on coal power plants, which present large sources of particle matters emissions. Modeling of PM_{10} dispersion from combustion process of thermal power plants Kostolac A and B (TEKO A and TEKO B) is performed, in order to examine impact of newbuilt TEKO B's Flue Gas Desulphurization (FGD) units, and results are presented in this paper. Two scenarios are discussed within this study, "without FGD" and "with FGD". AERMOD dispersion model, with hourly meteorological data (five years in row) from a representative measuring station, is used as modeling tool. Achieved results indicate that FGD has highly positive influence on air quality, not only on expected SO₂ concentration, but on PM_{10} concentration as well.

6.3 PM₁₀ AND PM_{2.5} EMISSION DURING THE PROCESS OF PREPARING THE MATERIAL FOR TIG WELDING

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Background and Aims: Welding is a common industrial and semi industrial process that generates complex aerosols of potentially hazardous metal fumes and gases. Large number of workers worldwide are exposed to welding aerosols everyday (Popović et al, 2014). The health of welders is difficult to assess because of differences in worker populations, work area ventilation, nature of welding processes, and other occupational exposures except welding aerosols (Schoonover et al, 2011). Most long-time welders experience some type of respiratory disorder during their time of employment (Jayawardana and Abeysena, 2009). Recent medical researches show that the risk for various health impacts increases with exposure to respirable and fine suspended particles (PM_{10} and $PM_{2.5}$) (Graczyk et al, 2015). The quantification of concentration levels of PM_{10} and $PM_{2.5}$ during the process of preparing the material for the tungsten inert gas (TIG) welding process was conducted in this study.

Methods: During the preparation of materials for the welding process submicron particles of TiO_2 were hand mixed with ethanol solution. The aim of mixing with ethanol solution was to create a coating intended to increase the penetration of tungsten inert gas (TIG) welding. The process of air sampling was conducted using active air sampler- Baghira. The mass concentrations of suspended particles in the air were determined by gravimetric analysis.

Key results of the study: During the measurement campaign concentrations of particulate matter PM_{10} fraction were in range from 10 to 471 µg·m⁻³ while the concentration levels of $PM_{2.5}$ fraction were in range from 5 to 370 µg·m⁻³.

Conclusions: In addition to the benefits that are achieved in the welding process, the staff participating in the process of preparing the materials for the welding are constantly exposed to a high concentration levels of respirable and fine suspended particles.

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6.4 CONVERGENCE CHROMATOGRAPHY AS AN EMERGING TECHNIQUE FOR DETERMINATION OF PAHS IN BIOMONITORS

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Polycyclic aromatic hydrocarbons (PAHs) are gaseous or particle-associated compounds formed in almost every process of the incomplete combustion from anthropogenic and natural sources. The US EPA has classified 16 PAHs as priority pollutants due to their mutagenic and carcinogenic properties. For the assessment of particlebound PAHs, biomonitoring using "moss bag technique" represents a complementary method to the convenient instrumental measurements (Aničić et al, 2017). The common analysis of PAHs in moss and air samples involve extraction, evaporation of the solvent, and cleaning steps before determination by high-performance liquid chromatography (HPLC) or gas chromatography (GC). Thanks to the novel upgrades, ultra convergence chromatography (UPC²) outperforms HPLC and GC in the domain of the PAH determination (Taylor, 2009; Welch et al, 2010). In this study, the method for determination of PAHs in moss samples by UPC² was developed. In UPC², the major component of the mobile phase is a supercritical fluid that has unique features lying between gas and liquid states. The critical temperature and pressure (T = 304 K, p = 74 bars) of carbon dioxide (CO_2) are easily attainable. The favorable properties of CO_2 over commonly used solvents are non-toxic and non-flammable nature and low cost. For the development of the method, 0.5 g of the moss material was spiked with standard solutions of 16 USEPA PAH. After ultrasonic-assisted extraction using dichloromethane, the extracts were injected into UPC² system with PDA detector (Waters, Milford, MA, USA). Separation was achieved at an UPC² Torus 2-PIC column (100 mm×3.0 mm×1.7 µm), which was kept at 40°C and the flow-rate was 1.5 mL min⁻¹. The injection volume was 5.0 μ L. The mobile phase consisted of compressed CO₂ and methanol. The PAH recovery was measured at different concentrations. The UPC² method separate 16 PAHs from the moss samples in less than four minutes. The method is eight times faster than HPLC and GC analyses, thereby reducing consumption of organic solvent by 85%. The improved speed of analysis is attributed to the inherent compatibility between UPC² and low polarity analytes, which minimises the risk of on-column degradation of the analytes. Moreover, the UPC² method used methanol as the co-solvent instead of often used toxic organic solvents, and without the need for time-consuming evaporation and reconstitution steps associated with HPLC and GC. The high throughput of the UPC² method is highly suited for laboratories routinely performing quality control and regulatory compliance monitoring where a large number of assays are required.

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6.5 PRESENTATION OF CURRENT ATMOSPHERIC PARTICULATE MATTER LEVELS WITHIN NATIONAL NETWORK FOR AIR QUALITY MONITORING IN SERBIA

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Background and Aims. Ambient air consist of compounds that is mixture of gases, vapors and particulate matter (PM). Particulate matter PM10 have dominant influence on the air quality in urban areas in the Republic of Serbia.Citizens over the Europe are at risk to be exposed to potentially harmful levels of air pollutants. According to national legislative that is adopted to EU legislative, PM10 and PM2.5 concentration in the Republic of Serbia have to be monitor in the aim of reporting daily and annual limit values and number of daily exceedances.

Methods. In accordance with the Law on Air Protection [Off. Gazette of RS, 2009, 2013] authority over the National Network for monitoring air quality in the Republic of Serbia is the Serbian Environmental Protection Agency (SEPA). Beside devices such as automatic monitors that may present data of main ambient air pollutants with resolution of 1min, PMs are collected with reference gravimetric samplers that are suitable for time weighed concentrations at daily level, 24h. Main pollutants data, including PM, collected with automatic monitors are qualified for official reporting in Annual Report of ambient air quality if there is available 75% of 1 hour validated data annually. In addition preliminary, not validated data of air quality monitoring in framework of National and Local Networks of AMS are presented in near to real time online with resolution of 1 hour, http://www.amskv.sepa.gov.rs/.

Results: In framework of National Network of AMS there has been operational 38 AMS. Taking in account all main pollutants in 2011. 94% collected enough 1h validated data, while in 2016. due to lack of adequate service and repair validated data set drop to 23%. In 2016. air quality assessment it was qualified 34 sites including 9 stations from Local Network. Including them there were 14 sites (1 regional background – EMEP station, 6 sites in Belgrade, 7 in other cities over Serbia) for PM monitoring. In 2016, at 10 of 14 sites annual limit value were over 40 μ g/m³. Exceedances of the daily limit values of 50 μ g/m³ during 2016 was at all stations and their number was from 5 days at the station Kamenički vis -EMEP till the 171 days recorded at the station Valjevo. The highest daily concentrations of PM10 in the 2016 were measured in Valjevo 566 μ g/m³ and Užice 438 μ g/m³.

Conclusions. In framework of National Network of AMS particulate matter in ambient is for years the dominant of main pollutant in the Republic of Serbia. For identification of sources of ambient air pollution it is important to perform more detail analyses of PM fractions content. In addition, it is necessary to enable monitoring fine particulate matter, PM_{2.5}, in framework of National Network of AMS; update location and improve maintains for automatic monitoring stations and sampling PM fractions with reference gravimetric devices.

Keywords: ambient air monitoring, PM₁₀, PM_{2.5}, National Network of Automatic Monitoring Station

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6.6 A CANDIDATE MEASUREMENT SYSTEM FOR THE STANDARDIZED ROUTINE MONITORING OF PARTICLE NUMBER CONCENTRATION IN AMBIENT AIR

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BACKGROUND AND AIMS: Ambient air monitoring data is used to understand and reduce urban haze, to assess the effectiveness of abatement measures (e.g. low emission zones), for epidemiological studies, and to derive recommendations for future action plans. While PM2.5 and PM10 measurements have been standardized for a long time (e.g. DIN EN 12341:2014), this is not the case for ultrafine particles (UFPs). On the other hand there is a growing awareness that UFPs could have significant effects on human health or our climate, especially as they are frequently present in large numbers due to traffic, residential heating, and other processes. They are best quantified using condensation particle counters (CPCs) as their contribution to the mass of atmospheric particles (PM) is essentially insignificant. A number of European monitoring networks including NABEL (EMPA, 2000) and GUAN (Birmili, 2015) have added CPCs to supplement gravimetric air quality measurements with a time resolved measurement of PNC. Comparing these data can be challenging when CPCs with different lower cut-offs (D50), operating conditions or even working fluids are used. In addition, different sampling systems can lead to large differences especially due to particle losses.

METHODS: The European Committee for Standardization (CEN) developed the Technical Specification CEN/TS 16976 as a first step of harmonizing the continuous measurement of PNC in ambient air. This Technical Specification was published in August 2016 and describes a standardized method by defining a set of requirements not only for the CPC, but also for its sampling and conditioning system, the measurement procedure and the reporting of measurement results. The CPC must be an n-butanol instrument with no flow splitting and single count mode measurement. The performance criteria for the CPC include flow rate accuracy, a lower limit of detection (D50) at 7 nm, low zero count rate and fast response time. The sampling system must ensure RH of the aerosol below 40% at the inlet of the CPC and particle losses to be less than 30% at 7 nm. In 2016 TSI Inc. (Shoreview, MN, USA) introduced the model 3772-CEN CPC and the model 3772200 sampling system, both fully compliant with the proposed CEN/TS 16976. This CPC operates with a volume flow rate of 1.0 L/min and uses an optimized coincidence and dead time correction method to count particles in single count mode up to concentrations of 50,000 particles/cm3. The counting efficiency is verified with sintered silver particles down to a D50 of 7 nm. It aslo includes a pulse height analyzer that monitors wick health, super-saturation state, and instrument status. The same technology of monitoring the pulse height of every signal has been used in CPC's designed for automotive type approval testing according to Euro 5b/6 legislations for many years. The customdesigned sampling system was designed to minimize diffusion losses of the airborne particles. It draws 16.67 L/min through a PM10 inlet, of which 5 L/min are dried by a single-tube Nafion® dryer (Perma Pure LLC, Lakewood, NJ, USA). Additionally it offers up to 3:1 dilution and continuous measurement of RH, t and p for automatic logging in the 3772-CEN CPC.

CONCLUSIONS: CEN developed the CEN/TS 16976 as a first step of harmonizing the continuous measurement of PNC in ambient air. This normative document will facilitate data collection and comparison in the future as it defines the measurement procedure and the reporting of measurement results, as well as a set of requirements for the CPC and for the sampling system. The new Model 3772-CEN CPC and its dedicated sampling system Model 3772200 (TSI Inc., Shoreview, USA) have been presented and it is shown that they fully comply with the requirements laid down in CEN/TS 16976. The measurement system employs technology that has been used in vehicle type approval testing according to Euro 5b/6 for many years and will ensure high accuracy as well as very tight tolerances for atmospheric researchers. In addition to the performance characterization results we will also give examples of the use of these new instruments.

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6.7 PRELIMINARY CHARACTERIZATION OF CARBONACEOUS AEROSOLS COLLECTED CLOSE TO A BUSY TUNNEL IN BELGRADE, SERBIA

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Carbonaceous compounds, organic carbon (OC) and elemental carbon (EC), are a significant component of atmospheric aerosols due to their impacts on global climate, air pollution as well as health effects. EC chemical structure is similar to impure graphite, mainly derived from incomplete combustion of fossil fuel, biomass burning and other carbon-containing materials. OC consists of a large variety of organic compounds, emitted from combustion sources or formed due to photochemical activity. In this paper, we presented preliminary characteristics of carbonaceous aerosols monitored close to a tunnel surrounding, where particles were predominantly derived from vehicle emissions.

Fine and coarse PM samples were collected during May 2016 close to Terazije tunnel, located in the Belgrade city center. The tunnel is 260 meters long, with an average hourly traffic density of 4000 vehicles in the period 7-22h, and around half that during the night. Reference gravimetric pumps, LVS Sven Leckel were used for collecting PM2.5 and PM10. The sampling was done during rush hours, in the morning and afternoon period, and for 24h. The mass concentrations of OC and EC were determined by the Sunset Laboratory (Model 5L) Carbon Aerosol Analyzer using the NIOSH protocol, following the thermal optical transmittance method (TOT).

It was found that the average mass concentrations of PM2.5 and PM10 exceeded WHO guidelines values at daily level for both fractions, and were up to 50% higher during morning and afternoon. Average mass concentrations in PM2.5 in the morning was similar for OC and EC (~ $8 \mu g/m^3$), while in the afternoon, those values were almost 80% higher. The results of comparison between PM fractions showed that OC was about twice higher in the morning and 1.5 fold higher in the afternoon, while EC was higher up 35% and 20%, in PM10. For 24h samples, average mass concentrations of OC were similar as in the afternoon samples, while concentrations of EC were about $3\mu g/m^3$.

EC concentrations range from 0.2 to 2.0 μ g/m³ in rural and remote areas to 1.5-20 μ g/m³ in urban areas (Seinfeld and Pandis, 1998). In general, the OC/EC ratios are more than 2 in the urban ambient air (Zhouet al., 2014). OC/EC ratio in most of the tunnel studies were about 1. In this study, maximum levels of OC/EC ratio for PM2.5 and PM10 were measured during afternoon (~ 1and 1.5). For 24h samples, OC/EC ratios were much higher for both PM fractions (~ 4 and 6). OC/EC ratio between 1 and 3 indicates a high probability that the emissions come exclusively from mobile sources (Mancilla and Mendoza, 2012) that is in line with results from this study.

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6.8 SCOPE OF AMBIENT AIR PM10 MONITORING WITHIN THE NETWORK OF LOCAL PUBLIC HEALTH INSTITUTIONS IN SERBIA

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Background and Aims. Elevated atmospheric particulate matter concentrations have significant adverse health effects (Samet et al., 2000; Peters et al., 2001; Pope et al., 2002) affecting ecosystems and visibility, also. Particulate matter (PM) consists of complex mixture of solid and liquid particles of organic matter, core elements, secondary inorganic aerosols and trace metals originating from variety of natural and anthropogenic sources, directly emitted in the atmosphere or formed secondarily in atmospheric chemical reactions (Juda-Rezler et al. 2011). Sources of PM_{10} in Serbia are of different nature: coal burning energy plants (Obrenovac, Lazarevac, Veliki Crljeni), household fossil fuel burning (Kraljevo, Ivanjica, Čačak), industrial contamination (Bor), traffic (Beograd), and topographic position of the urban setting, such as in Užice. Our aim was to present the scope of urban ambient air PM_{10} monitoring undertaken by the Air Quality (AQ) laboratories within the network local public health institutes (PHIs) in Serbia, being being part of a mixture of stations belonging to both State network of automatic stations and Network of local measuring stations, for the period 2012-2016.

Methods. Results of air quality monitoring at the local level, provided by the local IPHs are reported to the National IPH on regular, monthly and daily basis, according to its annually revised Program of National Interest towards the Ministry of Health. PM_{10} monitoring at the local level is, mostly, subject to the negotiation process among the local IPH and local selfgovernment, according to the local Programme of AQ monitoring, approved by the Ministry responsible for environment protection (Air Protection Act). PM_{10} monitoring and measuring procedures were aligned with the standards given by the Decree on the air quality monitoring conditions and requested air quality, such as standard gravimetric method for PM_{10} fraction determination and measurements obtained by automatic measuring instruments.

Key results of the study. Results were obtained for 19 urban settlements. Analyzing a 5-year monitoring period shows that only in 5/19 towns PM₁₀ concentration was monitored continuously (Beograd, Bor, Niš, Užice, and Šabac), in which a trendline of average annual PM₁₀ values shows a steep decline in Bor (28.55 - 73.85 μ g/m³), Užice (80 - 129 μ g/m³), and Šabac (14.8 - 17.1 μ g/m³), while in Belgrade the decline is of a moderate kind, although all values were above the limit value (42.83 - 55.7 μ g/m³), according to the national legislation (40 μ g/m³). This pollutant was monitored for 4/5 years in Čačak, Zrenjanin and Pančevo; 3/5 years in Veliki Crljeni, Grabovac, Lazarevac nad Obrenovac (coal mining and coal burning energy plants, IPH Belgrade); 2/5 years in Kikinda (oil extracting wells) and Sevojno (cement industry). From the limited data available, it is clear that 79.31% of all noted annual average PM₁₀ concentrations, exceed the ALV given by the national legislation (40 μ g/m³), meaning that PM₁₀ presence in urban ambient air in Serbia could be accounted as a serious public health risk for the exposed population (7).

Conclusions. Local programmes of AQ monitoring, conducted by the Network of PHIs give an incomplete and incomprehensive coverage of potential public health threats for the burden of disease originating from air pollution. Today, providing AQ monitoring services is accounted as a market economy activity, complicating involvement of PHIs laboratories in the competition process, despite the fact that they all have gone through extensive improvement of the measuring equipment in order to comply with current national legislation. The other important issue is inavailability of funds at the local level for financing programmes of AQ monitoring of higher performance value, for which local IPHs are equiped with both human and technical resources.

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6.9 EVALUATION OF THE TRAFFIC DENSITY AND METEOROLOGICAL CONDITIONS INFLUENCE ON PM2.5 CONCENTRATION LEVELS IN AMBIENT AIR ON HIGHWAY E75

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Abstract: It is undeniable fact that the ambient air quality is greatly affected by traffic. Research [Colvile, et al., 2000] show that increased concentrations of pollutants are forming in near-road ambient air. The main factors influencing the formation of those concentrations are traffic flow characteristics and meteorological conditions [Baldauf et al., 2008]. Taking into account that vehicle stop-start driving causes an increased emission of pollutants [WHO, 2000; BAICHOO, 1999], we have conducted a study in order to evaluate the influence of the traffic density and meteorological conditions on ambient $PM_{2.5}$ concentration levels at traffic conjunction places. The aim of this study was to determine functional relationship between $PM_{2.5}$ concentration levels and the traffic density and meteorological conditions at the conjunction places by using correlation analysis. Measurement of the $PM_{2.5}$ concentration levels and the meteorological parameters at toll booth Nais on highway E75 was carried out by automated measuring station "Airpointer®", in the period from 15th July to 15th October 2014, and the number of vehicles by categories was taken from the toll booth database. The determined correlation was positive or negative depending on the meteorological variable values.

Keywords: PM_{2.5}, meteorological variables, correlation analysis.

6.10 IMPACT OF STREET LEVEL TRAFFIC EMISSIONS (CO2, CO, NOX, PM AND VOC) ON OUTDOOR TEMPERATURE AND THERMAL COMFORT IN COMPLEX URBAN ENVIRONMENT

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Basic causes of the high outdoor temperature in summer period in large cities depend of the urban, meteorological parameters as well as pollution. High pollution levels have been often observed in urban street canyons due to the increased traffic intensity and reduced natural ventilation.

Urban planning solutions incorporate heat reduction strategies by natural based solutions of blue-green infrastructures, as well as the reduction number of vehicles in the urban environment. This directly influence to air quality and outdoor thermal comfort and can contribute to significant temperature drop in towns and cities in summer period. Apart from experimental evidence, quantification of applied mitigation measures is highly complex, especially in the case of planning new or renovation of urban structures. Methodologies of computational fluid dynamics (CFD) approach offers the possibility for reliable quantification of mitigation measures for outdoor temperature on the local urban scale.

For estimating outdoor temperature in complex urban environment with CFD simulations, a large number of parameters are required, most of them have to be additionally measured or calculated. Traffic emission in real times is very complex and the parameters used for the CFD simulation are obtained by traffic contamination modeling. As the one of the most comprehensive method of modeling the emissions of traffic for obtaining of the emission of CO₂, CO, NOx, PM and VOC, COOPERT method is used.

In the case of the complex urban geometry of the city of Belgrade and the measurements that have been completed, numerical simulations of the outdoor temperature were performed for part of Belgrade city centre presented at Figure 1.

Based on the obtained results, it is noted that ambient temperature is 1.5-3 °C higher near the street where traffic is higher or in places where the larger building than in other parts of the city, as it is show at Figure 2.



Area framed by Ruzveltova, Takovska, Kralja Aleksandra,....streets

Figure 1: Urban structure of Belgrade Center



Figure 2. Air temperature at 1.7m height at noon

Such research can be significantly used in the planning and design of urban environments, as well as smaller complexes within the urban environment. These types of research can greatly assist city planners, but also indicate that the person responsible for energy efficiency in construction and the environment should be involved in the design or reorganization of the urban environment.

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7. HEALTH EFFECTS II

7.1 HEALTH EFFECTS OF SHORT- AND LONG-TERM EXPOSURE TO AIR POLLUTION IN DENMARK: AN OVERVIEW OF EPIDEMIOLOGICAL METHODS AND MAJOR FINDINGS

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In this talk, an overview will be given of the air pollution levels and sources in Denmark, a low-air pollution area in global perspective. The talk will give an overview over epidemiological studies and main results from studies conducted in in Denmark. Health effects of short-term (hours, days, weeks) exposure to air pollution have been studied in Copenhagen in relation to cardiovascular and respiratory disease in elderly subjects and asthma in children, with time-series and case-crossover designs. Copenhagen has an ongoing routine measurements of nitrogen oxides (NO₂ and NO_x), carbon monoxide, ozone (O₃), particulate matter (PM) with diameter < 10 (PM_{10}) , < 2.5 µm $(PM_{2.5})$, and < 0.1 µm, so called ultrafine particles (UFPs). Copenhagen is one of the few cities worldwide measuring UFPs, which has facilitated several important studies on the health effects of this PM fraction. Health effects of long-term (years, decades, life-time) exposure to air pollution are typically studied in a prospective cohort framework, in two large Danish cohorts, the Danish Diet, Cancer and Health cohort, and the Danish Nurse Cohort, and include overall mortality, cardiovascular disease, lung cancer, breast cancer, asthma, chronic obstructive pulmonary disease (COPD), stroke and diabetes. Furthermore, a case-control study design has been utilized for rare outcomes such as brain tumors and Parkinson's disease. Epidemiological research on health effects of long-term exposure to air pollution in Denmark has benefited from AirGIS human air pollution dispersion modeling system, which predicts levels of PM2.5, PM10, NO2, NOx, CO, and O3 with high spatial (individual address) and time-resolution (annual mean level), all the way back since 1971, due to unique Danish historical residential address registration. While main focus in above mentioned studies has been on trafficrelated air pollution, better exposure data (at individual level) are needed on specific chemical components of PM as well as specific PM sources, including biomass burning for heating, agricultural emissions, shipping emissions, crustal material, etc.

7.2 PARTICULATE MATTER IN NIS, SERBIA: LEVELS, SOURCES AND MAJOR HEALTH EFFECTS

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A large body of evidence has documented that particulate matter (PM) in the ambient air has adverse effect on human health as well as on the environment (Mukherjee, Agrawal, 2017.). Air pollution monitoring in Nis (Serbia) started in 1966 by Public Health Institute, for the presence of sulphur dioxide and soot in ambient air. Analysis of air quality indicated that the city of Niš belongs to a group of cities characterized by the third category of air quality (excessive air pollution) (SEPA, 2010.). An investigation of levels and potential sources affecting ambient particulate matter (PM) and associated risk to public health by regional Public Health Institute was started at Nis in 2011. Also, particulate matter monitoring (PM2.5; PM10) in the city was conducted by means of two automatic monitoring stations, owned by the Environmental Protection Agency of the Government of the Republic of Serbia. In 2012 and 2013, the Faculty of Occupational Safety in Niš conducted measurements of PM2.5 concentrations in ambient air, as part of the scientific project, funded by the competent Serbian Ministry. From 2011, degradation of ambient air quality in the city of Niš is primarily caused by high PM10 concentrations. According to the "Annual Report on the Environment in the Republic of Serbia" by the Ministry of Environment, Mining, and Spatial Planning, the mean annual ambient air PM10 concentration in 2010 was 51 μg/m3(maximum allowed level: 50 μg/m3), whereby limit values were exceeded during 123 days. According to Public Health Institute monitoring, in the period 2011-2016, the annual mean concentrations of PM10 were over limit together with a large number of days with PM concentrations over limits. The most likely sources of PM in the Niš city, especially during the winter, are vehicular traffic, combustion activities and domestic fuel burning, as well as industrial activities. Several epidemiological studies (Đorđević A. et al, 2016; Stanković , Nikolić M, 2016; Nikolic et al, 2014.) regarding health impact of ambient PM on population were performed on risk groups (pre-school children, school children, pregnant women and persons older than 65). Our studies demonstrate that PM significantly affect health of the vulnerable population and increase of morbidity. The findings are useful for developing risk management actions for PM on the local and national level. Although most sources of outdoor air pollution are well beyond the control of individuals, there is still space for personal action, like healthy behaviour. Further development of a network and system for monitoring ambient PM in Serbian urban areas can significantly contribute to disease prevention, primarily for vulnerable population. Emission reduction policies with epidemiological studies are needed to understand the benefits of sustainable control measures for PM mitigation.

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7.3 THE DEVELOPMENT OF WHO AIRQ+ TOOL TO ASSESS THE IMPACTS OF AIR POLLUTION ON HEALTH

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In May 2016 World Health Organization (WHO) released AirQ+, a software that assesses the burden of air pollution on mortality and morbidity. AirQ+ is the updated version of AirQ, developed by WHO to support the collection and analysis of air pollution data fifteen years before.

WHO is currently working on developing a new version of AirQ+ to take into account suggestions, recommendations and the experience cumulated in fifteen years of use of AirQ. A review of the use of AirQ will be presented as well as the comments and suggestions received by experts and users of AirQ+ in the last year.

The aim of the work is to promote the assessment of air pollution impacts on health, support the implementation of agreed methodologies in Member States and stimulate policies aiming at improving air quality in the WHO European Region (WHO, 2014). The information gathered by WHO on the use of AirQ and other tools that quantify the impacts of air pollution suggest several indications for further developments, for improving communication processes and capacity building opportunities. The review and evaluation of the past, current and potential utilization of these tools can provide useful information for policy interventions and awareness raising.

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8. PM COMPOSITION AND MODELING III

8.1 CONCENTRATION WEIGHTED BOUNDARY LAYER HYBRID RECEPTOR MODEL FOR ANALYZING PARTICULATE MATTER ALTITUDE DISTRIBUTION

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Throughout more than 30 years, several statistical models have been developed and upgraded for identification of remote emission source regions (Hsu et al, 2003), which is considered important for air pollution management, as well as for better understanding of atmospheric pollutant transport patterns and the ability of the atmosphere to dilute and disperse the pollutant species. In addition to conventionally applied hybrid receptor models, such as potential source contribution function (PSCF) (Zeng and Hopke, 1989), concentration weighted trajectory (CWT) analysis (Seibert et al, 1994) and residence time weighted concentration (Stohl, 1996), a few advancements have been proposed recently, including the concept of three-dimensional (3D) PSCF (Kim et al, 2016). In their study, Kim et al. (2016) calculated PSCF by simply ignoring the trajectory segment endpoints above the arbitrary threshold, although the existing knowledge suggests that meteorological factors determine the volume of air into which pollutants are emitted and govern the vertical distribution of pollutant concentrations.

In this study, we present concentration weighted boundary layer (CWBL) hybrid receptor model designed to provide a representation of pollutant altitude distribution along transport pathway by coupling planetary boundary layer (PBL) height with preprocessed pollutant concentrations obtained at the receptor site (Stojić and Stanišić Stojić, 2017). As explained by Stull (1988), pollutants emitted at the ground level are mostly trapped within the PBL that exhibits diurnal fluctuations in a wide range from several tens to several thousands of meters, whereas their concentrations in the upper atmosphere remains low. To illustrate an application of the CWBL model approach, PM₁₀ concentrations measured from January 2011 to December 2015 at New Belgrade urban site and PBL heights at the receptor site calculated using GDAS1 (Global Data Assimilation System, 2015) and MeteoInfo software (Wang, 2014) were used. The CWBL derived PM₁₀altitude profiles showed that the bottom layer is severely affected by ground emissions throughout the year, while the pollutant concentrations rapidly decrease with height. These findings are in compliance with pollutant altitude distribution described by Stull (1988). Similar patterns were observed for all seasons, despite the significant differences in winter and summer PBL height. As can be concluded, CWBL model presented herein considering PBL height enables reliable representation of pollutant altitude distribution over the receptor site.

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8.2 ESTIMATION OF PM EMISSIONS FROM CRUISE SHIPS IN KOTOR BAY

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Cruise ship tourism has experienced massive growth in the last years. However, some of the most popular cruise ship destinations are those which are the most sensitive to environmental disturbances. Cruise ships generate hundreds of tons of waste of every kind, including exhaust emission of pollutants and green house gasses as fossil fuels are burned. City of Kotor, positioned at the end of Kotor Bay, as the leading cruising destination on the Montenegrin coast, experienced multiple advantages of the cruising tourism development. Emission of pollutants from cruise ships, along with emissions from road traffic, represents majority of anthropogenic emissions of pollutants in the Bay area, since there are no larger industrial plants. In this paper, exhaust emission of PM from cruise ships in the Kotor Bay was estimated by implementing Tier 3 EMEP/EEA emission inventory. This inventory considers specific cruise ship data (main engine type, engine nominal power, fuel type, engine load factors, time and emission factors) relating to the defined two operating modes, maneuvering and hoteling. Years 2014 and 2015 were taken into consideration. At this period there was an increase in cruise ship calls from 354 in 2014 to 412 in 2015. Since there are no regulations regarding sulfur level in marine fuels in Montenegro, two scenarios were taken into account, one when cruise ships in defined operating modes use only HFO with two year average sulfur content of 2,67% m/m and the second when ships use only destilate marine fuel oils with max sulfur content of 0,1 % m/m. In high sulfur scenario, total estimated PM emission from cruise ships entering the Kotor Bay area increased from 54,65 t y-1 in 2014 to 65,73 t y-1 in 2015. In low sulfur scenario, total estimated PM emission from cruise ships entering the Kotor Bay area increased from 20,5 t y-1 in 2014 to 25,09 t y-1 in 2015. Somewhat larger increase of estimated PM emission in this period (high sulfur scenario 20,3 % and low sulfur scenario 22,4 %) than cruise ship calls (for 16,4 %) is associated mainly due to change of the classes of cruise ships and its retention times in port of Kotor area.

8.3 PRACTICAL APPLICATION OF SHORT-RANGE CALPUFF MODELLING FOR PM_{2.5} ASSESSMENT FROM PULP AND PAPER MILL IN CANADA

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This paper presents the results of a CALMET/CALPUFF validation study undertaken at the Corner Brook Pulp and Paper Mill (CBPP) operated by Kruger Inc. The facility's main boiler, Boiler #7, supplies steam to the mill for the paper making process. Boiler #7 burns a combination of bark (hog fuel) and oil. Emissions from Boiler #7 are controlled with a wet scrubber. In this study, emission rates prorated based on daily steam production records and the most recent stack sampling data were developed for the year 2011.

This study evaluates three aspects of air dispersion modelling:

- Generation of on-site meteorology in the absence of on-site meteorological observations with the use of a meso-scale forecasting model;
- Validation of CALMET/CALPUFF (Earth-Teck,2006) in short-range mode (less than 50km) with one year of hourly ambient PM_{2.5} data at two nearby monitoring sites; and
- Modelling in a setting that involves both complex terrain and a shoreline (land-water interface).

The meso-scale Non-Hydrostatic Meso scale Model (WRF-NMM) (Janic et al. 2004: Janic at al, 2000; Janic.Z.I, 2003), was run with fine resolution (\sim 3km), to produce forecasts on an hourly basis over a large modelling domain. The outputs from the meso-scale model were used to generate three-dimensional wind fields and temperature that were used as input into the CALMET meteorological preprocessor. A series of "pseudo" surface, upper air and over-water stations were created to generate meteorology in the 20 km by 20 km modeling domain with a horizontal resolution of 200 m. This fine resolution was necessary to resolve a detailed shoreline and distinguish the water/land interface near the stack.

At CBPP, the major pollutant of concern was $PM_{2.5}$, which is emitted from the 45.7 m tall Boiler #7 stack. Data from two nearby hourly ambient air monitoring stations for the year 2011 were used to validate the model output. The results of the model predictions are well within a factor of two at these monitoring stations. Based on the complexity of the source location and the terrain, CALPUFF performed exceptionally well and the results are used to demonstrate CBPP's compliance with regulatory requirements.

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8.4 EFFICIENT TOOLS FOR CREATION AND VALIDATION OF LUR BASED MAPS

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Aim and background: One of the most important aspects of high resolution mapping using land use regression (LUR) approach is creation of explanatory variables with sufficient resolution. Buffer type variables typically induce most of the CPU and memory cost, and if the employed algorithm is inherently slow it will be very challenging (sometimes even impossible) to create high resolution explanatory variables. Starting from input dataset, such as CORINE (Bossard, 2000), buffer type variables, e.g. total area of green and natural surfaces, are usually calculated in the following maner. First step is to create buffer layer with appropriate buffer radius and appropriate buffer placement. In this step, in QGIS (QGis Devel. team, 2011), it is also needed to specify polygon which will approximate the circular buffer. Second step is to intersect each feature in input layer with each buffer. This step creates large temporary layer with size proporational to product of number of buffers and number of input layer features. Large feature count can hinder computation and common mitigation strategies include reduction of grid resolution, simplification of input layer, subdivision of input layer or subdivision of buffer layer. Third step is to calculate length or area of each intermediate layer feature and assign it (add it) to appropriate grid points. This step finalizes the layer creation. While procedure described above uses common GIS tools, it has disadvantages, since for certain combination of inputs it can perform very poorly. In this work we explain, in detail, more simple and efficient algorithm for creation of circular buffer type explanatory variable.

Method: Workflow for the proposed algorithm is the following. <u>First step</u> is to mesh (triangular or linear mesh) input layer. <u>Second step</u> is to iterate over each mesh element and add its area (or length) to all grid points which are within buffer radius distance from center of mesh element. This step introduces several simplifications compared to the typical workflow and is efficient since each feature is iterated over and meshed only once. Algorithm for determining weather a grid point belongs to a circular buffer was inspired by general ray object intersection algorithm (Srisukh, 2002) adapted to planar circle and grid line intersection.

Results: Figure below shows CORINE input layer for Belgrade master plan with 5km margin, 5km buffer variable corresponding to green areas and water surfaces. These layers (in addition to several others) were used to calculate and validate NO2 mass concentration map for Belgrade based on Wang European model (Wang, 2014).



Figure 1. a) CORINE input later for Belgrade master plan b) green areas in 5km buffer c) water areas in 5km buffer

Conclusion: New algorithms enabled simple and efficient layer creation of LUR based maps. Map of NO2 mass concentration for Belgrade was created, having high resolution and later validated, giving mean normalized gross error from 21 to 28% depending on the traffic model.

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9. EXPOSURE TO TOXIC AND INFECTIVE PM AGENTS

9.1 PROCEDURE OF MICROBIOLOGICAL QUALITY CONTROL OF AIR IN MEDICAL LABORATORIES

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Background and Aims: In special theatres such as pharmaceutical facilities, quality of air is strictly regulated by contemporary standards, which do not allow presence of pathogenic bacteria with total number of bacteria above 100 cfu/m³. The microbiological quality of air is assessed by special devices in controlled space. The isolation and identification of bacteria are difficult and the results are often depending on method of sampling and detection (Karkkainen PM, et al 2010, Pietarinen VM, et al 2008, Radakovic SS, et al 2014). The aim of this study is to investigate qualitatively and quantitatively the microbiological quality of air in controlled space, to compare the sensitivity of different sampling methods, and to investigate the efficacy of filter cleaning.

Methods: The conditions in pharmaceutical theatre were as follows: air in controlled space ISO8 class passes through prefilter EU9 class, than HEPA filters H13 class. This space is overpressured, and pressures are blanaced according to specific activities, with determine number of air changes. The ratio of fresh air is 100%. Temperatures and relative air humidity are monitored and regulated within prerequested ranges (22 ± 3 °C, and $45\pm15\%$ respectively). In pharmaceutical facility before filter cleaning we collected 44 samples using automatic impinging method, and 34 samples using passive sedimentation method (Petri dish left for 30 minutes). The samples were analyzed after 48 h incubation on 37° C, following 48 h on 20° C, and isolation and identification was performed using BBL crystals.

Key results of the study: Before filter cleaning, there were 41 (93,18%) positive impinged samples and 26 (76,47%) positive sedimented samples. After filter cleaning, positive samples significantly decreased, either collected by impinging or by sedimentation method, to 5 (23,81%) and 2 (8,70%), respectively. The number of colony forming units (cfu/m³) was also significantly higher in samples collected by impinging method compared to sedimentation method, both before and after filter cleaning (13,84 cfu/m³ in positive impinged samples before vs. 0,38 cfu/m³ after filter cleaning; 2,97 cfu/m³ in positive sedimented samples before vs. 0,13 cfu/m³ after filter cleaning. The highest cfu/m³ number was 80, and was recorded by impingig method before filter cleaning. Both sampling methods provided the identification of the same types of saprophytic bacteria: before filter cleaning the most dominant were *Micrococcus spp* (39 positive samples collected by impingig and 21 positive samples by sedimentation), then *Staphylococcus epidermidis* (in 27 and 1 sample respectively), and *Bacillus spp* (in 10 and 1 sample respectively). In some samples more than one bacteria were identified. After filter cleaning, only *Sarcina spp* and *Staphylococcus saprophyticus* remained, and formed very poor colonies.

Conclusions: According to results, the microbiological quality of air in investigated facility is on appropriate level, even before filter cleaning. Not one pathogenic bacteria was isolated. In all samples number of cfu/m³ was under 100. Automatic impinging method was more sensitive compared to passive sedimentation. Filter cleaning provides efficient improving of microbiological quality of air in controlled spaces.

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9.2 DEVELOPMENT OF AN EVIDENCE BASE FOR RESPIRATOR SELECTION FOR BIOAEROSOLS

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A method for selection of respiratory protection for airborne biological particulates based on control banding has been developed for use in the 2011 edition of the Canadian Standard for "Selection, Use and Care of Respirators", CSA Z94.4-11. This is for use where workers may encounter airborne biological hazards without exposure limits and where exposure measurement is not straightforward.

The selection method uses a semi-quantitative assessment of critical factors in bioaerosol exposure and their combination to recommend an appropriate respiratory protection level. Three factors are involved in the 2011 method: the hazard of bioaerosols in the exposure environment according to US National Institutes of Health rating; their generation rate and the control measures in place – notably ventilation. Each is assessed on a four-level scale, converted to a score and these are combined in an algorithm to determine a recommended protection level which directs the user to a range of choices of respiratory protective equipment. The procedure has been calibrated to match existing published guidance as far as possible, and it usefully fills gaps and addresses a wider range of potential exposure situations. Since issue of this standard, a similar protocol with some differences has been developed and adopted by the Province of Québec.

The selection protocol in the Canadian standard is now being updated with building of an evidence base to identify needed changes, improve guidance and to incorporate of additional data through several activities:

- User Survey: A wide-ranging survey was undertaken of users of the Canadian standard and those in workplaces where it is not used but where it is appropriate for the selection guidance to be followed. It included assessment of the nature of the workplace, classification of bioaerosols encountered, types of protective equipment used, the extent of application of a respiratory protection programme including training and fit testing. A total of 414 responses was received. Among many things, the survey illustrated the level of understanding of the current standard and deployment of applicable training and fit testing in key sectors such as healthcare, and the correlation of respiratory protection usage with the hazard level of bioaerosols present in various workplaces. The outcomes will be used to focus updated information on critical respirator programme requirements and the targeting of examples and training materials.
- Critical Appraisal of the Literature: building of an evidence base for the selection guidance was undertaken through a comprehensive literature search to establish supporting data for nine key questions. These covered:
 - Aspects of respirator usage in workplaces involving biological aerosols and the corresponding incidence of infection or adverse health effects including proper fit and donning/doffing;
 - Influence of respirator type on infection resulting from bioaerosols in the workplace;
 - Evidence for the effect of dispersion process, ventilation and the physical characteristics of bioaerosols on workplace infection or adverse health effects.
 - Specific publications were subjected to critical appraisal in which the relevance and quality of key research was evaluated and summarized.

Bioaerosol Concentration Measurements: determination of ranges of biological aerosol concentrations were made for various types of workplaces in Canada between 2001 and 2017; additional studies from the United States have been identified and incorporated to the database in the guidance.

Bioaerosol Persistency on Inanimate Surfaces: published data were collated to provide guidance on the viability of biological agents on surfaces.

All of these studies are being used to revise the respirator selection method and associated guidance. Twenty scenarios have been developed to provide examples to aid users, and correspondence with existing guidance demonstrated where available. The literature survey indicated that there have been limited suitable studies correlating acquired infection to respirator usage or not, but the current selection method is basically supported. The studies above have also been used for a comprehensive revision of the risk assessment requirements with respect to workplace exposure, including division of the assessment into protocols for chemicals, non-infectious and infectious bioaerosols.

The improvements in risk assessment and selection protocol combine to improve the guidance of workers and the selection of respiratory protection and so contribute to reduction of avoidable adverse health effects.

9.3 AEROSOL TRANSMISSION OF INFECTIVE AGENTS: POSSIBLE IMPACTS

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Background and Aims: Aerosol transmission of infective agents has been considered as the most effective way of their dissemination that can produce mass casualties because the airborne pathogens may disperse over great distances and be inhaled, ingested, or come into contact with susceptible individuals (Mohr, 2005). Their release could go undetected for hours or days. According to the particle diameter we could delineate between airborne ($\leq 5\mu$ m) and droplet (> 5μ m) transmission (Fernstrom&Goldblatt, 2013). The infective aerosol particles up to 100 µm they can be inhaled into the oronasopharynx, while the smaller particles < 10 µm penetrate into the trachea and lung (Radakovic et al, 2014). Aerosol derived pathogens present a unique challenge in infection control in the environment, health care facilities, office buildings, travel and leisure settings (Roy, 2010) as well as for biodefence because many possible B agents could be transmitted by aerosols (smallpox, variola, Ebola, Marburg, influenza, SARS, anthrax etc.) (Ristanovic, 2015). Our aim is to discuss all the risks of aerosol transmission of infective agents, its possible consequences and considerations as well as prevention procedures.

Methods: Critical review analysis based on the knowledge, literature data and own experience .

Key results: It is particularly important to understand the basic principles of aerobiology and physics due to which infectious particles can be transmitted as well as microbiological characteristics of infective agents and possible consequences of their spreading across office buildings, hospitals, travel/leisure settings in order to develop adequate prevent and control measures. The modern era of bioterrorism pose a new light on these considerations.

Conclusions: The airborne transmission of infectious disease is a problem considering public health, infection prevention, hospital-acquired multiresistant infections as well as biodefence. In the lack of new expensive technologies, high-efficiency filtration remains the most widely deployed technology for this purpose.

Key words: infective agents, aerosols, particles, transmission

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10. ADVANCES IN PM CHARACTERIZATION II

10.1 DEVELOPMENT OF REAL-TIME REACTIVE OXYGEN SPECIES MONITORS

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WHO has estimated that atmospheric pollution is responsible for more than 7 million premature deaths each year. A large contributor to this mortality is due to atmospheric particulate matter (PM), with PM being linked to lung cancer, cardiovascular disease, and lung disease. A proposed mechanism to explain these health outcomes is through oxidative stress, wherein PM generated through combustion processes introduce a group of free radicals known as reactive oxygen species (ROS) to the body. These ROS impede cell function creating oxidative stress, which can lead to inflammation and cell death.

To investigate this hypothesis, instrumentation to accurately measure PM ROS concentrations (oxidative load) is essential. The ideal system should be: sensitive to a wide range of species; collect ultrafine PM with high efficiency; and collect and measure rapidly. Quantification of ROS is a difficult problem both chemically and physically. In order for measurement to take place, PM containing ROS must in most cases be collected into a liquid containing a chemical probe. The degree to which this probe reacts with the PM sample is measured in order to ascertain a value for the concentration of ROS, which is termed oxidative load.

Several systems have been developed to address this, using both commercially available and in-house designed instrumentation coupled with a variety of chemical probes for the detection of ROS. Some probes, including POHPAA, ascorbic acid, and DTT, are only sensitive to narrow ranges of ROS species; making them unsuited for quantification of total ROS activity (Fang et al, 2015; Zhou et al, 2017). DCFH-DA combined with a horse radish peroxide (HRP) catalyst is currently one of the most commonly used ROS probes in literature (Huang et al, 2016; Fuller et al, 2014). In addition, an in-house designed probes based on profluorescent nitroxides (PFN) have also been used (Stevanovic et al, 2012).

Beyond the implementation of a chemical probe, there are several properties of ROS and combustion aerosols which make oxidative load measurements difficult. The high reactivity of ROS causes them to react readily with the atmosphere and other surroundings; leading to ROS on ultrafine particles having estimated half-lives of under 15 minutes. Therefore, delays between capture and measurement typical of filter collection methodologies can lead to significant underestimations in ROS concentrations. This indicates that the best approach for ROS measurement is to collect particles directly into liquid for analysis. This further complicates the process as particles from combustion process are predominantly in the ultrafine size range (< 100 nm) and can be very hydrophobic. These attributes make direct collection into liquid a difficult process.

In this presentation an overview of the current real-time methods for ROS measurements will be presented with a critical overview of their characteristics and performance. Results on a prototype system based on the in-house developed PFN probe will be presented.

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10.2 COMPARISON OF LOW-COST AND CONVENTIONAL PM SIZERS AND COUNTERS IN INDOOR AMBIENT ENVIRONMENT

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Aim: Low cost particulate matter (PM) sensors can potentially bring PM level monitoring to a much wider audience, thus providing relevant information, at affordable cost, to all interested stakeholders. However, there are a lot of unknowns about low cost PM sensors and their performance compared to lab-grade equipment (Tasić, 2016). Aim of this work was to explore potential of several low cost sensors as reliable PM monitors. The definition of term low cost sensor itself can be somewhat ambiguous, and in this work we opted for more inclusive definition i.e. we use the term for either commercially available low cost instrument or for prototype that includes barebone sensor and supporting electronics.

Method: Several low cost sensors and lab-grade instruments were collocated in laboratory office space in Institute Vinca and the results were collected for few weeks in the period November-December 2016. Low cost instruments included two Sharp GP2Y1010AU0F compact optical dust sensors connected to Arduino platform, Alphasense Compact OPC sensor and Dylos DC1700 PM unit. Lab grade instruments included TSI NanoScan SMPS Model 3910 (13 channels from 10 nm to 0.4 μ m) and TSI Optical particle sizer 3330 (17 channels from 0.3 μ m to 10 μ m), however in this work only the data from TSI Optical particle sizer was used in order to simplify analysis. All instruments and sensors, except for the Arduino connected optical dust sensor, sampled aerosol via internal pump, while the Arduino dust sensor used internal thermal resistor to increase aerosol flow. Time resolution of instruments was set to 1 minute, which for Arduino dust sensor required averaging of about 40 samples per minute.

Results: Cross-correlation matrix of all relevant signals was done as a part of exploratory analysis (Fig. 1a)



Figure 1. (a) Cross-correlation matrix of normalized measurements: Sharp 1, Sharp 2, Dylos - small particles, Dylos - large particles, TSI OPS channels 1-17, total of 21 individual signals (b) Normalized Arduino and TSI OPS 3330 ch. 1, from 2016-11-29 12h to 12-02 11h.

It can be seen that Sharp sensors have very high correlation ~ 0.98. We can also conclude that signals from Sharp dust sensors are most correlated with channel 1 (0.3 μ m) of TSI OPS 3330 ~ 0.75 (signals match quite well, as seen in Fig. 1b), and that correlation steadily decreases toward channel 17. Signal from Dylos – large particles has highest correlation ~ 0.98 with channels around channel 10 of TSI OPS (2.156 μ m). Alphasense CompactOPC results were not included in Fig. 1a because they correlate extremely well with corresponding TSI OPS 3330 channels, above ~ 0.90 for almost all channels.

Conclusion: Low cost sensors showed potential to measure certain ranges of particle sizes with very high accuracy. Sharp dust sensors had high reliability and consistency among themselves, and correlated to particle sizes meas. in 0.3um - 1.4um range. Note that normalized values were compared and that real word deployment would require separate calibration of each sensor, due to differences in absolute levels among signals.

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10.3 ARTIFICIAL INTELLIGENCE MODELS WITH MULTIVARIATE INPUTS FOR CALIBRATION OF LOW COST PM SENSORS

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Aim: Particulate matter (PM) level and content in ambient air have been recognized as an extremely important factor that may cause negative effects on the human health and environment (Ghio and Huang, 2004). Sometimes PM may contain toxic compounds, which contribute, in various ways, to their potential for inducing negative health effects (Schwarze et al., 2006). In order to examine the PM exposure and health effects as reliable as possible, monitoring systems need to be improved. In order to be convenient for collecting data with high spatial and temporal resolution it is especially important that novel devices have small dimensions and to have affordable calibration and maintenance procedure. On the other hand, novel PM devices aim for as much as possible in stability, selectivity and sensitivity, having characteristics of reference/equivalence monitors required by current legislation and standards (EC, 2008) as long-term ambitious goal.

Method: This paper presents the results of testing sophisticated calibration models for improving the measurement properties of low cost sensors for $PM_{2.5}$ and PM_{10} fractions that are embedded in the AQMESH devices (http://www.aqmesh.com/). AQMESH PM sensors are optical sensors with the ability to detect number concentration, which can then be readily converted using on-line system to $PM_{2.5}$ and PM_{10} mass concentration. During 2015, we performed two consecutive data collecting campaigns using 25 AQMESH platforms co-located with reference/equivalence PM monitors located in Belgrade and belonging to National Network: Zeleno Brdo – ZB (21.4.-7.7.) and Stari Grad – SG (14.7.-16.10.).

Results: A multi-dimensional approach was applied for calibration of PM low cost sensors. Artificial neural networks (ANN's) were used to develop calibration models which establish best dependence between input and output signals. Also, several multivariate linear regression (MLR) models have been developed for comparison with ANN's. For ANN models, the input parameters were selected by calculating partial mutual information by forming a mixed embedded vector. This vector is formed through a progressive embedded algorithm based on the conditional mutual information (Vlachos & Kugiumtzis , 2010; Kugiumtzis , 2013). The performance of the developed models was tested using standard statistical tests which are shown in Table 1.

Conclusion: ANN models for 25 AQMESH sensors collocated in same period at reference stations give better results than MLR models. ANN's, unlike MLR's, have demonstrated the ability for automatic modeling of non-linearities and a greater adaptability when environmental conditions are changed.

Model	AMS	R	RMSE	MGE	NMGE
Mmlr,pm2.5	ZB	0.67	1.14	0.83	0.48
	SG	0.81	4.28	3.14	0.26
MANN,PM2.5	ZB	0.83	1.03	0.76	0.38
	SG	0.90	3.25	2.37	0.20
MMLR,PM10	ZB	0.75	3.41	2.36	0.24
	SG	0.85	7.52	4.95	0.17
MANN,PM10	ZB	0.86	2.71	1.88	0.19
	SG	0.88	6.82	4.60	0.16

Table 1. Results of calibration AQMESH PM sensors collocated at ZB &S G with built MLR & ANN models

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10.4 ANALYSIS OF PARTICULATE MATTER AND SMALL ION CONCENTRATIONS IN INDOOR ENVIRONMENT BASED ON BALANCE EQUATION

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Aim: Aim of this work was to explore a relation between particulate matter (PM) and small (cluster) air ions (SI) concentration in a typical indoor environment. Changes in SI concentration are due to several factors. First, SI are constantly created, in pairs, by ionizing radiation that exists in the environment. They are also continually destroyed in processes of recombination, attachment to aerosols (PM) and deposition on electrostatic surfaces. Because of this, a change in PM concentration directly results in a change in SI concentration. SI balance equation can be used to quantitatively describe above mentioned processes.

Method: Wide range of relevant air quality parameters were measured in indoor environment, occupied on work days, in March 2017. The measurements included negative SI measurements by Gerdien-type air ion detector (Kolarz, 2012), PM concentration in 10 nm to 10 um diameter range using TSI NanoScan SMPS Model 3910 and TSI Optical particle sizer 3330, gravimetric measurements of particles in 3 fractions, and local temperature, pressure and humidity. In addition, hourly radon concentration measurements describe steady state, radon concentration gives insight into rate of volumetric ion pair generation and 1 minute PM measurements give insight into main loss mechanism for SI.

Results: Relation between negative SI concentration and PM concentration was derived using quasi steady state approximation of SI balance equation. Form of this relation suggests that the use of linear regression in modelling is sound and well justified approach, and that the regression coefficients can be interpreted as ion-particle attachment coefficients. Since there was a large number of individual channels (13 Nanoscan and 16 OPS channels), with significant cross correlation, ordinary least squares was not a reliable method, producing unphysical results. To ensure regression coefficients have physical meaning we used non-negative least squares solver (Lawson, 1995), and aggregation of channels into total counts and typical PM fractions. Results are shown in Fig. 1.



2017-03-21 2017-03-22 2017-03-23 2017-03-24 2017-03-25 2017-03-26 2017-03-27 2017-03-28 2017-03-29

Figure 1. Comparison of negative small ion measurements and 3 models based on total counts and PM fractions **Conclusion:** All models show daily variations of ion concentration, however, it seems that models are prone to overestimation, which occurs in periods of low particle counts, which are inherently less accurate. In the case of a model based on total counts, attachment coefficient is estimated to be 8.45e-06 cm3 s-1. Note, however, that interpretation of regression coefficients as attachment constants is somewhat approximate, since there is a significant correlation between individual channels.

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10.5 CURRENT STATUS OF APPLICABILITY OF LOW-COST PARTICULATE MATTER SENSORS FOR AMBIENT AIR POLLUTION AND EXPOSURE ASSESSMENT

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Clean air is considered to be a basic requirement for human health and well-being. More than 85 % of population nowadays lives in areas where the level of regulated air pollutants are far above the WHO air quality (AQ) guidelines values. Such situation is in most European cities [EEA, 2015] and therefore citizens in Europe are at risk to be exposed to potentially harmful levels of air pollutants. In addition, Serbian Environmental Agency (SEPA) reported that more than 30% of citizens of Serbia were exposed to air that is considered not healthy in 2014. In recent years 85% of exceedance of main air pollutant that was evidenced at the Serbian Air Quality State Network was attributed to particulate matter (PM) pollution.

In this paper we review recent research activities in development, testing and application of PM low-cost sensors. There are many challenges related to measuring PM, but they still need to be quantified in order to control emissions, which contribute to improving the quality of indoor and outdoor air. The information on AQ and related hazards is currently mostly generic, and seldom personally relevant. It would be necessary to offer information to a person about AQ level in microenvironment, on the route and what does that mean for her/him. By using affordable personal monitors or by establishing a dense network of monitoring units, in which low-cost sensors for various air pollutants including PM fractions are embedded, AQ monitoring gains novel and innovative tools ready for future challenges.

PM sensors integrated in units are typically based on optical particle counters, and usually do not detect particles smaller than 0.3 µm. First generation was able to detect the amount of opacity, while newly developed sensors detect PM2.5 and PM10. Some of them stated that they may measure particles in different particle sizes, [Sousan et at, 2016]. However, there is a disparity in the scientific literature related to PM low-cost sensors performance assessment including calibration procedure, which makes it complex to evaluate the quality of sensor data obtained in different studies and to make comparisons between them [Rai et al. 2017]. Results for same sensor when tests were performed in laboratory and in field conditions may be very different. E.g. in office indoor environment, we compared Alphasense OPC N1 to TSI OPC 3330 device and obtained the same results as in the low-cost sensor datasheet. Sousan et at [2016] for the first time test detection efficiency of Alphasense OPC N1 in control test atmosphere: chamber with NaCl generated polydisperse aerosol, welding fume and ARD. The number concentrations measured with the OPC-N2 agreed fairly well to those measured with the PAS-1.108 and two reference instruments for coarse particles, but underestimated number concentrations for sub-micrometer particles. Mass concentrations from both OPCs firmware were highly linear with the reference instruments, coefficient correlation R>0.97. In EPA field study [2017] it was reported that R between OPC N2 sensor integrated into a prototype UN multi-pollutant sensor pod, collocated in duration of 1 month next to GRIMM EDM 180 monitor, were 0.08 and 0.1 for PM2.5 and PM10 respectively. We obtained similar results for mass concentration during collocation in the field of twelve AS510, Atmospheric Sensors, nodes with integrated OPC N2 sensors with GRIMM EDM 180 monitor. Between twelve low-cost devices and one reference monitor R was in the range 0.03-0.34 and 0.05-0.23 for PM2.5 and PM10 respectively. While R within twelve AS510 nodes varied between 0.52-0.86 (PM2.5) and 0.50-0.80 (PM10).

As the discrepancy in the performance of these sensors in laboratory and field studies is rather large, common procedure for assessment of their performance is necessary to be able to apply low-cost PM sensor as a personal monitor or to establish a large-scale sensor network.

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AUTHOR INDEX

Author	Section(s)
Adamović, D.	6.3
Adamović, S.	6.3
Aničić Urošević, M.	6.4
Arandjelović, M.	7.2
Atanasievska, S.	9.3
Baloš, S.	6.3
Bartoňová, A.	4.2, 10.3, 10.5
Bengalli, R.	3.4
Bešlić, I.	1.4
Bischof, O.F.	6.6
Božilov, A.	6.9
Broday, D.	2.5
Brown, R.A.	10.1
CITI-SENSE Consortium	4.3
Camatini, M.	3.4
Castell, N.	4.2
Ciglenečki, I.	2.1
Cocić, M.	1.5
Cvetković, A.	1.2
Cvitešić, A.	2.1
Dahlkötter, F.	6.6
Dauge, F. R.	4.2
Davidović, M.	6.7, 8.4, 10.2, 10.3, 10.4, 10.5
Deljanin, I.	2.4
Dikanović, S.	1.2
Dramićanin, M.	6.3
Dubroecq, S.	6.6
Frka, S.	2.1
Gagic, R.	8.2
Glogovac, J.	9.1
Godec, R.	1.4
Grossberndt, S.	4.2
Ignjatović, Lj.	2.2
llić, L.	5.3
Janjatović, P.	6.3
Janjić, O.	6.8
Janković, M.	6.4
Jarosinska, D.	4.1
Jovanović, M.	6.5
Jovanović, M. V.	6.7
Jovanovic-Andersen, Z.	
Jovasevic-Stojanovic, M.	1.2, 1.3, 0.7, 8.4, 10.2, 10.3, 10.4, 10.5
	0.3
JOVOVIC, A. Korličić N	0.2
Karlicic, IN.	0.2
ΝΙΖΟΙ, Γ. Κποτονιά	2.J 6.5
Kildzevic, J.	0.5
Kounan, D.	4.5 0 1
Kovacevic, I.	7.1
Kovačević, R.	1.3, 1.5
---------------------------------	---------------------------
Kuzmanoski, M.	5.3
Lazović, I.	1.5, 6.10
Longhin, E.	3.4
Manojlović, D.	1.3
Mantecca, P.	3.4
Marchetti, S.	3.4
Maric, J.	9.1
Marić–Tanasković, L.	6.5
Matijević, D.	1.2
Matić, B.	6.8
Mijić, Z.	5.3, 5.4, 6.1
Milićević, T.	6.4
Mirkov, N.	6.1
Morais, S.	2.3
Močnik. G.	1.1
Mudu. P.	3.1. 4.1. 7.3
Ničković. S	5.1
Nikolic, D	8.2
Nikolić. M	2.4
Nikolić M	3372
Obradović M	62
Onija A	2.2
Paunovic E	4 1
Perišić M	54 61
Popović A	6.4
Predrag Kolarž	10.4
Protic-Diokic V	93
Radakovic S	9193
Radić D	62
Radonić I	63
Padonija 7	0.3 8 2
Radonjic, Z. Padagavljavić I	0.5
Dalzić II	3.2
Rakic, U. Distanovia E	0.1, 0.0
Ristanović, E.	5.1, 5.5 6 7 10 1 10 5
RISLOVSKI, Z. D.	0.7, 10.1, 10.3
Robinson, J. A.	4.5
Sam D	2.4
Sari, D.	5.2
Savic, J.	0./
Schweiden D	0.0
Schneider, P.	4.2
Smith, S.J.	9.2
Spielvogel, J.	6.6
Stamenkovic, I.	6.9
Stanisic Stojic, S.	0.1, 8.1
Stankovic, A.	5.5, 7.2
Stanojevic, M.	0.2
Stevanovic, S.	0.7, 10.1
Stević, N.	2.4

Stojić, A.	5.4, 6.1, 8.1
Tambur, Z.	9.1
Tasić, V.	1.3, 1.5, 2.1, 6.8, 6.10
Telenta, B.	8.3
Todorović, D.	6.2
Todorović, M.	5.3
Todorović, Ž.	2.2
Tomašević, M.	2.4
Topalović, D. B.	6.7, 8.4, 10.2, 10.3, 10.4, 10.5
Tritscher, T.	6.6
Turanjanin, V.	6.1
Urošević, M. A.	2.4
Viša Tasić,	10.2
Vukadinović, A.	3.2
Vukicevic, M.	8.2
Vuković, G.	2.4, 5.4, 6.4
Vuković, N.	1.2
Yang, H.	4.1
Zerboni, A.	3.4
Zivanovic, A.	9.1
Özkurt, N.	5.2
Čačković, M.	1.4
Đorđević, A.	3.2
İncecik, S.	5.2
Šega, K.	1.4
Šimić, I.	1.4
Šoštarić, A.	1.2, 5.4
Živković, M.	1.5
Živković, N.	6.9