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Milena Jovašević-Stojanović
and Alena Bartoňová, eds.

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Particulate Matter: Research and Management,
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Milena Jovašević-Stojanović
Alena Bartoňová

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ATMOSPHERIC PARTICULATE MATTER - PHYSICAL AND CHEMICAL PROPERTIES

- *sources and formation of particulate matter*
- *particulate matter composition and levels outdoors and indoors*
- *environmental modeling*
- *nanoparticles in the environment*

PARTICULATE MATTER AND HEALTH

- *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*

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. Atmospheric particulate matter arises both from primary emissions and from secondary formation in the atmosphere. It is one of the least well-understood local and regional air pollutants, has complex implications for climate change, and is perhaps the pollutant with the highest health relevance. It also poses many challenges to monitoring.

By WeBIOPATR, we aim to link the research communities with relevance to particulate matter with the practitioners of air quality management on all administrative levels, in order to facilitate professional dialogue and uptake of newest research into practice. The workshops usually draw an audience of about 70, and attract media attention in Serbia. It enjoys support of the responsible authorities, Ministry of Health, Ministry of Environment, and the Serbian Environmental Agency whose sponsorship is indispensable and gratefully acknowledged. We enjoy also support of international bodies such as the WHO.

The 1st WeBIOPATR Workshop was held in Beograd, 20.-22. May 2007, associated with a project funded by the Research Council of Norway. The 2nd workshop was held in Mecavnik, Serbia, 28.8.-1.9. 2009. WeBIOPATR2011 was held in Beograd 14.-17. 11. 2011 and for the first time, included a dedicated student workshop. WeBIOPATR2013 was held in Beograd 2.-4. 10. 2013. It covered the traditional PM research and management issues, discussions on how to encourage citizens to contribute to environmental governance, and how to develop participatory sensing methods. WeBIOPATR2015 was held in Beograd 14.-16.10. 2015. Own sessions were devoted to sensor technologies for air quality monitoring, utilizing information and input from the EU FP7 funded project CITI-SENSE (http://co.citi-sense.eu) and the EU COST action EuNetAir (www.eunetair.it).

We have now the pleasure to present to you the proceedings of the 6th conference held in Beograd 6.-8.9. 2017. We are excited to have contributions from old friends and new acquaintances, and we are especially pleased with a wider than before Western Balkan participation. The contributions were reviewed. The language editing was performed by Dr Simon Smith, PhD, to whom we would like to extend out sincere thanks. Technical manuscript preparation was graciously done by Dr Milos Davidovic, PhD, to whom we are very grateful.

We are hoping that you, the reader, will extend your support to WeBIOPATR also in the future. The issues of atmospheric pollution, with their wide implications for climate change, human health and ecosystem services, are no less important today than before. Addressing them requires a strong scientific community and commitment of all societal actors. Your contribution will make a difference.

Milena Jovašević-Stojanović and Alena Bartoňová

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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 PARTICLE-ASSOCIATED POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) IN THE VICINITY OF A STEELMAKING INDUSTRY (SMEDEREVO, SERBIA)

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ABSTRACT

Particle-associated polycyclic aromatic hydrocarbons (PAHs) concentrations were analyzed in ambient air, in a residential region of Smederevo city, a site with strong influence of industrial activities of a steelmaking industry located nearby. PM_{10} were analyzed for a total of 16 PAHs by Gas Chromatography with Mass Selective Detector. In the period November 2016 - July 2017, 185 particulate matter (PM) samples were collected.

Campaigns were performed in cold periods where officially heating is used (H), October 15th to April 15th (116 samples) and in warm periods where heating is not required (NH), April 15th to October 15th (69 samples). The total PAH concentration in the campaigns was 59.38 ng/m^3 in heating and 5.77 ng/m^3 in non-heating seasons. This is similar to concentrations measured during campaigns performed in the period 2012-2014. High molecular weight PAH (including 4-6 rings) species occurred in the high fractions. Toxic equivalent factors analysis gave the potential carcinogenic risks in ambient air in a residential area of Smederevo. Health risk assessment (BaPeq value) showed that the most negative impact was found in H season - 9.52 ng/m^3 while in NH it was 1.00 ng/m^3. By diagnostic ratio analysis, traffic emission and combustion (coal or wood) were potential sources for PAHs at this sampling site. The ratio of InP/(Bpe +Inp) and Baa/Chr was 0.46 during both seasons and 0.91 and 0.67 during winter and summer seasons while Ant/(Ant+Phe) was 0.19 and 0.15, respectively. For coal combustion, the BaP/Chr ratio was above 0.5 (0.8 in NH and 1.25 in H season). The highest value for cancer risk we obtained in H (0.00083) was 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). Finally, a Positive Matrix Factorization (PMF) receptor model was used to identify potential sources of PAHs and to determine their mass contribution to total PAH concentrations. Three potential groups of sources were identified: (1) traffic-diesel and gasoline exhaust, (2) stationary sources, (3) wood combustion and coal combustion. The contribution of traffic was 44.4% and 36.6%, stationary sources 36.9% and 50.4% and combustion (wood and coal) 18.8 and 13.1% during non-heating and heating seasons, 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.

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

INTRODUCTION

Air pollution has the potential to affect the environment, human health and ecosystems at all scales. It can cause adverse health effects, local and regional environmental damage and global problems such as climate change, loss of biodiversity: it is a complex problem posing multiple challenges in terms of management and mitigation of harmful pollutants. According to EEA, 2016, the obtained results indicate that air-quality policies have delivered many improvements.

Reduced emissions have improved air quality in Europe but a large proportion of European populations and ecosystems are still exposed to air pollution that exceeds European standards and, especially, World Health Organization (WHO) Air Quality Guidelines (AQGs). For example, concentrations of particulate matter (PM) continued to exceed the EU limit and target values in large parts of Europe in 2014 (EEA,2016).

For PM with a diameter of 10 μm or less (PM_{10}), concentrations above the EU daily limit value were registered in 21 of the 28 EU Member States and for PM with a diameter of 2.5 μm or less ($PM_{2.5}$), concentrations above the target value were registered in four EU Member States. A total of 16 % of the EU28 urban population was exposed to PM_{10} levels above the daily limit value and approximately 50 % was exposed to concentrations exceeding the stricter WHO AQG value for PM_{10} in 2014. Regarding $PM_{2.5}$, 8 % of the urban population in the EU28 was exposed to $PM_{2.5}$ levels above the EU target value and approximately 85 % was exposed to concentrations exceeding the stricter WHO AQG value for PM $PM_{2.5}$ in 2014 (EEA, 2016).

The decrease in PM_{10} concentrations was particularly marked in Italy, Portugal and Spain. In Poland, an average increase in PM_{10} concentrations was registered in rural background stations, while urban stations registered an

average decrease. In other countries there was no statistically significant average increasing trends in $PM_{10.}$ Exposure to benzo[*a*]pyrene (BaP) pollution is quite significant and widespread, in particular in central and eastern Europe. Only 20 Member States reported measurements of BaP with enough valid data in 2014 (EEA, 2016). More than one-third of the reported BaP measurement stations in Europe had values above the EU target value in 2014, mostly in urban areas. About 24% of the European urban population was exposed to BaP annual mean concentrations above the European target value in 2014 and about 88% to concentrations above the estimated reference level.

Air pollution continues to have significant impacts on the health of Europeans, particularly in urban areas. Estimates of the health impacts attributable to exposure to air pollution indicate that $PM_{2.5}$ concentrations in 2013 were responsible for about 467.000 premature deaths originating from long-term exposure in Europe (over 41 countries), of which around 436.000 were in the EU28 (EEA, 2016).

EXPERIMENTAL METHOD

In the period November 2016. - July 2017. the total of 185 PM samples were collected at one sampling site with huge influence of industry - Smederevo, Serbia. It is a city on the right bank of the Danube, the seat of the Podunavlje District, about 45 kilometres downstream of the capital Belgrade (Figure 1). According to official results of the 2011 census (Statistical Off. of Republic of Serbia, 2014), the city-urban area has a population of 64.105, and 108.209 people live in its administrative area. Among other things, air quality is subject to a huge impact of a steel manufacturing (steel plant, hot and cold mill). Considering the total flow of the Danube through Serbia, the sampling site is located at 1116 km.

All PM_{10} samples were collected, prepared and analyzed as described in previous studies (Cvetkovic et al., 2010a,b). We analysed 16 priority EPA PAHs (EEC, 1999; CEN, 1998; ISO 12884:2000, US EPA 1999).

TEF, BaP equivalent and Lifetime lung cancer risk are also calculated as prepared in previous studies (Akyüz at al., 2008; Knafla et al., 2006 ; WHO, 2000; Cvetkovic et al., 2010a,b).

Figure 1. *Sampling site*

RESULTS AND DISCUSION

The total PAH concentrations in the campaigns performed was 59.54±59.83 ng/m^3 in heating and 5.74±7.94 ng/m^3 in non-heating seasons, which is similar as during campaigns performed in period 2012-2014. Mean concentrations for sum of PAHs were about than 10 times higher in winter than in summer campaign. Seasonal variation of PAHs concentrations were showed on Figure 2.

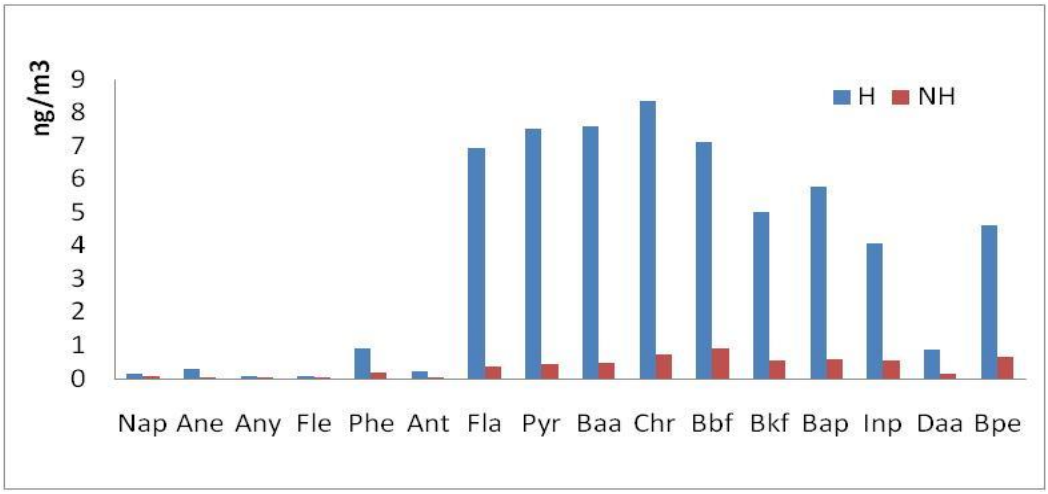

Figure 2. *Mean PAHs concentration during H and NH season*

The sum of total PAH concentrations during previous campaigns (2012-2014) were between 4.83 ng/m^3 and 71.10 ng/m^3 in 2012; 9.45 ng/m^3 and 45.98 ng/m^3 in 2013 and 4.20 ng/m^3 and 62.20 ng/m^3 in 2014 during summer and winter, respectively. In 2012 almost all values for B[a]P in winter season were above the limit value. In 2013 and 2014 only few B[a]P concentrations were above 1 ng/m^3. In 2016-2017, B[a]P total mean concentrations were between 0.59 to 5.77 ng/m^3. About 17 % of B[a]P concentrations were above the limit value during NH (with max value 4.73 ng/m^3). During H season 95% of B[a]P concentrations were above the limit value (with max value 29.30 ng/m^3). These concentrations and seasonal trends are similar in the other studies in urban areas all over the world (Mantis et al., 2005; Akyz et al., 2010; Agudelo-Castaned et al., 2014; Albuquerque et al., 2016).

The total BaPeq value during the winter season was 9.52 ng/m^3, and 1.00 ng/m^3 during the non-heating season. The carcinogenicity activity contribution of B[a]P was about 60 % during both seasons (Yang et al., 2010; Agudelo-Castaned et. al., 2014, Cvetković et al., 2015b). The contribution of DahA was 8.2-11.7% and contribution of Baa 11.1-6.7% during H and NH, respectively (Figure 3).

The highest value for cancer risk we obtained in H (0.00083) was due to the increase emission of PAHs in ambient air and the proximity of a mining industrial complex. All values for the lifetime cancer risk were above the target individual lifetime risk, which is 10-6 (US EPA, 2012) (Figure 4).

The PAH diagnostic ratio was used for identification of potential emission sources (Rogge et. al.,1993. ;Khalili et .al. 1995; Simick et al., 1999.; Tang at al., 2005 ; Akyuz and Cabuk et al., 2010; Yunker et al., 2002; Kim at al., 2003; Zencak at al., 2007; Toiszewski and Nameisnik, 2012). According to the PAH diagnostic ratio Ind/(BghiP+Ind): 0.45-0.47 (2012-2014) and 0.47 during H and 0.46 during NH in this study and BghiP/Ind: 1.1 **diesel** was dominant emission source at Smederevo. The ratio of Flt/(Flt+Pyr) and BaA /Chry was 0.48(H), 0.47 (NH) and 0.91(H), 0.67(NH) (in previous study:0.46-0.48 and 0.65-1.11) have shown that **gasoline** has also significant impact to source emmisionfor PAHs in air in both seasons. **Coal combustion** was dominant source in the winter season in all period (the ratio of B[a]P/BghiP was 1.25 (H) and 0.91(NH) while in previous study was 1.11-1.45). Ratio Ant/(Ant+Phe) confirm impact of **wood combustion** in both season in both campaigns (>0.1).

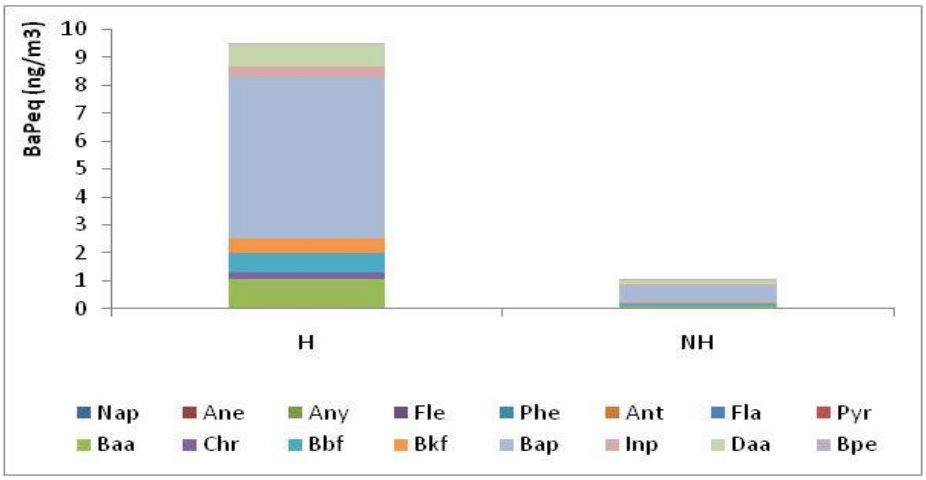

Figure 3. *The carcinogenicity activity contribution of individual PAHs*

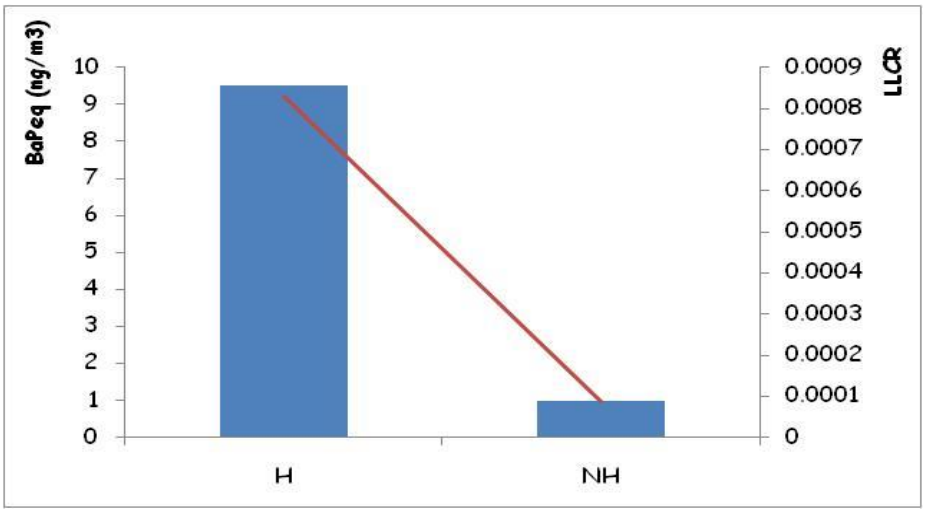

Figure 4. *Lifetime lung cancer risk and BaPeq*

In this paper we established a new PAH ratio: B[a]P/(BkF+BfF). It was 0.48 in H and 0.40 in NH; in the previous study it was from 0.34-0.46 at Smederevo and 0.34-0.43 at Obrenovac, a site with huge influence of stationary sources. As a conclusion we can say that new established ratio of PAH is B[a]P/(BkF+BfF) with values 0.3-0.5 for stationary sources.

PMF application confirmed this conclusion for emission sources: we determined the mass contribution of potential factors to total PAH concentration (Paatero,1999; Hopke, 2001; Polissar et al., 1998; Watson at. al., 2004). Some PAHs are markers for source emission and we used literature data for identification emission sources (Abrantes et al., 2004; Ho et al., 2002; Harrison at al., 1996; Lee et al., 2004; Howson and Jones, 2010; Boostrom et al., 2002; Ravindra et al., 2008; Riddle et al., 2007; Wang et al., 2009; Teixeira et al., 2012; Da Rocha et al., 2009; Martins et. al., 2012; Park et al., 2011; Jang et al., 2013; Papageorgopoulou at al., 1999; Akyüz at al., 2008; Yang et al., 2010; Mostert et al., 2010; Kulkarni and Venkataraman, 2000; and also traffic Roge et al., 1993; Khalili et al., 1995)

Three potential groups of sources were identified: (1) traffic-diesel and gasoline exhaust, (2) stationary sources, (3) wood combustion and coal combustion. The contribution of traffic was 44.4% (2.56 ng/m^3) and 36.6% (21.79 ng/m^3); stationary sources 36.9% (2.13 ng/m^3) and 50.4% (30.00 ng/m^3) and combustion (wood and coal) 18.8% (1.08 ng/m^3) and 13.1% (7.80 ng/m^3) during non-heating and heating season, respectively (Figure 5).

PMF results confirm that the major sources were vehicle emissions, steel industry emissions, and coal combustion for both heating and non-heating seasons, which agreed with the results from the diagnostic ratio analysis.

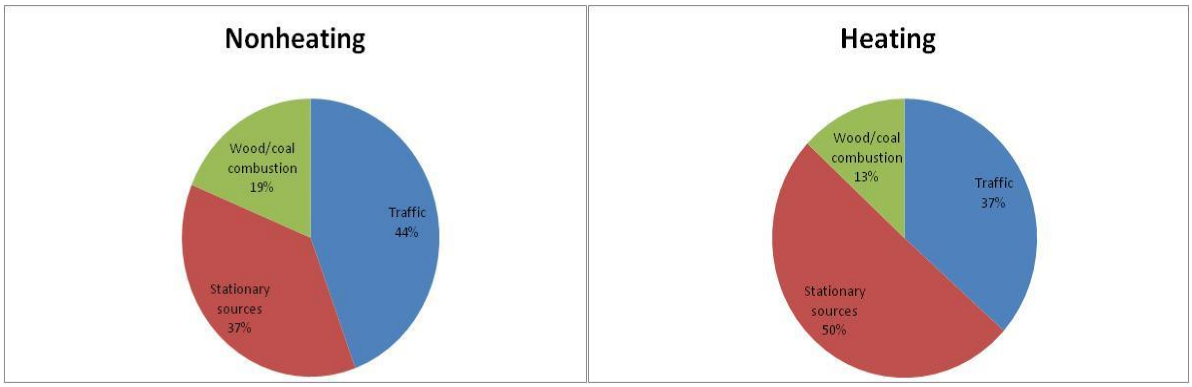

Figure 5. *Identified sources of ambient air pollution at Smederevo im heating and non-heating seasion*

CONCLUSION

This study presents reported long-term measurements of PAHs in the ambient air in Smederevo. The average concentrations of the sum of PAHs as well the as sum of their BaPeq equivalents were about ten times higher in winter than summer. Comparison of ratios of some PAHs with published literature data were used for source diagnosis and proved that stationary sources, traffic, wood and coal combustion could be identified as potential emission sources. Application of PMF to resolve source contribution of 3 different factors has shown that major contributions to total PAH concentrations depend on the sampling site and industry influence. The contributions of stationary sources at Obrenovac, a sampling site with industry influences are sigmilar to Smederevo (14.3% in summer and 40% in winter). Thermal power plants around Obrenovac represent the dominant source of air pollution but there are many heavy-duty vehicles in the thermal power plant complex and influence of vehicle exhaust and resuspended dust is much higher at these places than at sites without influence of industry. As a conclusion at Smederevo the hihgest contribution is: from the stationary sources in winter, about 50%, and contribution from the traffic in non-heating season, 44%.

AKNOWLEDGEMENTS

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

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ABSTRACT

Positive matrix factorization (model EPA PMF 5.0) was used for source apportionment and characterization of PM_{10} collected during the period from September 2009 to July 2010 in the vicinity of copper smelter in Bor, Eastern Serbia. Nine different sources were identified: fuel combustion, industrial dust, dust from tailings, storage and preparation of raw materials, secondary nitrate, Cu smelter, traffic, cadmium and gold drive.

INTRODUCTION

In the framework of the Project 21009 funded by Ministry of Education, Science and Technological Development of the Republic of Serbia**:** "Characterization of respirable particulate matter in outdoor and indoor environment in Serbia" we focused on characterization of particulate matter, PM_{10}, in the vicinity of the industrial complex of mining and metallurgy in Bor, Eastern Serbia. In order to get better insight into particulate matter characterization and emission sources in the vicinity of copper smelter. Positive Matrix Factorization (PMF 5.0) was applied to an outdoor PM_{10} chemical composition data set measured at Bor.

Out-dated pyrometallurgy technology of copper production, utilizing the smelting of the chalcopyrite-pyrite type of ores with increased content of arsenic, is the main source of environmental pollution of large areas surrounding the smelter (air, water, and soil). Industrial activities release gaseous contaminants such as SO_2 and particulate matter into the atmosphere. During last decade several studies have shown increased concentration of SO_2, arsenic and sulphide-related toxic elements in the atmosphere of Bor (Dimitrijević et al., 2009; Kovačević et al., 2010, Djordjevic et al., 2013; Serbula et al. 2010, 2013, 2014; Tasić et al., 2010, 2012, 2017).

An estimated 60% of global anthropogenically-generated atmospheric arsenic is attributed to copper smelting and coal combustion (Matschullat 2000). According to Serbula et al. 2010, one of the highest As concentrations in TSP in the world was recorded in the Bor area (669 ng/m^3). Inhalation exposure to arsenic-bearing dusts and aerosol, in both occupational and environmental settings, has been definitively linked to increased carcinogenic and non-carcinogenic health outcomes (Duker et al., 2006). Inhabitants living in the vicinity of an arsenic emission source have an increased risk of additional exposure through inhalation of arsenic-contaminated particulates (Martin et al., 2014).

No previous study quantified the Cu-smelter contribution to PM_{10} in the Bor region, nor has there been an assessment of source contribution in any industrial area in Serbia. Our study is the first to quantify source contribution using Positive Matrix Factorization applied to analyze outdoor PM_{10} chemical composition data collected in an industrial site in Serbia.

METHODOLOGY

The city of Bor (population about 50000 inhabitants) is located on the Balkan Peninsula, in the eastern part of the Republic of Serbia. This city has a historic relation with mining and metallurgical activities related to the production of copper for more than a century.

The sampling site (a kindergarten) is located downwind of the copper smelter and dumped tailing soils of mining activities and related manufactures (Figure 1). A total of 104 samples were taken between September 2009 and July 2010 by Sven Leckel LVS3 low volume sampler. Filters were weighed and analyzed at the Mining and Metallurgy Institute, Bor. The collected 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. The data were divided into the four observation periods: heating season (HS), non-heating season (NHS), smelter working (SW) and smelter out-of-work (SOW).

Figure 1 *- Location of the sampling site*

In this study, the EPA PMF receptor model (version 5.0) was used for each sampling season separately to identify the major sources of ambient PM_{10} and quantify their relative contributions to total PM_{10} mass. PMF is a factor analysis model that solves the chemical mass balance equations using a weighted least-squares algorithm and by imposing non-negativity constrains on the factors (Reff et al., 2007).

RESULTS AND DISCUSSION

During sampling period the average PM_{10} and SO_2 were 42.0 μg/L and 196.8 μg/L, respectively (Kovacevic et al.,2016)

Source identification was carried out by inspection of key species in each identification factor and by comparison with published source profiles. The following nine sources were identified during campaign: fuel combustion, industrial dust, dust from tailings, storage and preparation of raw materials, secondary nitrate, Cu smelter, traffic, cadmium and gold drive. 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 work (SOW) and when it works (SW), and six factors during the non-heating season (NHS).

The marker species for identified PM_{10} sources and percentage contribution of sources resolved by the PMF model are given in Table 1. Figure 2 a-d shows the factor contributions as a pie chart for the total mass (PM_{10}) during HS, NHS, SW and SOW.

Table 1 *- Summary of the marker species for identified PM_{10} sources and percentage contribution of sources resolved by the PMF model*

Source	**Marker species**	Percentage contribution of individual factors (%)			
		NHS	**HS**	**SOW**	**SW**
Fuel combustion	SO_4^{2-}, NH_4^+, Se, Sn, K, Cd, As	17.8	22	10.2	33.3
Industrial dust	Mn, Ca, Al, Fe, Cr, Ni, Sb, Ti, Mo, As, Cl, Cu	**58.3**	**36.5**	25.6	**38.0**
Dust from tailings	Na, Ti, Sr, Mn, Mg	3	12.2	**30.5**	6.9
Storage and preparation of raw materials	Cu, Fe, Ni, Ag, Mo, Ti, Cr, Mn, As	0.7	9.6	16.1	0.8
Secondary nitrate	NO_3^-, NH_4^+	7.8	1.4	0.3	6.0
Cu smelter	Pb, As, Cd, Cr, Zn, Mn	12.3	9.3	-	11.8
Traffic	K, Mo, PO_4^{3-}, Cd, Pb, Mg, Cl, Se, Ni	-	-	7.7	-
Cadmium	Cd, Pb, As, Cu, Ag, Sb, Se	-	-	-	3.3
Gold drive	Ag, NO_3^-, Sr	-	9.1	9.6	-

The PMF analysis parameters are summarized in Table 2. The model was run 20 times with 6 or 7 factors. During NHS, HS and SOW the Q(robust) values was about 2% lower than the Q(true), indicating no impact of outliers on the Q-value. The Q(robust) was about 15% lower than the Q(true) during SW, indicating some, but not heavy, impact of outliers on the Q-value.

Table 2 *- Summary statistics of the PMF analysis parameters*

PMF analysis parameters	**NHS**	**HS**	**SOW**	**SW**
n	25	24	27	26
m	58	46	61	46
$Q_{teor.}$	952	614	1031	923
f	6	7	7	7
s/w	19/6	11/12	10/16	9/16
b	-	1	1	1
Q_{robust}	1404.0	1096.7	1303.3	1486.3
Q_{true}	1406.4	1112.2	1327.6	1740.9
R^2	0.71	0.80	0.79	0.80
F_{peak}	-0.5	-0.1	-0.4	-0.2

n-number of species, m-number of the analyzed samples, $Q_{teor.}$-theoretical value, f-number of factor, s- number of species with strong correlation, w- number of species with weak correlation, b- number of species with bad correlation, Q_r -Q robust value, Q_t -true value, F_{peak} value

Table 3 presents the slope, intercept, and coefficient of determination (R^2) of the linear regressions between daily resolved measured ambient PM_{10} and estimated PM_{10} mass concentrations, calculated by the sum of PM mass apportioned to each identified factor. It can be inferred that the PMF model was able to effectively estimate the measured PM_{10} mass concentrations during all observation periods (slope varying from 0.79 to 0.94 and R^2 ranging from 0.71 to 0.94).

Table 3 *- Summary statistics of the linear relationship between daily resolved measured ambient PM_{10} and estimated PM_{10} mass concentrations obtained from the PMF model.*

	Equation	R^2
NHS	y = 0.79 x + 4.81	0.71
HS	y = 0.94 x + 2.34	0.94
SOW	y = 0.93 x + 0.56	0.79
SW	y = 0.87 x + 2.85	0.80

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%).

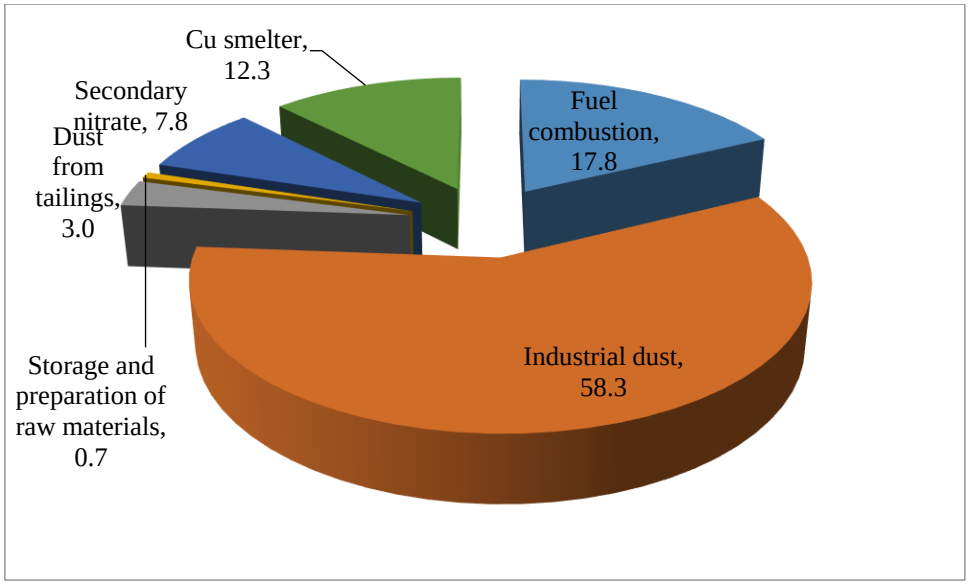

Figure 2a *- Distribution of mass for PM_{10} during NHS*

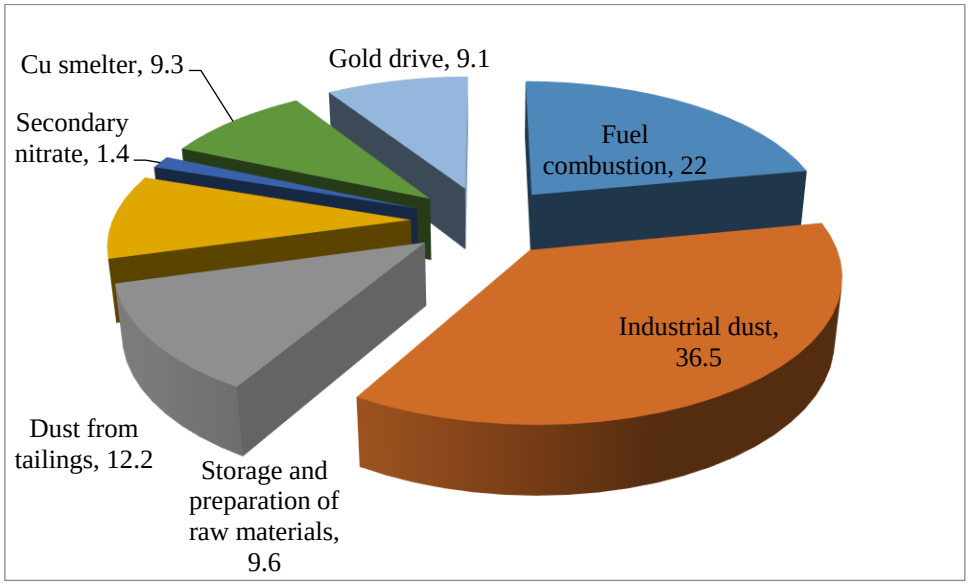

Figure 2b *- Distribution of mass for PM_{10} during HS*

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 periods. The smelter source was absent only during the period when the smelter does not work. The contribution of this source is approximately 10%. Cadmium was isolated as separate source only during the period when the smelter works (3.3%), while the source traffic contributed 7.7% only during the period when the smelter does not work. One more independent source, marked as Gold drive, was identified during the period of the campaign covering processing anode slimes (GS and SNW).

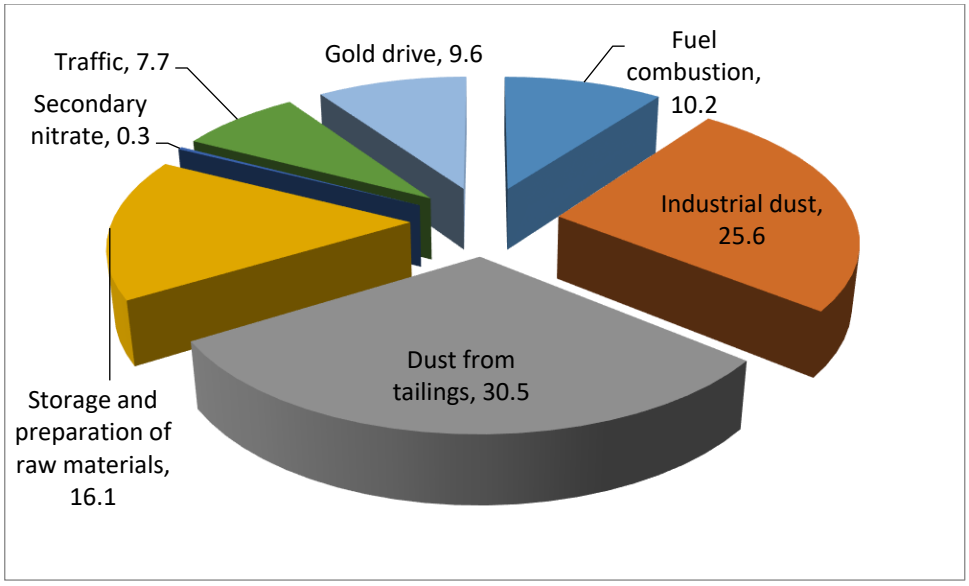

Figure 2c *- Distribution of mass for PM_{10} during SOW*

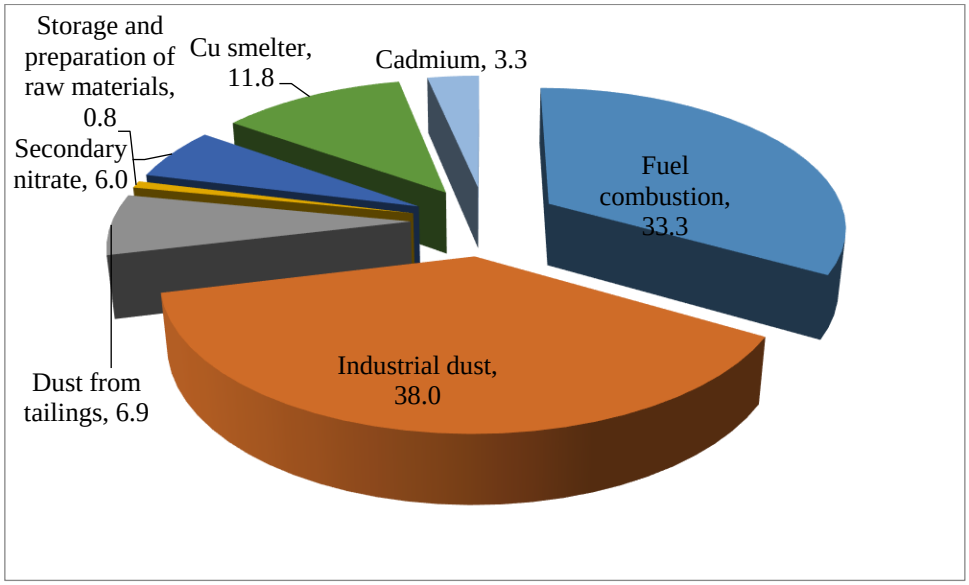

Figure 2d *- Distribution of mass for PM_{10} during SW*

CONCLUSION

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 specific 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 PM_{10} particles emitted from pollution from the RTB complex is 2.3-fold lower (35.8%) compared to the period when the smelter operates.

The overall action plan to reduce PM_{10} concentrations will need to concentrate on local sources as a priority, as reduction of these source strengths will give maximum benefit in terms of lower exposure to air pollution.

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1.4. SPATIAL DISTRIBUTION OF CARBON MASS CONCENTRATIONS IN CROATIA

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ABSTRACT

The purpose of this study was to determine the distribution of carbon mass concentrations in different types of environment in Croatia and to see if carbon mass contributions to overall PM_{10} mass and elemental and organic mass concentrations change with the seasons of the year. The sampling sites (urban background, semi-rural industrial, rural and rural background) were located at four different parts of Croatia. Samples of PM_{10} particle fraction were collected on quartz fibre filters, pre-fired at 900 °C for three hours. Reference samplers were used for sample collection and PM_{10} mass concentrations were determined gravimetrically. Organic carbon and elemental carbon in PM_{10} fraction were determined by the thermal-optical transmittance method. 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 than the concentrations measured in the warmer part of the year.

INTRODUCTION

Particulate matter

The term particulate matter (PM) is a general term used for particles suspended in air for long periods, from several hours to several weeks, even months, caused by various natural or anthropogenic activities. Atmospheric particles originate from primary and secondary sources. Primary particles are those emitted directly from the source, while secondary particles are formed in the atmosphere from gases emitted directly from the source (Pöschl, 2005). PM is characterized according to size, composition, shape, colour, number and balance between the gaseous and the particle phase (Šega, 2004).

An individual particle: a small unit of matter, of a regular shape with a density approximately equal to the intrinsic density of the substance from which it is made.

Aggregate: A group of individual particles that are held together by molecular forces. When moving, they behave like single particles.

Agglomerate: A group of individual particles held together by weaker forces of adhesion and cohesion.

Flocculants: A group of even weaker-bound individual particles that easily breaks by shake or shuffle. When moving, it behaves very differently from individual particles.

Fibres: natural (biological or mineral origin) or artificial origin. The following conditions must be satisfied to define the particle as a fiber: L> 5 μm and L / D> 3 (Figure 1).

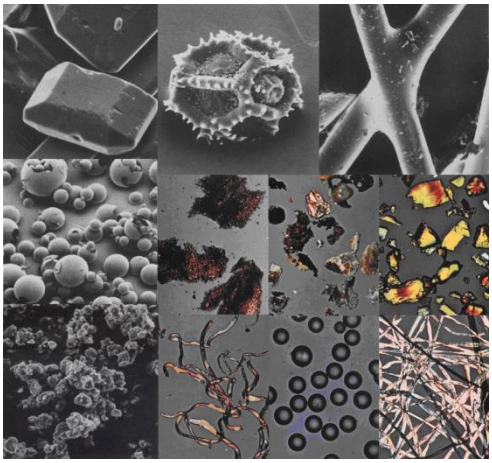

Figure 1. *Picture of different types of particulate matter*

Harmful action of PM on human health can be from minor irritation of the upper respiratory tract to chronic respiratory and cardiovascular diseases, lung cancer, and acute respiratory infections in children and chronic bronchitis in adults, aggravating existing heart and lung diseases, or asthmatic seizures.

Carbon in particles

The main forms of carbon in particulate matter are elemental carbon (EC), organic carbon (OC) and carbonate carbon (CC). EC is a visible component of the PM which is inert, non-volatile, insoluble under atmospheric conditions and may be called soot, black carbon (BC) or carbon that absorbs light (LAC) depending which type of analyses is used for its determination. EC has a large specific surface with adsorbed polluting gases and particles on it. These gases and particles may have carcinogenic and mutagenic properties and that is why we investigate EC; because of potential harmful effects on human health and the environment. EC is a primary pollutant and it is all directly emitted into the atmosphere from various natural and anthropogenic sources, for example: incomplete combustion of fossil and biomass fuels, biomass burning, industrial processes, forest fires, etc. Unlike EC, OC is a fraction of organic matter which is complex and contains hundreds of organic compounds which may have mutagenic and carcinogenic properties. OC can be primary (POC) and secondary (SOC). Sources of primary OC are natural (photochemical oxidation of gaseous organic precursors, emissions of plant, spores and pollen, forest fires, volcanic eruptions) and anthropogenic (combustion of fossil fuels and biomass, etc.). Secondary OC is made by conversion of gaseous pollutants in the air and the condensation of organic compounds onto pre-existing particles (Karanasiou et al., 2015; Kumagai et al., 2009; Mkoma et al., 2010; Park et al., 2012; Pio et al., 2011; Wu and Yu, 2016)(Figure 2).

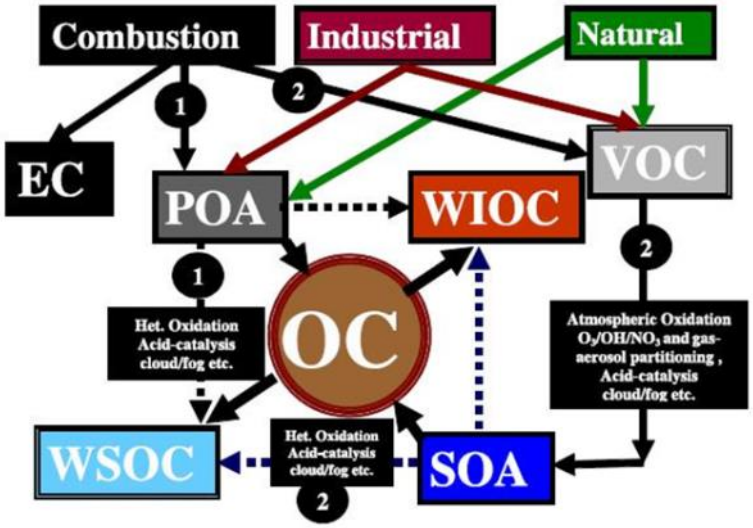

Figure 2. *Mechanisms of sources of EC, OC, primary organic aerosol (POA,) secondary organic aerosol (SOA), water soluble (WSOC) and water insoluble organic carbon (WIOC) in the atmosphere* (Pathak et al., 2011)

The purpose of this study was to determine the distribution of carbon mass concentrations in different types of environment (urban background, semi-rural industrial, rural and rural background) in Croatia and observe if carbon mass contributions to overall PM_{10} mass, as well as elemental and organic mass concentrations, change with the seasons of the year. Furthermore, this was the first time measurements of EC and OC were carried out at rural sites in Croatia and the results are presented here.

METHODOLOGY

Sampling sites and sampling

The sampling sites were located at four different parts of Croatia (Figure 3) and they were defined as:

site **A** - urban background site,

site **B** - semi-rural industrial site,

site **C** - rural site,

site **D** - rural background site.

Sampling site **A** was situated in the yard of the Institute for Medical Research and Occupational Health located in the northern part of Zagreb city, where the main sources of pollution are residential heating and moderate traffic.

The population of Zagreb was about 790,000 inhabitants during measurements. This monitoring station is described as an urban background monitoring station. Site **B** was situated at the north-eastern outskirt of Delnice, away from the town centre and close to the economic zone, 685 m above sea level in the hills of Gorski Kotar. The population of Delnice was 5,952 at the time of measurement. Air pollution at this site originated from wood used as fuel for cooking and space heating, as well as from the local wood pellet industry. The winters there are long and harsh, with abundant snowfall, while summers are short and crisp in the morning and evening. Site **C** is a typical rural place with a small population and low traffic density. It was located in a village in the continental northern part of Croatia with about 1,300 inhabitants. Households mostly use wood as fuel for cooking and space heating. Site **D** was a village situated in eastern Croatia inhabited by around 5,000 people and with air pollution which originated mostly from agriculture.

The number of collected and analysed PM_{10} samples are presented in Table 1, as well the measurement periods for each sampling site. The numbers of samples in which the EC and OC mass concentrations are determined are listed in bold while the numbers of samples for which PM_{10} mass concentration was gravimetrically determined are in brackets.

Table 1. *Number of collected and analysed PM_{10} samples and measurement periods on different sites*

Site	Number of samples		Measurement periods	
	2010	**2011**	**2010**	**2011**
A	**365** (363)	**38** (38)	1st January - 31st December	1st January - 7th February
B	**121** (121)		15th January - 16th March and 24th June - 22nd August	
C	**65** (64)		17th March - 20th April and 28th July - 26th August	
D	**30** (29)	**32** (32)	25th June - 24th July	7th January - 7th February

In bold - the number of samples in which EC and OC mass concentrations were determined; in brackets - the number of samples for which PM_{10} mass concentration was gravimetrically determined.

Daily samples of PM_{10} particle fraction were collected from approximately 55 m^3 of ambient air on quartz fibre filters (Pallflex Tissuequartz 2500QAT UP, Pall Life Sciences), pre-fired at 900 °C for three hours in a furnace to reduce carbon content in filters before collecting PM_{10}. Sven Leckel LVS3 and Sven Leckel Sequential Sampler SEQ47/50 (Sven LeckInginierbüro, Berlin, Germany) reference samplers were used for sample collection and PM_{10} mass concentrations were determined gravimetrically according to the HRN EN 12341:2005 standard. That means that filters conditioning and weighing were carried out under conditions of constant temperature (20 ± 1) °C and relative humidity (50 ± 5) %. For filter weighing, Mettler Toledo MX 5 microbalance with a golden Faraday case for removing static electricity and resolution of 10-6 g was used. Blanks were analysed one per 10-15 samples, always from the same batch of pre-fired filters, and passed the same procedure of conditioning and weighing.

Carbon analyses

Organic carbon and elemental carbon 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., 2016, 2012) according to the CEN / TR 16243:2011. A portion of each sample (1.5 cm^2) was used to determine OC and EC with the TOT method. To ensure QA/QC and prove the consistent operation of the instrument, an inner standard, external sucrose aqueous solution and cross-method procedure were used. A recovery method was used for the efficiency evaluation: two sets of filters (blank samples and real samples) were analysed after being spiked with a known concentration of carbon. The results of recovery ranged between 96 % and 104 % with relative standard deviation RSD < 5 % (Godec et al., 2012). The detection limits were determined and calculated ($\gamma + 3\sigma$) on the basis of an average taken from ten measurements of blank samples (unexposed filters). The detection limits were:

0.02 μg cm^{-2} for EC and 0.82 μg cm^{-2} for OC. The detection limits expressed in μg m^{-3} in 55 m^3 of air were 0.01 μg m^{-3} for EC and 0.18 μg m^{-3} for OC (Godec, 2013).

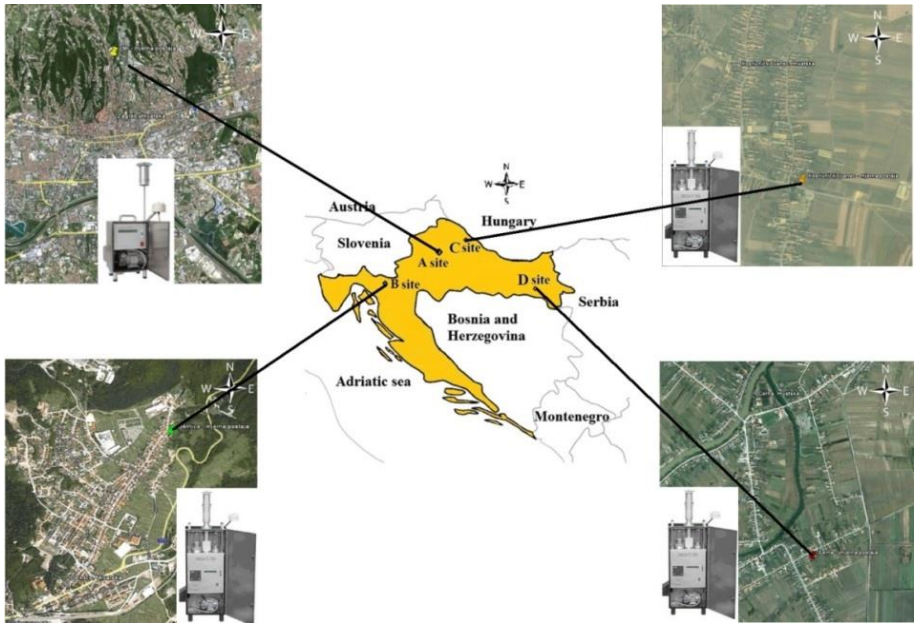

Figure 3. *The sampling sites*

DISCUSSION AND RESULTS

Table 2 presents the statistical parameters of PM_{10}, OC and EC for different monitoring sites in Croatia during 2010-2011. Average PM_{10} mass concentrations at sites A, B and C were all under the yearly average limit value of 40 μg m-3 prescribed by the Regulation on Limit Values of Pollutants in the Air from OG 133 2005, while at site D the limit value was exceeded.

The average mass concentrations of OC and EC varied in order of C < A < B < D and C < D < A < B, respectively. The highest average OC mass concentration was observed at site D, which was characterised as a rural background site where the main source of pollution was incineration of agricultural fields.

Table 2. *Statistical parameters for PM_{10} and carbon species concentrations (μg m^{-3}) at different monitoring sites in Croatia during 2010-2011*

Site	Statistical parameters																			
	PM_{10}							OC							EC						
	$\overline{\gamma}$	σ_γ	γ_{min}	γ_{25}	γ_{50}	γ_{75}	γ_{max}	$\overline{\gamma}$	σ_γ	γ_{min}	γ_{25}	γ_{50}	γ_{75}	γ_{max}	$\overline{\gamma}$	σ_γ	γ_{min}	γ_{25}	γ_{50}	γ_{75}	γ_{max}
A	31.7	21.7	3.1	16.8	25.3	38.8	163.3	8.86	7.08	1.46	4.29	6.59	11.01	62.34	1.15	0.80	0.13	0.62	0.91	1.42	6.35
B	33.1	24.0	2.7	16.6	27.0	45.5	155.8	12.39	13.19	0.82	4.84	7.89	15.68	91.49	1.35	1.51	0.12	0.36	0.65	1.86	5.68
C	25.5	12.3	3.7	17.9	22.2	31.6	67.4	6.92	3.21	2.43	4.93	6.00	7.92	18.41	0.65	0.34	0.23	0.44	0.55	0.70	1.71
D	52.1	31.1	9.5	27.5	39.1	79.6	137.3	17.75	12.23	4.54	7.71	13.63	25.74	49.24	0.85	0.41	0.18	0.53	0.76	1.11	2.16

$\overline{\gamma}$ - average, σ_γ - standard deviation, γ_{min} - minimum measured value, γ_{25} - 1st quartile, γ_{50} - median, γ_{75} - 3rd quartile, γ_{max} - maximum measured value, PM_{10} - particle matter with aerodynamic diameter less than 10 μm, *EC* - elemental carbon, *OC* - organic carbon

Figure 4 shows the spatial distribution of carbon mass concentrations between the urban (**A**) and rural (**B, C** and **D**) sites.

The significance of difference among EC, OC and TC mass concentration between different sampling sites was tested with analysis of variance at a significance level of 0.05.

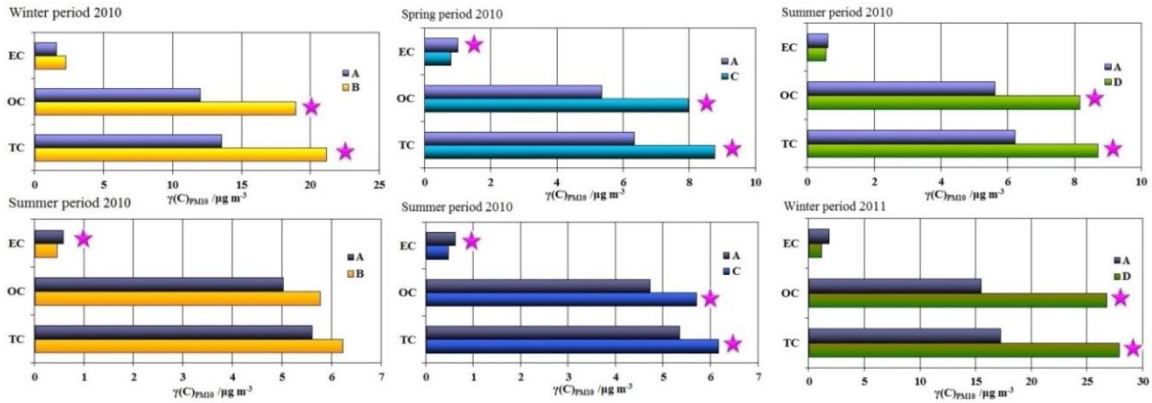

Figure 4. *Spatial distribution of carbon mass concentrations in PM_{10} particles in the air*

During the winter period, the mass concentrations of OC and TC determined at site **A** differed statistically significantly from the concentrations determined at site **B,** while during the summer measurement period, there was a significant difference in the mass concentration of EC in the particles PM_{10} in the air between these two measuring stations. Mean concentrations of OC and TC concentrations in the PM_{10} particles in air at site **C** were statistically significantly higher while EC concentrations were statistically significantly lower than at site **A**. The mean values of the OC and TC concentrations in PM_{10} particles in the air at site **D** were statistically significantly higher than at site **A**. The mass concentrations of EC and OC in the PM_{10} particle fraction at the rural sites were significantly higher (at a significance level of $p = 0.05$) in the cold part of the year (winter and spring) than the concentrations measured in the warmer part of the year (summer). In the cold part of the year (winter and spring), the OC mass concentrations determined at site **A** were significantly lower (at a significance level of $p = 0.05$) than the concentrations determined at sites **B**, **C** and **D**.

EC and OC mass contributions to the total PM_{10} mass during the entire measuring periods at all of the sites are shown in Figure 5. At site A, the highest OC contribution was noticed in autumn and the lowest in spring. EC mass contribution in winter and summer as well as in spring and autumn were the same, which was not expected. EC mass contribution to the total PM_{10} mass was higher in winter than in summer at site **B**, while OC mass contribution remained the same. In colder months, higher EC concentrations originated from increased traffic and vehicle fuel combustion. At site **C**, OC mass contribution to the total PM_{10} mass was higher in the summer than in the spring, because of incineration of agricultural fields while at site D, OC mass contribution to the total PM_{10} mass was higher in the winter. At both sites **C** and **D**, EC mass contributions were equal in both periods, because of low traffic density.

According to Castro et al., (1999) the production of SOC was calculated from the following equation:

$$SOC = OC - \left(\frac{OC}{EC}\right)_{minimum} \cdot EC$$

As shown in Table 3, most of the average and minimum values of OC/EC concentrations ratio in the seasons are above 3, indicating that the SOC particles were considered to be formed in the observation period.

Table 3. *Average and minimum values of OC/EC mass concentration ratio for each season at different monitoring sites in Croatia during 2010-2011*

Measurement periods	**Sampling site**							
	A		**B**		**C**		**D**	
	$\bar{x}$	x_{min}	$\bar{x}$	x_{min}	$\bar{x}$	x_{min}	$\bar{x}$	x_{min}
spring	6,67	2,68			11,22	5,89		
summer	8,32	2,75	14,03	6,87	12,32	6,69	15,48	8,27
autumn	8,53	1,74						
winter	9,49	2,68	10,72	3,36			23,52	14,50

$\bar{x}$ - average OC/EC ratio, x_{min} - minimum value of OC/EC ratio

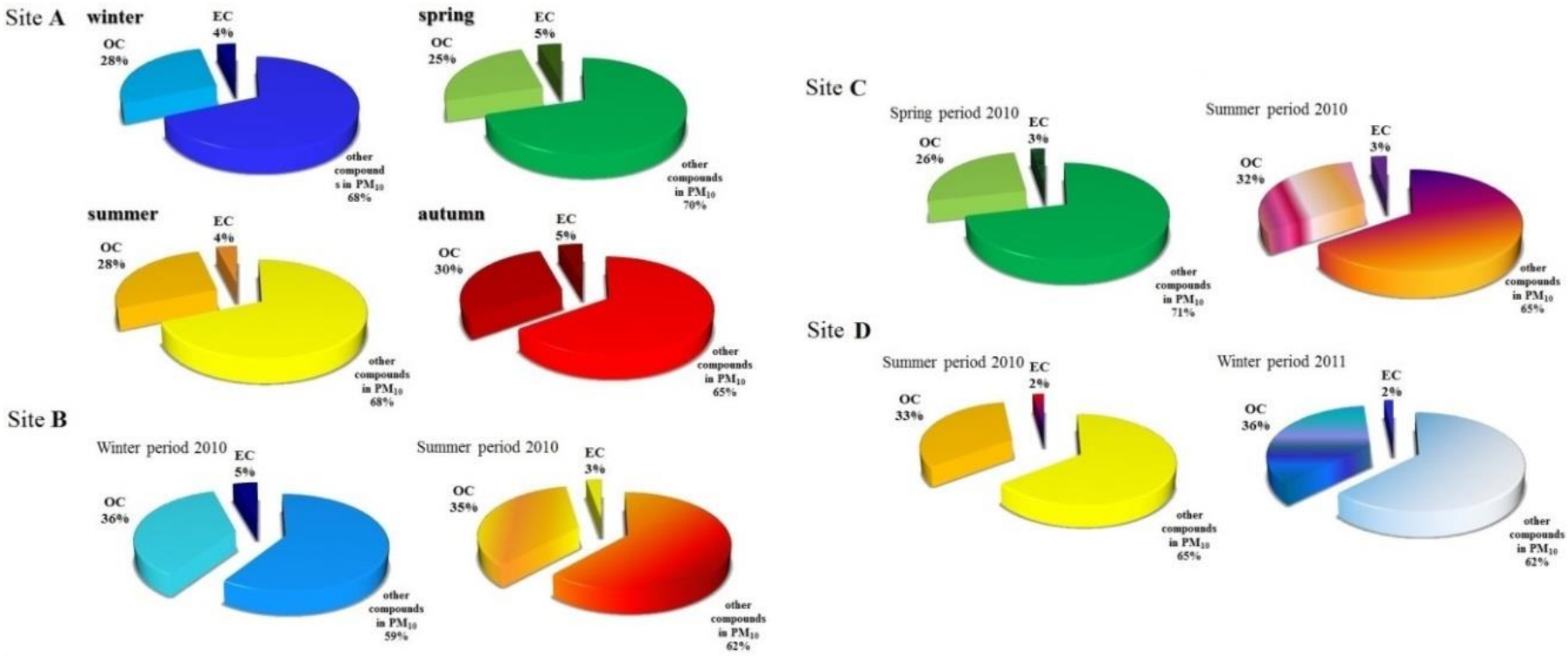

Figure 5. *EC and OC mass contribution to the total PM_{10} mass during the entire measuring periods at all of the sites*

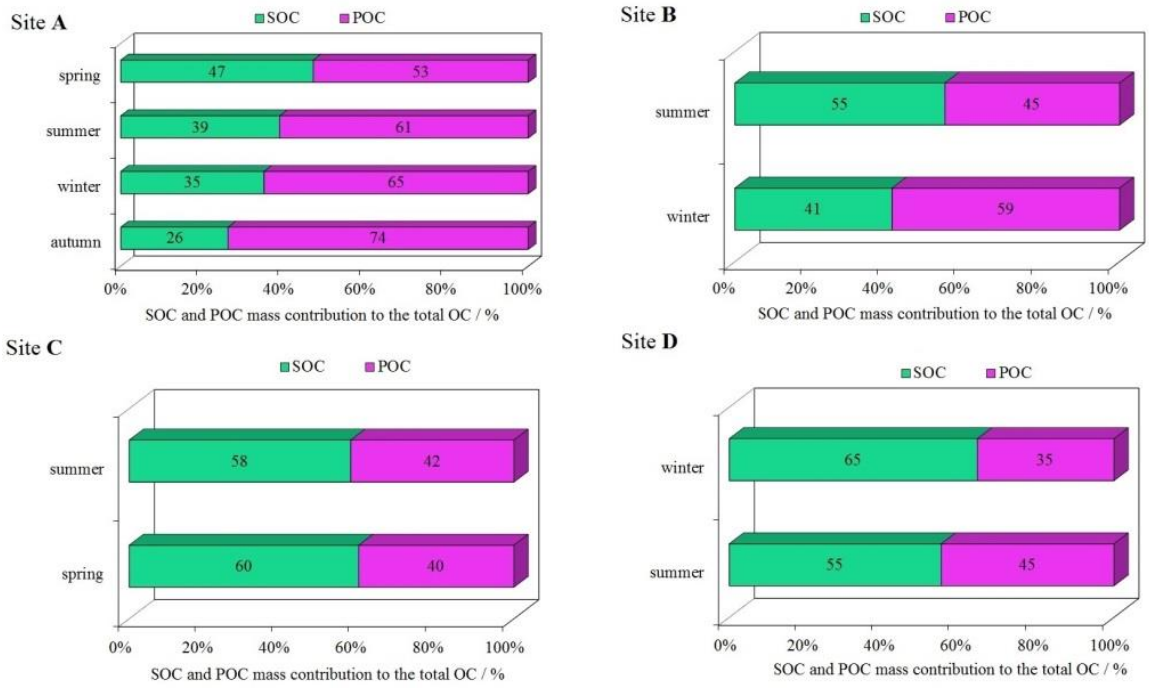

Figure 6. *POC and SOC mass contribution to the total OC mass for each season at all of the sites during the sampling periods*

POC and SOC mass contributions to the total OC mass during the whole measuring periods at all of the sites are shown in Figure 6. The mass contribution of POC in the total OC mass increased through the seasons: spring < summer < winter < autumn at site A. This increase of POC at site A originated from traffic during the colder part of the year, while the increase of SOC during the warmer part of the year originated from a higher temperature which favours the condensation of organic compounds onto pre-existing particles and higher OC mass concentrations and SOC content in OC. At site **B**, the increase of POC in winter originated from traffic and wood used as fuel for cooking and heating. The increase of SOC in summer originated from a higher temperature which favours the condensation of organic compounds onto pre-existing particles and higher OC mass concentrations and SOC content in OC. POC and SOC mass contributions to the total OC in PM_{10} were almost identical across summer and spring at site **C**. Higher SOC mass contribution during summer at site **D** was unexpected and it was in reverse in relation to all of the other places (**A, B** and **C**). This fact may be explained by the fact that incineration of agricultural fields was the main source of pollution at site **D**. Higher SOC values were observed at all of the sites during the warmer part of the year except at site **D** where the main source of pollution was agriculture and where the incineration of agricultural biomass was common.

CONCLUSIONS

The mass concentrations of EC and OC in the PM_{10} particle fraction at the rural sites were significantly higher (at a significance level of $p = 0.05$) in the cold part of the year (winter and spring) than the concentrations measured in the warmer part of the year (summer). In the cold part of the year (winter and spring), the OC mass concentrations determined at site **A** were significantly lower (at a significance level of $p = 0.05$) than the concentrations determined at site **B, C** and **D**. EC and OC mass contributions to the overall PM_{10} mass were also higher during the colder period of measurements. Higher SOC values were observed at all of the sites during the warmer part of the year except at site **D** where the main source of pollution is agriculture and where incineration of agricultural biomass is common.

ACKNOWLEDGEMENTS

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

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ABSTRACT

The exposure to particulate matter (PM) pollution has been associated with the respiratory and cardiovascular disease. In the indoor environment, both indoor and outdoor sources contribute to PM levels. Indoor air quality in educational buildings is of great importance since children and students spend a large part of their time in classrooms. This work presents results of an ongoing study on students' and teachers' exposure to suspended particles in the selected classrooms and offices at the University of Belgrade, Technical Faculty in Bor, Serbia.

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 non-heating (April-September) and heating seasons (October-March) in the time interval from 2011 to 2016. The measurement of PM was conducted for a period of at least 14 days per classroom/office in each season. In the first week of measurements, Sven/Leckel low-volume samplers LVS3 were co-located with the OSIRIS monitor to collect the PM_{10} and $PM_{2.5}$ gravimetric samples.

The average indoor daily concentrations of suspended particles in the non-heatingseason were within the ranges from 19.9 to 59.3 $\mu g/m^3$ for TSP, 12.9 to 39.6 $\mu g/m^3$ for PM_{10}, and 4.6 to 13.4 for $PM_{2.5}$. Similarly, the average outdoor daily concentrations of suspended particles in the non-heatingseason were within the ranges from 50.3 to 98.2 $\mu g/m^3$ for TSP, 35.9 to 75.2 $\mu g/m^3$ for PM_{10}, and 18.5 to 36.7 for $PM_{2.5}$.

The average indoor daily concentrations of suspended particles in the heating season were within the ranges from 20.8 to 41.3 $\mu g/m^3$ for TSP, 13.3 to 24.2 $\mu g/m^3$ for PM_{10}, and 5.2 to 11.8 for $PM_{2.5}$. Similarly, the average outdoor daily concentrations of suspended particles in the heating season were within the ranges from 33.8 to 77.9 $\mu g/m^3$ for TSP, 21.1 to 55.6 $\mu g/m^3$ for PM_{10}, and 10.4 to 32.7 for $PM_{2.5}$.

The average I/O ratios in the non-heatingseason 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 PM_{10}, and 0.18 to 0.86 for $PM_{2.5}$.

Exceeding of the daily limit of PM_{10} in the ambient air was observed in 17% of days during the heating season and in 40% of days in the non-heatingseason. The exceeding of the daily limit of $PM_{2.5}$ in the ambient air was observed in 21% of days during the heating season and in 48% of days in the non-heatingseason.

In contrast to that, exceeding of daily limits of PM in the indoor air was observed during the very few cases (exceeding of PM_{10} in one office in 5% of days during the non-heatingperiod). Also, the lowest PM concentrations in the indoor air were detected during non-working days (weekends).

INTRODUCTION

The town of Bor with a population of about 40,000 people is situated in the eastern part of the Republic of Serbia. It is assumed to be representative of a hot-spot urban-industrial environment in the country. Because of the emissions of sulfur oxides and particulate matter from the copper smelter facilities situated close to the urban area, air pollution is the main environmental problem in Bor [1]. According to the SEPA annual report for 2010 [2], the annual mean PM_{10} concentration at the Bor at sampling site Town Park was 31 g/m^3. In fact, annual mean PM_{10} concentrations recorded in Bor were among the lowest compared with PM_{10} concentrations in other Serbian cities. In most of the Serbian cities, PM_{10} concentrations have been much higher in the cold than in the warm period of the year. However, in Bor, PM_{10} concentrations were just 10% higher in the cold period than in the warm period [3].

Exposure to particulate matter (PM) pollution has been associated with respiratory and cardiovascular disease [4-8]. It is very important to determine the impact of indoor PM concentrations on human health because that people spend most of their lives indoors [9]. In the indoor environment, both indoor and outdoor sources contribute to PM levels. PM in indoor air originates from outdoor infiltration and additional indoor sources such as cooking and heating devices, tobacco smoking, building materials, etc. 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 students' and teachers' exposure to suspended particles (PM_{10} and $PM_{2.5}$) in selected classrooms and offices at the University of Belgrade, Technical Faculty in Bor, Serbia.

METHODOLOGY

Technical Faculty in Bor consists of several buildings situated about 1 km NW from the copper smelter facilities, as shown in Figure 1. The measurements of the suspended particles mass concentrations (TSP, PM_{10} and $PM_{2.5}$) were conducted throughout several sampling campaigns in the non-heating(April-September) and heating seasons (October-March) in the time interval from 2011 to 2016. At all places of interest (4 offices and 2 classrooms) the measurements lasted at least two weeks per season.

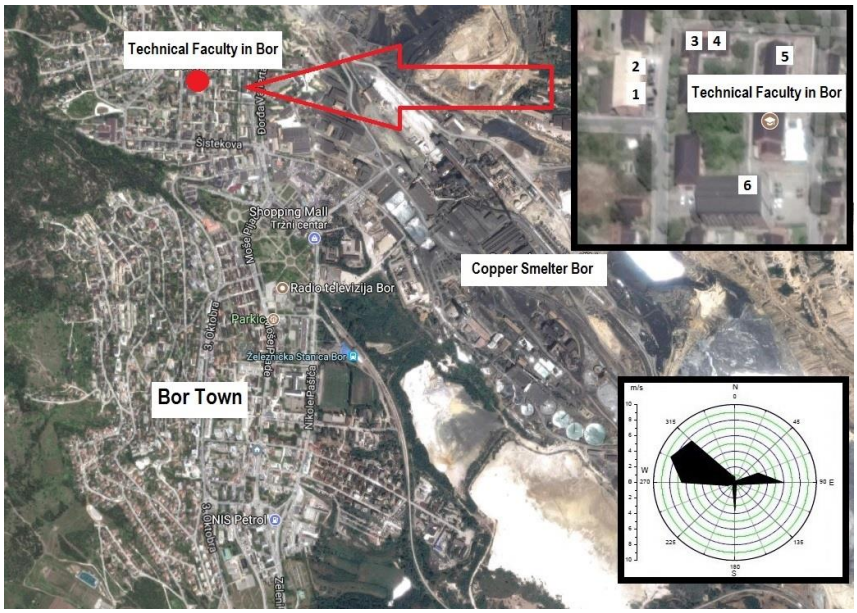

***Figure 1**. The position of the Technical Faculty on the Bor town map*

A real-time air particulate monitor, Turnkey OSIRIS (Model 2315), was used to provide continuous real-time readings of TSP, PM_{10}, $PM_{2.5}$, and PM_1 mass concentrations. It uses a light scattering technique to determine the concentration of airborne dust in the particle size range from about 0.4 μm to about 20 μm [10]. In the first week of measurements, Sven/Leckel low-volume samplers LVS3 [11] were co-located with the OSIRIS monitor to collect the PM_{10} and $PM_{2.5}$ gravimetric samples. The daily average PM concentrations obtained by the gravimetric method were used to correct results obtained by the OSIRIS monitor as suggested by Ramachandran et al. [12]. The measurement locations were selected in such way to cover all the main buildings at the Technical Faculty, as shown in Figure 1. The selected offices (labeled as 1, 3, 4, and 6 in Figure 1) were occupied by 2-5 persons only during work hours (8 AM - 2 PM). The selected classrooms (labeled as 2 and 5 in Figure 1) were occupied by up to 20 persons during lectures and exercises in the period from 8 AM to 6 PM. The floor of the office 1 was covered with carpets, the floors of the offices 3, 4, and 6 were covered with laminate, as well as the floor of the classroom 5, while the floor of the classroom 2 was covered with worn wooden parquet. There was no air conditioning system in the offices and classrooms. The surface areas of windows in the offices and classrooms were about 2-4 m^2. In the non-heatingseason, the windows in the offices usually remained open during working hours. The offices' volumes were 40-50 m^3, whilst the classrooms' volumes were 50 and 70 m^3.

RESULTS AND DISCUSSION

The average daily PM mass concentration measured in the selected offices/classrooms during the non-heatingand heating seasons are presented in Tables 1 and 2. The indoor average daily concentrations of suspended particles in the non-heatingseason were within the ranges from 19.9 to 59.3 μg/m^3 for TSP, 12.9 to 39.6 μg/m^3 for PM_{10}, and 4.6 to 13.4 for $PM_{2.5}$. Similarly, the outdoor average daily concentrations of suspended particles in the non-heatingseason were within the ranges from 50.3 to 98.2 μg/m^3 for TSP, 35.9 to 75.2 μg/m^3 for PM_{10}, 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 μg/m^3 for TSP, 13.3 to 24.2 μg/m^3 for PM_{10}, 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 μg/m^3 for TSP, 21.1 to 55.6 μg/m^3 for PM_{10}, and 10.4 to 32.7 for $PM_{2.5}$.

Table 1. *Average daily TSP, $PM_{10,}$ and $PM_{2.5}$ concentrations detected during non-heatingseasons (μg/m^3)*

Location	TSP indoor	TSP outdoor	PM_{10} indoor	PM_{10} outdoor	$PM_{2.5}$ indoor	$PM_{2.5}$ outdoor
1	54.4	74.6	33.7	55.1	9.4	23.7
2	59.3	98.2	39.6	75.2	13.4	32.6
3	19.9	50.3	12.9	35.9	4.6	18.5
4	26.4	68.3	18.1	48.8	8.5	27.7
5	25.0	81.3	16.4	56.9	4.8	28.4
6	25.5	89.3	19.2	63.8	10.1	36.7
Average	35.1	77.0	23.3	56.0	8.5	27.9

Table 2*. Average daily TSP, $PM_{10,}$ and $PM_{2.5}$ concentrations detected during heating seasons (μg/m^3)*

Location	TSP indoor	TSP outdoor	PM_{10} indoor	PM_{10} outdoor	$PM_{2.5}$ indoor	$PM_{2.5}$ outdoor
1	20.8	33.8	13.3	21.1	5.2	10.4
2	41.3	45.1	24.2	27.8	11.8	13.9
3	21.6	50.3	14.7	35.9	6.5	22.4
4	26.0	34.0	15.1	21.3	5.6	10.6
5	23.2	73.3	14.5	52.4	6.2	28.7
6	22.5	77.9	16.5	55.6	8.0	32.7
Average	25.9	52.4	16.4	35.7	7.2	19.8

***Table 3**. Average daily TSP, PM_{10}, and $PM_{2.5}$ I/O ratios during the heating and non-heating season*

Location	TSP I/O no heating	TSP I/O heating	PM_{10} I/O no heating	PM_{10} I/O heating	$PM_{2.5}$ I/O no heating	$PM_{2.5}$ I/O heating
1	0.70	0.59	0.61	0.61	0.39	0.51
2	0.59	0.90	0.52	0.87	0.40	0.86
3	0.40	0.44	0.36	0.42	0.25	0.30
4	0.38	0.76	0.37	0.72	0.31	0.55
5	0.36	0.33	0.32	0.28	0.20	0.21
6	0.33	0.33	0.35	0.31	0.32	0.18
Average	0.46	0.56	0.42	0.54	0.31	0.44

The geographical position of the Technical Faculty in Bor is such that a wind from the N/NW directions reduces the PM levels in the heating period. In the non-heatingperiod the frequency of winds from N/NW directions are much lower. This is the main reason why the average concentration of suspended particles in the ambient air near the Technical Faculty in Bor were higher in the non-heatingseasons compared to those measured in the heating seasons [1]. As a consequence, the average TSP concentrations were 47% higher, PM_{10} concentrations were 57% higher, and $PM_{2.5}$ concentrations were 41% higher during the non-heatingseasons compared with respective concentrations measured during the heating seasons.

According to data shown in Table 3, the average I/O ratios in the non-heatingseason vary from 0.33 to 0.70 for TSP, from 0.32 to 0.61 for PM_{10}, and from 0.20 to 0.40 for $PM_{2.5}$. Similarly, the average I/O ratios in the heating season vary from 0.33 to 0.90 for TSP, from 0.28 to 0.87 for PM_{10}, and from 0.18 to 0.86 for $PM_{2.5}$. The exceeding of the daily limit of PM_{10} in the ambient air was observed in 17% of days during the heating season and in 40% of days in the non-heatingseason. The exceeding of the daily limit of $PM_{2.5}$ in the ambient air was observed in 21% of days during the heating season and in 48% of days in the non-heatingseason.

In contrast to that, exceeding daily limits prescribed for PM_{10} and $PM_{2.5}$ in the indoor air were observed just in a few cases (exceeding of PM_{10} limit in the classroom 2 in 5% of days during the non-heatingperiod). It is known that human activities lead to the re-suspension of deposited particles from horizontal surfaces, such as floors, carpets and furniture [13]. Accordingly, the lowest TSP and PM concentrations in the indoor air were detected during non-working days (weekends). Moreover, the re-suspension rates increase with particle size [14]. Also, the coarse airborne particles were positively affected by the presence of a large number of occupants and by cleaning activities [15]. Accordingly, the highest TSP and PM concentrations in the indoor air were detected in the classroom 2 during working days. This classroom is covered with worn wooden parquet which significantly contributes to the re-suspension of the dust compared to other observed premises.

CONCLUSIONS

This study presents TSP, PM_{10}, and $PM_{2.5}$ levels measured at the Technical Faculty in Bor. The exceeding of daily limits prescribed for PM_{10} and $PM_{2.5}$ in the ambient air were observed in both heating (17% and 20% respectively) and non-heatingseasons (40% and 48% respectively). In contrast to that, exceeding daily limits for PM_{10} and $PM_{2.5}$ in the indoor air were observed just in a few cases. No significant difference was found between PM_{10} I/O ratios in the non-heatingand heating seasons. These findings point to the absence of the significant indoor sources of PM particles at the observed premises. So it can be concluded that most of the indoor TSP and PM particles originate from the outdoor air. Differences in the concentration of suspended particles in the observed rooms should be attributed to the different number of occupants, as well as to the various habits of ventilation and cleaning of rooms.

ACKNOWLEDGEMENTS

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2. ADVANCES IN PM CHARACTERIZATION I

2.1. ELECTROANALYTICAL METHODS IN AEROSOLS PARTICULATE MATTER CHARACTERIZATION

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ABSTRACT

Electroanalytical methods with a mercury electrode were used for the first time for determination of surface active substances (SAS) and reduced sulphur species (RSS) in the water soluble (WS) particulate matter fractions ($PM_{2.5}$) of marine aerosols, and in indoor school air environments. Marine aerosols were collected in the vicinity/area of unique euxinic environment on the Adriatic coast, Rogoznica lake, RL (43.53° N, 15.95° E), while indoor aerosols were collected in the school Vožd Karađorđe in the city of Niš, Serbia. A typical WSOC sampling technique included sample collection on glass fibre followed by extraction in water.

RL aerosol samples were collected in the autumn, when water layer mixing was occurring in the lake. Two types of non-volatile RSS peaks were detected in WS fractions, and attributed to the presence of organic mercapto-type and inorganic sulphide/S^0-like compounds. In the studied WS aliquot samples, the concentration of SAS ascribed to the presence of macromolecular compounds ranged between 0.35 and 0.55 mg/l equivalent to Triton-X-100. In indoor aliquot samples more adsorbable SAS were recorded, while only presence of mercapto type compounds were evident there.

INTRODUCTION

Electrocanalytical methods (EA) provide a simple measurement procedure and prompt response for relatively low cost. Combined with the high sensitivity and selectivity, along with possibility to conduct in-situ measurements, EA methods are a strong analytical tool for characterization and quantification of different SAS and S species in water environment [1-8]. Features of EA methods, especially voltammetry, make them appropriate for use as monitoring tools in assessment of water quality in natural environment, i.e. trace pollutant analyses: S species [5-7], organic compounds [1-4,7-9], trace metals [10-12], engineered and natural nano-particles (NPs) [13-15]. On the other hand, in AC voltammetric *out-of phase* measurements at the Hg electrode, the decrease of the AC current value at the initial deposition potential -0.6 V (vs. Ag/AgCl) with respect to the base-line of the pure electrolyte (0.55 mol dm^{-3} NaCl) is the result of the SAS adsorption [1,2,9]. In some cases volumetric curves show different shapes (characteristic hump, different position of desorption waves, or non-expressed well-defined peaks) which is a base for qualititave characterization of SAS by comparing the obtained adsorption curves to those of different model substances. In our previous studies, a number of adsorbable organic substances (nonionic, anionic, and cationic surfactants, polyaromatic hydrocarbon, monocarboxylic, dicarboxylic acids, humic (HA) and fulvic (FA) acids, polysaccharides, proteins and lipids), representing either naturally occurring substances in the aquatic systems or potential pollutants, have been studied under same conditions as natural water samples [1-4,8,9]. In general, there are differences in adsorption behaviour between strongly adsorbable, relatively small molecules and hydrophylic large polymer molecules. The high, sharp and well-defined desorption peaks are characteristic for relatively low molecular mass substances while the low and extended desorption waves indicate the presence of macromolecular organic substances.

Atmospheric climate, air quality and its impact on human health are now being considered central topics in environmental research and its protection. The atmospheric aerosol system is composed of solid or liquid particles (in the range of 10^{-9} to 10^{-4} m) suspended in the air [16]. The focus of today's research is that they directly and indirectly affect climate, atmospheric chemistry, air quality, and people's health. Indoor air quality, i.e. chemical composition of smaller particles ($PM_{2.5}$ and smaller) is very important for people's health [17]. Concentration, size, structure and particle chemical composition are the primary parameters that determine the effect of aerosols on human health and climate, and are largely subject to spatial and temporal variability. Organic matter (OM) in aerosols need special attention due to its surfactant properties and their influence on the microphysical properties of the airborne particles [16,18,19].

Surface-active substances (SAS), as the most reactive part of OM in natural aquatic systems that accumulate at the different phase boundaries, are an important OM fraction in the airborne particles [18,19]. Many of the organics identified in atmospheric aerosols are known to be surface-active in aqueous solutions, contributing to the aerosol water-soluble organic compounds (WSOC) pool [8,18-20]. Moreover, S compounds are central to the aerosol budget in the marine atmosphere because their oxidation products (predominantly sulphate) affect aerosol pH and hygroscopicity [21,22]. Recent studies have presented evidence that the reactive uptake of principal gas-phase oxidation products on aerosols involves organosulphate formation as well as other so far unidentified organosulphur species [23, 24]. Today organic aerosols still represents one of the last understood fractions of atmospheric aerosol, although it typically comprise a large fraction of ambient particulate matter.

In this work a simple, fast and non-destructive voltammetric methods developed within our group applied were for the first time for monitoring of organic matter with surface active properties and reduced sulphur species in WS fraction of marine aerosols ($PM_{2.5}$) collected in the area of Rogoznica Lake (RL), central Dalmatia (Middle Adriatic, 43º32'N 15º58'E) and in indoor aerosol samples ($PM_{2.5}$) collected in the school Vožd Karađorđe in the city of Niš, Serbia. The WSOC fraction of both airborne particle solutions was followed by HTCO measurements. A typical WSOC sampling technique included sample collection on glass fibre followed by extraction in water; the volume of water used for the extraction per unit of the area of the filter analysed (V/A) for RL samples was 11.53 ml /cm^2, while this ratio for indoor samples was 2.3 ml/cm^2.

METHODOLOGY

TheRogoznica Lake, RL aerosol samples (aerodynamic diameter <2.5 μm) were collected on glass-fibre GF/F filters (φ=47 mm) by a low-volume sampler, Sven/Leckel SEQ 47/50 (2.3 m^3/h, sampling time: 48 h). Before exposure, the filters were pre-heated at 650°C for 5 h and after the sampling these were carefully packed in aluminium foil (pre-heated at 450 °C, 5 h) and stored in a freezer until the analysis. Blank filters were prepared in the same way as filters for sampling but without exposure to air. Samplings were performed in Autumn (October 2016) at RL marine system in the central Dalmatia (Middle Adriatic, 43º32'N 15º58'E). RL can be considered as an extreme, naturally eutrophic system which feels all effects of the Adriatic atmospheric and ocean conditions [25]. The influence of these conditions due to the lake's semi-closed nature might be several times stronger than in other coastal and open sea Adriatic waters. The whole region is characterised with extensive tourism, with a low impact of industrial activities.

Mass concentrations of indoor $PM_{2.5}$ fractions were measured with a low volume sampler, Sven/Leckel LVS3 (2.3 m3/h, sampling time: 24 h) in the school Vožd Karađorđe in the city of Niš, Serbia [26]. Quartz fibre filters (Whatman QMA, φ=47 mm) were used for this ambient air sampling.

Sample pre-treatment

The water-soluble (WS) aerosol fraction was extracted by placing 10% (RL samples) and 50% of the filters in cca 20 ml of high purity de-ionised MilliQ water (Millipore Corp.) for 24 h, following the work of Frka et al. [8]. The extracts were then filtered through 0.7 μm GF/F filters pre-heated at 450°C for 5 h and directly used for electrochemical measurements and WSOC analysis. The samples of the filtered extracts for WSOC analysis were preserved by adding 100 μL of 2 g dm^{-3} $HgCl_2$.

Sample analysis

Characterization of organic matter and RSS in the WS fraction of sampled aerosols was performed by fast and easily-performed EA methods that have been developing in our group for characterization and measurements of SAS, and different RSS in natural waters [1-9,12]. For the quantification of the SAS content in the WSOC fraction, a calibration plot of the nonionic surfactant Triton-X-100 was used, which is shown to be a good representative of the most reactive part of SAS in natural waters [1-9].

AC voltammetry *out-of phase* measurements were used for SAS characterization, while RSS were measured by square wave voltammetry (CSSWV). EA measurements were performed with an electrochemical analyser μAutolab-type (Eco Chemie B.V., The Netherlands) equipped with GPES 4.6 software (Eco Chemie B.V., The Netherlands). A standard polarographic Metrohm cell of 50 cm^3 equipped with a three-electrode system was used. A hanging Hg drop electrode (HMDE, Metrohm, Switzerland) with the surface area A=0.01245 cm^2 was used as a working electrode, an Ag/AgCl/3 mol dm^{-3} KCl as the reference electrode and a Pt as the auxiliary electrode. A saturated solution of NaCl was added to the WS sample to adjust ionic strength of 0.55 mol dm^{-3} electrolyte solution prior to the SAS and RSS measurement [8]. The RSS presence, based on acidification and purging step [5-7, 9]

and calibration plot of the methyl 3-mercaptopropionate (3-MPA) was characterized by the CSSWV; experimental conditions: Ed = -0.2/-0.1 V, A = 25 mV, f = 80 Hz, ta = 120 s.

A sensitive high-temperature catalytic oxidation analyser TOC-VCPH (Shimadzu, Japan) with Pt-coated silica catalyst and a non-dispersive infrared detector for CO_2 measurements was used for WSOC measurements.

RESULTS AND DISCUSSION

A typical voltammetric curve of RSS recorded in the WS fraction of marine aerosols (pH around 6) collected in the area of Rogoznica lake in October 2016 (Autumn sample, A1) is presented in Figure 1. In the voltammogram recorded in the WSOC original aliquot (water to filter ratio, V/A = 11.53 ml /cm^2), several voltammetric peaks are visible: peaks at around -0.4 V and -0.75 V, which correspond to redox proces of sulphide/S^0 at the Hg electrode, while small and much wider peak at around -0.56 V was attributed to the presence of mercapto compounds. As visible in Figure 1, lower blue curve, this smaller peak was even more expressed in 2x diluted sample. Standard addition of the methyl 3-mercaptopropionate, 3-MPA (used here as standard for mercapto compounds) directly into electrochemical cell containing sample A1 caused an increase of the peak around -0.56 V, pointing to similar electrochemical behaviour as the 3-MPA at the Hg electrode. The addition of sulphide caused a shift to a more negativeHgS reduction peak (around -0.75 V). It is important to notice that all RSS recorded peaks were not visible under diffusion controlled conditions, and were not sensitive to a purging and acidification step which is common procedure in electrochemical characterization of RSS, indicating the presence of non-volatile RSS. In the case of the HgS peak (peak around -0.75 V), the acidification and purging step caused a decrease up to 20% [5,6,9].

The appearance of the negative HgS peak in RJ A1 sample could be likely associated with a sudden and fast mixing process between oxic and sulphide rich anoxic waters in the lake, and establishment of holomictic euxinic and anoxic conditions, followed by enhanced release of volatile S compounds [27]. In other words, during lake mixing, milimolar concentrations of sulphide from the bottom anoxic layer reach the surface where the oxidation mainly to S^0 is favoured as well as its further loss into the atmosphere. Such an explanation is supported by the fact that the more negative peak (HS-/S^0-like compounds) was decreasing with time after layer mixing was oberved to start, and has not been recorded in other analysed samples collected in the same area during spring and winter of 2015/2016.

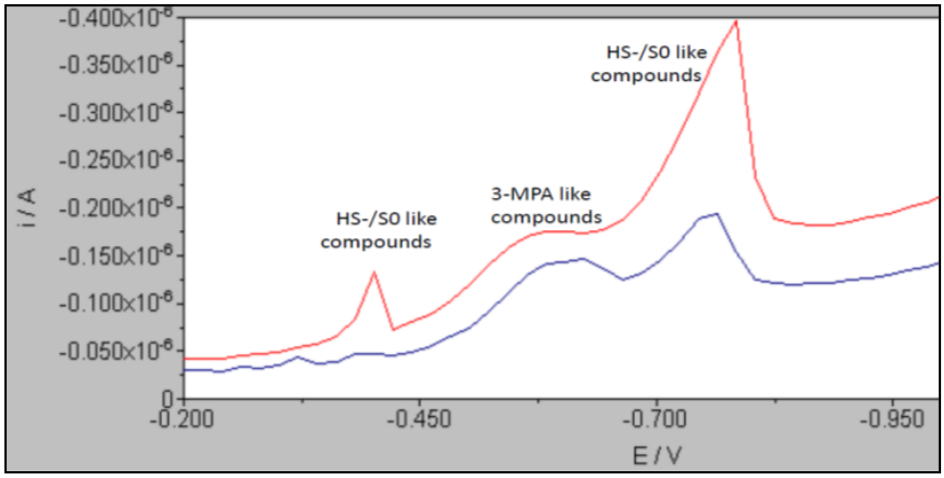

***Figure 1**: CSSWV curves recorded in the WS fraction of autumn RL aerosol sample A1, accumulated time of 120s at starting potential E= -0.2 V. Upper red curve: original aliquot with V/A= 11.53 ml/cm^2; lower blue curve is 2x diluted original A1 aliquot. Concentration of 3-MPA like compoundes in diluted aliquot sample is 31.23 nM, and HS-/S^0 was 12 nM.*

The characteristic AC *out of phase* voltammetric curves which reveal the suppression of the capacity current in comparison to the capacity current of the pure electrolyte (0.55 M NaCl) due to adsorption of unknown SAS in WS aerosol fraction, are presented in Figure 2 for the RJ A1 sample, and for comparison in the indoor school sample (Figure 2, insertion). A rough characterization of SAS, performed by comparing the shapes and intensities of the

electrochemical responses with those obtained with different model substances [1-4,7-9,28-30] indicate prevalence of similar (there was no difference in the curve shapes) large macromolecular molecules (more adsorbable than humic type compounds), visible through appearance of wide and flat desorption peaks between -1.25 and -1.5 V. Highly adsorbable macromolecular compounds are even more visible in the indoor sample by observing very high suppression of the capacity current, which was at the saturation level in this aliquot sample. Approximately the same concentrations of the aerosol mass were recorded for the both aerosol samples, around 25 μg/m^3.

In view of the above discussion, we have concluded that the WSOC in our studied samples consists mainly of high molecular weight substances. However, our preliminary results indicate that is very important how the WSOC fraction is obtained i.e. ratio between volume of water used for extraction of WSOC and the filter surface area/mass of the PM, and influence extraction process. Different ratios can largely influence WSOC extraction results especially in the case of highly hydrophobic material, as already referred in the literature [31]. Also in our previous work we noticed that dilution effect could largely influence AC voltammetric results [9]. Very often stronger adsorption effects in diluted samples is caused by the presence of strongly-adsorbable compounds which are present in smaller amounts. In such cases, the adsorption effect of more predominant polymer material is diminished by dilution, and more strongly adsorbable compounds (more hydrophobic in its nature), present in a lower concentration range were measured in the diluted sample [1, 9]. In other words, the WSOC fraction depends on its concentration in the airborne particulate phase, its solubility and the water used for the WSOC extraction [31].

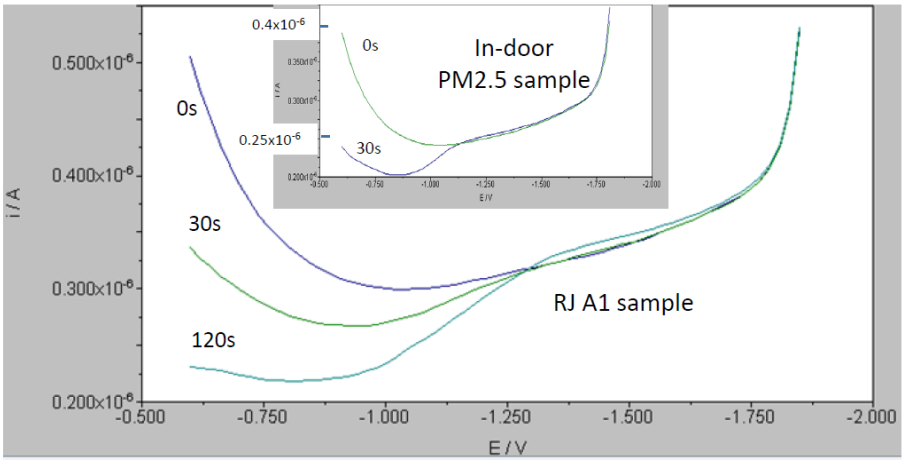

Figure 2. *AC voltammetric curves (out-of-phase measurements) recorded in the WS fraction of autumn aerosol sample, A1 2x diluted original aliquot (V/A= 11.53) sample; accumulation times with stirring at the starting potential E=-0.6 V, 0,30,120 s. Insertion is AC curves recorded in indoor $PM_{2.5}$ sample, V/A= 2.3 ml/cm^2. SAS concentration in A1 sample is 0.33 mg/l eq.T-X-100 (WSOC=0.41 mg/l; org.C tot =1.68 μgC/m^3), and in the indoor sample 0.51 mg/l (at saturation, eq.T-X-100) (WSOC= 1.29 mg/l; org.Ctot = 9.63 μgC/m^3 air). In this indoor sample no RSS presence was recorded.*

It is interesting that in some of the indoor samples, a typical reduction process for mercapto compounds at the Hg electrode is recorded as well, as shown in Figure 3. Again non-volatile RSS were recorded, for which cathodic peaks were similar in height as for measurements with deposition potentials at -0.1 and -0.2 V, after acidification and apurging step, and adjustment of pH to the starting/original one. Unfortunately this sample was not spiked with standard addition of the 3-MPA but these were ascribed to the presence of the mercapto compounds due to the peak's position and behaviour.

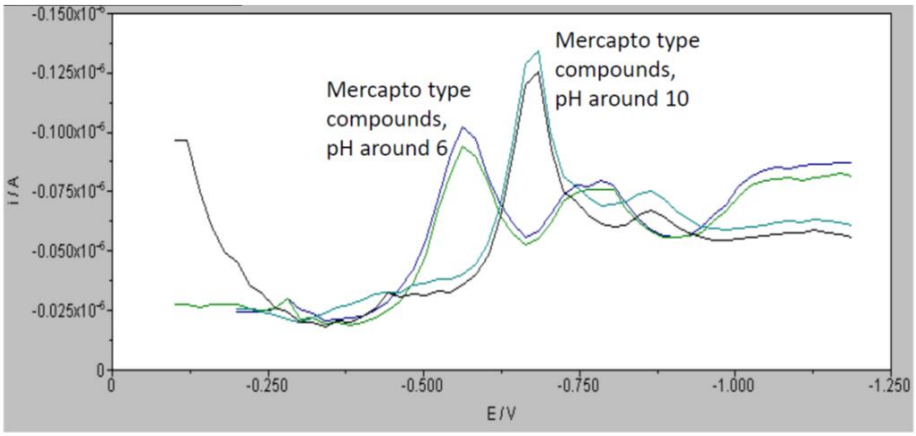

Figure 3. *CSSWV curves recorded in the WS fraction of indoor $PM_{2.5}$ aerosol sample. Be aware that green and blue curves were recorded in original aliquot sample, pH around 6 (peaks recorded around -0.55 V, after deposition at -0.1 and -0.2 V for 120 s), while negative peaks (cyan and black) were recorded after an acidification and purging step, and re-adjustment of pH around 10 (peaks recorded around -0.70 V, after deposition at -0.1 and -0.2 V for 120 s). Concentration of the 3-MPA compounds was estimated to be 50 nM. In the same sample WSOC= 0.82 mg/l; org C tot= 4.507 µgC/m^3 air.*

CONCLUSIONS

Results from this study clearly prove the already recognised great potential of electrochemistry at the Hg electrode for fast and simple qualitative and quantitative water sample analyses. This is especially efficient for rough characterization and tracing of naturally occurring organic material with surface active properties and sulphur content. For the first time, this methodology is used for SAS and RSS characterization in the water-soluble particulate matter fractions ($PM_{2.5}$) of marine aerosols, and indoor school air environments. Our preliminary study indicate that results obtained can be very influenced by the procedure of how the WS fraction is obtained. It appears that a different ratio between volume of water used for extraction of WSOC and filter surface area/mass of the PM can largly influence WSOC extraction results, especially in the case of highly hydrophobic material with sulphur content, as already obtained in our research for dilution effects.

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2.2. TIME SERIES ANALYSIS OF LOW MOLECULAR WEIGHT ORGANIC ACIDS IN ATMOSPHERIC AEROSOLS BY ION CHROMATOGRAPHY

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ABSTRACT

Low molecular weight (LMW) organic acids constitute a significant fraction of atmospheric water-soluble organic aerosols. 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). All extracted filters were analyzed on a Dionex IC system with AS11 analytical column and hydroxide eluent. Oxalate was the most abundant organic species detected. Its concentration ranged from 15.87 to 282 ng/m^3 with an average of 95.70 ng/m^3. Malonate was the second most abundant species followed by succinate, with average concentration of 19.43 ng/m^3. Formate, glyoxylate, succinate and malate are present in similar concentration ranges. Glutarate is present in the lowest concentration with mean value of 7.12 ng/m^3. Time-series analysis strongly suggests that concentrations of LMW organic acids in aerosol samples are linked to the dominant contribution from anthropogenic sources.

INTRODUCTION

In urban areas particulate matter can cause air quality problems such as visibility reduction and health problems. One of the most significant contributions to atmospheric loadings comes from anthropogenic sources, and this contribution is in a significant increase in industrial and urban areas. In urban region water-soluble ions are major components of the atmospheric aerosols (Zhang et al., 2011; Kawamura et al., 2016). Detection of the chemical composition of atmospheric aerosols would be valuable for understanding their chemical and physical behaviour, and to trace their origin. Examination of water-soluble ions is very important for getting information of the sources of aerosols, their characteristics, formation mechanisms and behaviour (Fang et al., 2011; Wang et al., 2015). Water-soluble components of atmospheric aerosol contain many important compounds such as low molecular weight (LMW) organic acids. These components can affect to the solubility of toxic organic compounds and significantly increase their toxicity. They are emitted from primary sources such as fossil fuel combustion and biomass burning and make secondary organic aerosols. LMW contributes only a small part of the total aerosol mass, but they are very important factor for different processes (human health, cloud condensation nuclei, climatic process, acid precipitation, hygroscopic properties, ice forming nuclei, optical properties) (Tsai et al., 2008). Local sources, weather and reaction conditions and long-range transportation significantly influence on concentrations and particulate distributions of ions in atmospheric aerosol particles (Zhao et al., 2011).

The separation of LMW organic acids can be undertaken using IC and gas chromatography with mass spectrometry (GC-MS). GC-MS is a suitable technique after a derivatization step, in order to get these acids in their volatile form. Disadvantages of GC-MS are complex extractions and the large amount of organic solvent consumed. The derivatization process is often troublesome. The application of IC is more advantageous such is simpler sample preparation, minimizes the use of hazardous solvents, maximizes the efficiency of recovery and shortens the analytical time (Fritz and Gjerde, 2000; Ng et al., 2016). Improved separation in chromatography can be accomplished by applying optimization criteria. IC separations can be realized either by isocratic or gradient elution. The advantage of gradient elution is that both weakly retained and strongly retained ions can be separated in the same run. Optimization of IC methods is sometimes difficult due to the high number of parameters which can affect the separation. Optimization of IC separations is achieved first of all with a choice of appropriate stationary phase and then by changing the compositions of eluent.

In this work seven LMW organic acids (formate, glyoxilate, glutarate, succinate, malate, malonate and oxalate) in 100 atmospheric aerosol samples, collected in a suburb of Belgrade (Serbia), were analysed on a Dionex IC system with AS11 analytical column and hydroxide eluent. Concentration levels and the seasonal variations of the measured species are also studied.

METHODOLOGY

Atmospheric aerosol samples for determination of LMW organic acids were collected between September 2013 and June 2014 at the Mirijevo, outskirt of Belgrade. Located to the south-east of the city, the sampling site is characterized by the following environment: (1) a suburban residential and commercial area (near commercial area, retail stores, houses and restaurants), (2) a municipal incinerator in the vicinity; (3) a city landfill in the vicinity; (4) a petrochemical industry in the vicinity; (5) oil refinery in the vicinity.

A 100 daily samples 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 in afreezer until the time of analysis. A portion of each loaded filter (1.0 cm^2 punch) was 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 DX-300 IC system (Dionex, Sunnyvale, CA, USA) with Dionex IonPac®-AS11 (250 x 4 mm) analytical column and hydroxide eluent. An Anion Self Regenerating Suppressor (ASRS ultra 300) was used. For instrument control, data collection and processing, Dionex Peaknet 5.1 software was employed. A Spectra-Physics model AS3500 autosampler was used for the direct programmed injection of samples. The system operated with a flow rate of 2.0 ml/min.

Commercially supplied standards or high-purity chemicals were used to prepare individual solutions of organic acids. Milli-Q system (Millipore Co., Bedford, MA, USA) processed water (18 $M\Omega cm^{-1}$) was used for preparation of working mixture. As a quality control measure, duplicates, blanks and spike samples were also analysed. A mixture of HPLC grade methanol and hydroxide ions, at flow rate of 2.0 ml/min, was used as the eluent. The following gradient program was applied: (1) time: 0.0 min, KOH: 0.175 mM, CH_3OH: 5.0 %, (2) time: 6.0 min, KOH: 0.575 mM, CH_3OH: 5.0 %, (3) time: 26.0 min, KOH: 8.575 mM, CH_3OH: 17.0 %, (4) time: 30.0 min, KOH: 10.175 mM, CH_3OH: 5.0 %.

RESULTS AND DISCUSSION

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 sulphates which tend to overlap the peaks of LMW organic acids. Therefore, a complicated gradient program must be applied.

For the separation of anions, a multi-step gradient provided simultaneous separation of both inorganic ions (chloride, nitrite, nitrate, sulphate) and the ionic form of LMW organic acids (formate, glyoxylate, methanesulphonate, glutarate, succinate, malate, malonate, oxalate). In addition to these anions, several other anions (bromide, phosphate, sulphite, benzoate, caproate, pimelate, fumarate, phtalate, acetate, lactate, glycolate, pyruvate, tartarate and azelate), which are detected in some samples, are not included in this statistical evaluation. The reason was incomplete data for most of the samples. Besides, some of these anions were often either below the quantification limit of the applied method (pyruvate, tartarate, bromide, phtalate, caproate, fumarate) or there were co-elution problems (fluoride/lactate/acetate, acetate/glycolate) or a problem with the stability of analyzed anions (sulphite, azelate). Therefore, 7 LMW organic acids were quantified in all analysed samples. The organic acid concentrations (mean value) of aerosol samples was in the following order: oxalate > malonate > succinate > formate > malate > glyoxilate > glutarate.

The arithmetic means, minimum values, maximum values and standard deviations for the obtained concentrations of all analyzed LMW organic acids in the studied aerosol samples were calculated (as shown in Table 1).

Oxalate was the most abundant organic species detected. Its concentration ranged from 15.87 to 282 ng/m^3 with an average of 95.70 ng/m^3. Malonate was the second most abundant species followed by succinate, with concentrations ranging from 0.10 to 103.49 ng/m^3 and with an average of 19.43 ng/m^3. Formate, glyoxylate, succinate and malate are present in similar concentration ranges with average values of 16.98, 12.00, 17.99 and 15.82, respectively. Glutarate is present in lowest concentration with mean value of 7.12 ng/m^3. Vehicle emissions and biomass burning in the vicinity of the sampling site are primary sources of LMW organic acids.

Table 1. *Descriptive statistics for the data for the studied water-soluble substances in atmospheric aerosols [ng/m^3] at one site in the outskirts of Belgrade in the period of September 2013 until June 2014*

Variable	Mean	SD*	Min.**	Max.***
Formate	16.98	8.632	4.54	44.11
Glyoxylate	12.00	11.42	1.03	61.00
Glutarate	7.12	5.643	0.65	30.96
Succinate	17.99	14.41	3.39	82.28
Malate	15.82	18.95	1.39	93.40
Malonate	19.43	25.43	0.10	103.49
Oxalate	95.70	61.27	15.87	282.00

* - standard deviation, ** - minimum value, *** - maximum value.

To examine the trends of the concentration changes over investigated period (autumn 2013 to summer 2014), the average concentrations of analysed LMW organic acids were plotted for all samples for a period of ten months. The time-trends of these variables were also fitted by quadratic curves. The obtained graphs are presented in Fig. 1. All of the analysed 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. 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.

For the presence of LMW organic acids in atmospheric aerosols in Belgrade, no data have been presented and published so far. There are data in the literature for different urban and background regions. Analytical procedures in these studies were based on different analytical instruments, including IC, HPLC-MS, GC-FID and GC-MS. Oxalate is the most abundant species which is consistent with data from the literature. Malonate is the second abundant species. Kawamura and Bikkina (2016) reported that global atmospheric distribution of LMW organic acids shows higher abundances over continental sites than over marine regions which are probably linked to the dominant contribution from anthropogenic sources. In the urban and rural atmosphere, this acids originate from a variety of anthropogenic sources and, as expected, higher concentration were found in urban compared to background areas.

CONCLUSIONS

Application of IC methods in analysis of atmospheric aerosol samples with great differences in concentration between inorganic anions and LMW organic acids, strongly depends on the concentration of hydroxide eluent. Variation of the concentration of hydroxide eluent influences the retention time of fluoride and chloride ions, which is crucial for the analysis of these ions together with organic acids. Therefore, optimization of separation of the LMW organic acids and inorganic anions is a necessary step prior to their analysis. Gradient elution with four steps was developed using Dionex AS 11 IC column. By application of the gradient to atmospheric aerosols samples good separation of peaks even in the presence of high concentrations of inorganic anions was achieved. Seven LMW organic acids (formate, glyoxilate, glutarate, succinate, malate, malonate and oxalate) were detected in atmospheric aerosol samples. Oxalic acid was found to be the most prevalent LMW organic acid. The time trend shows an increase in concentration in autumn and spring.

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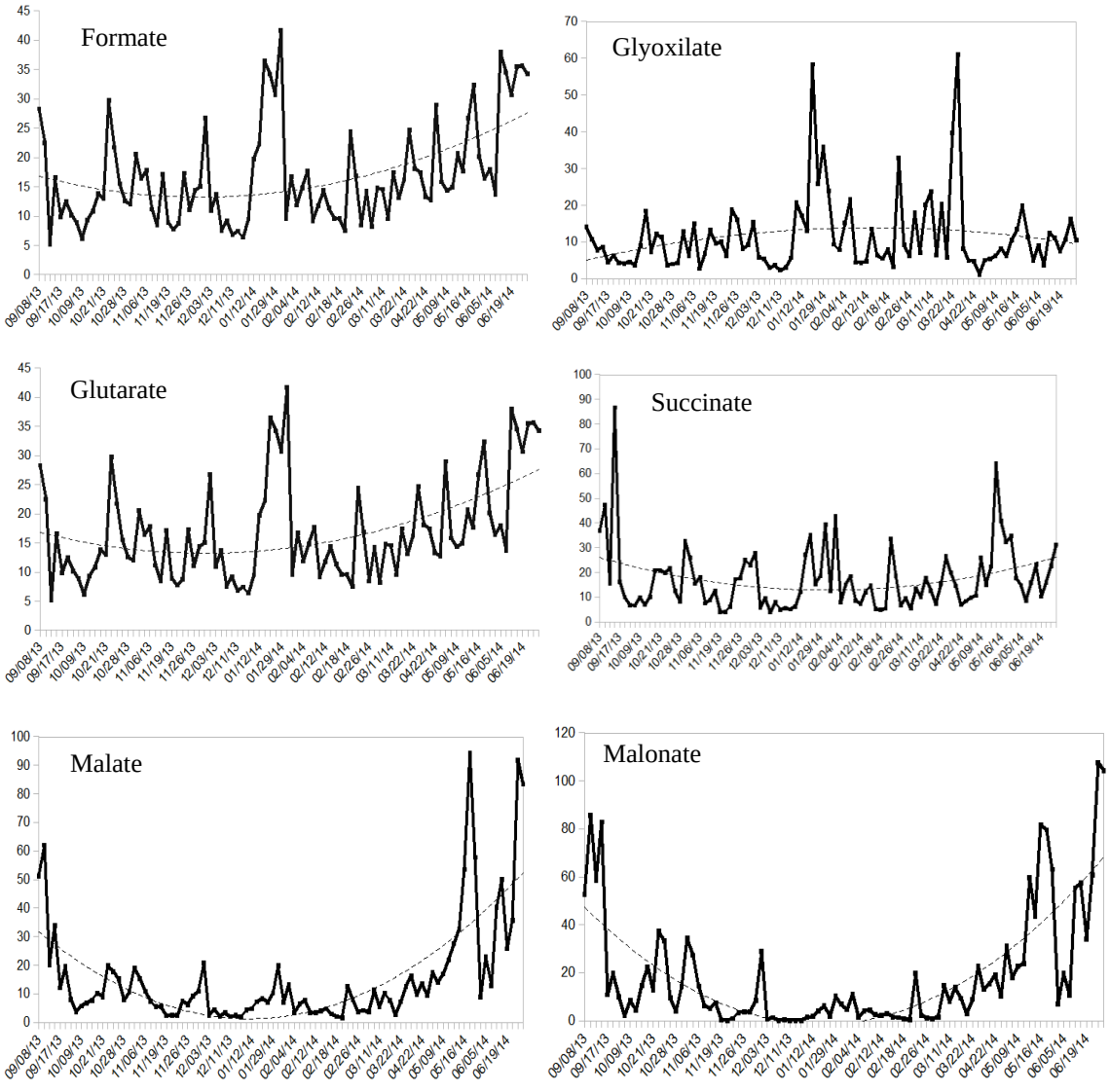

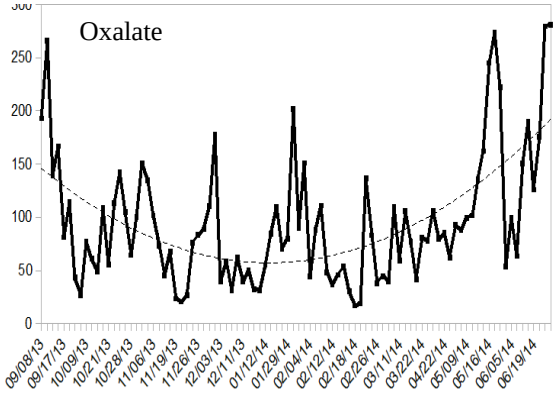

Figure 1. *Variation of atmospheric aerosol concentrations of formate, glyoxilate, glutarate, succinate, malate, malonate and oxalate in outskirt of Belgrade during the period 2013 to 2014. The lines indicate the moving average, n=4 (solid line) and quadratic fit (dot line).*

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

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ABSTRACT

The concentrations of eighteen polycyclic aromatic hydrocarbons (PAHs) in indoor and outdoor air of preschools (3-5-years old) and in the breathing air zone of firefighters, as well as the contribution of air on the urinary excretion levels of six monohydroxyl-PAHs (OHPAHs) were reviewed. Compounds with 2-3-rings contributed the most for airborne total PAHs. Urinary 1-hydroxynaphthalene and 1-hydroxyacenaphthene were the most abundant compounds (66-96% of total OHPAHs), followed by 2-hydroxyfluorene (1-16%), 1-hydroxyphenanthrene (1-11%), 1-hydroxypyrene (1-7%); 3-hydroxybenzo(a)pyrene, the PAH biomarker of carcinogenicity, was never detected. Positive and moderate-to-strong correlations were found between levels of total PAHs in school total indoor air and firefighters' personal air at fire stations with the urinary concentrations of total OHPAHs found in preschool children and firefighters, respectively. In general, a strong contribution of airborne PAHs to children and firefighters' total PAH body burden was found.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a group of hydrocarbons composed of aromatic rings that are formed during the incomplete combustion of organic materials. PAHs present cytotoxic, mutagenic and carcinogenic properties (IARC 2010b), being also classified as endocrine disrupting chemicals (WHO, 2013). Some compounds may cause neuro-, immuno-, hemato-, cardio-, reproductive and developmental toxicities in humans. As a consequence, 16 PAHs are classified as priority pollutants (USEPA, 2005): naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(a,h)anthracene, benzo(ghi)perylene, and indeno(1,2,3-cd)pyrene. Benzo(a)pyrene is the only known compound with proven carcinogenic properties to humans (IARC group 1; IARC, 2010b), while naphthalene, benz(a)anthracene, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, chrysene, and indeno(1,2,3-cd)pyrene are classified as possible carcinogenic (group 2B; IARC, 2002, 2010b). Dibenzo(a,l)pyrene and dibenz(a,h)anthracene, probable carcinogens (group 2A; IARC 2010b), have also been under consideration because of their higher carcinogenic potency comparatively with benzo(a)pyrene (Okona-Mensah et al, 2005; Slezakova et al, 2013). The most relevant sources of PAHs are traffic emissions, coal and petroleum combustion, emissions from several industial processes including electrical stations, waste treatment, and burning of biomass and wood products (Kamal et al, 2015). Indoor sources of PAHs are originating from outdoor air penetration (open doors and windows) and by activities conducted in indoor microenvironments mainly related with smoking, cooking and candle burning. However, assessment of PAH exposure is complicated due to their partition between particulate and gas phases and by exposure through several routes, namely inhalation, food ingestion, and skin contact. Therefore, biological monitoring has been used in combination with environmental data to better assess total exposure to PAHs. PAHs are absorbed into the blood stream through the skin, lungs and gastrointestinal tract and tend to accumulate in the lipophilic tissues of the human body where it is expected to exert their toxicity (Franco et al, 2008; Kamal el al, 2015; Needham et al, 2007). Human body has the capacity to metabolize PAHs through some enzymatic mechanisms that may occur in nasal tissues, red and white blood cells, platelets, the uterus, hair follicles, brain, spleen, placenta, liver, lungs or kidneys (Kamal et al, 2015). However, the liver presents the highest rate of metabolization, followed by the lungs, intestinal mucosa, skin and kidneys (Kamal et al, 2015). Metabolization will transform the absorbed PAHs into intermediated compounds (hydroxylated metabolites; phase I) that can be conjugated with biological macromolecules such as glutathione, glucuronide or sulphate (phase II) in order to be easily eliminated from the human body (Kamal et al, 2015; Lewtas, 2007; Toriba and Hayakawa, 2007). Among the different elimination routes, urine is the easiest and cheapest human matrix to assess biomarkers of exposure to PAHs. Urinary 1-hydroxypyrene (1OHPy) and 3-hydroxybenzo(a)pyrene (3OHBaP) are the principal metabolites of pyrene (marker of exposure to PAHs) and benzo(a)pyrene (marker of exposure to carcinogenic PAHs), respectively. PAHs with 2-3 aromatic rings, namely acenaphthene, fluorene, and phenanthrene are frequently found in environmental samples, being 1-hydroxylacenaphthene (1OHAce), 2-hydroxylfluorene (2OHFlu), and 1-hydroxyphenanthrene (1OHPhe) their major urinary metabolites, respectively (Gomes et al, 2013; Cirillo et al,

2006; Oliveira et al, 2015a, 2015b). 1-hydroxynaphthalene (1OHNaph) 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 (OHPAHs) may 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.

This work aims to review data from some case studies (Oliveira et al, 2016a, 2016b, 2017a, 2017b) related with preschool children environmental (3-5 years old attending preschools) and firefighters' occupational exposures (at fire stations and after fire combat activities) to 18 PAHs (16 USEPA priority PAHs, dibenzo(a,l)pyrene, and benzo(j)fluoranthene recommended by EU Directive 2004/107/EC). The contribution of indoor and personal airborne individual and total PAHs on the excretion of six main urinary OHPAHs (1OHNaph, 1OHAce, 2OHFlu, 1OHPhe, 3OHBaP) was explored.

METHODOLOGY

Characterization of the study populations and sampling sites

Several outdoor and indoor air sampling campaigns were performed at two urban Portuguese preschools during the regular schoolar period. Preschool one (A1) was situated in Paranhos, Oporto Metropolitan Area (2nd largest Portuguese city) where main emission sources of PAHs include vehicular traffic, an international shipping port, petrochemical complex with oil refinery situated nearby, and an incineration unit. Peschool two (A2) was located 150 km northeast of Oporto, in the city of Chaves (municipality with 2nd highest population in Vila Real district). A2 was located directly next to a road, which is the major thoroughfare to city center with a mall and a gas station that contributed to a consistent vehicular traffic throughout the day.

Firefighters´occupational exposure to PAHs was determined by the monitorization of PAHs in the breathing air zone of professional (and non-smoking) firefighters´ during a regular work shift at different fire corporations situated in the district of Bragança (North of Portugal).

Sample collection

Gaseous and particulated PAHs were simultaneously collected in the indoor and outdoor air of both preschools. Collection of indoor air samples was performed at classrooms where educational, physical exercising and entertaining activities occurred throughout the school day. Ambient air samples were collected in preschools yards where children daily played. Sampling was performed with constant flow samplers (model Bravo H2; TCR TECORA, Italy) and using different combinations of PM EN LVS sampling heads (Norm EN14907); an air flow rate of 2.3 m^3/h was used. Each sampling head was assembled at 1.5 m of height, 1 m from walls and in a way to guarantee children safety. Particulate fractions and gaseous samples were respectively collected on polytetrafluoroethylene membrane filters (PTFE; 2 μm porosity, Ø 37 and 47 mm, SKC Ltd., United Kingdom) and polyurethane foams (PUF; 75 mm, SKC Ltd., United Kingdom), which were immediately frozen at -20ºC until chromatographic analysis.

Firefighters' personal air sampling campaigns were performed during a consecutive period of 4-h at a normal work day in the fire corporation, i.e, without the active participation in firefighting activities. Each firefighter was informed that he should perform his routine tasks at the fire station during the period of sampling campaign. Air samples were collected on PTFE filters (SKC Ltd., United Kingdom) with personal constant flow samplers (Gilian, models GilAir3 and ProValue3; Sensidyne, USA) that were positioned at the firefighter' breading area; an air flow rate of 2 L/min was used.

A questionnaire was prepared based on previously validated questionnaires (WHO, 2002) and delivered to children´ parents and to each firefighter to fill it out. Parents of all children and firefighters who accepted to participate in the study confirmed the volunteer participation in the study by signing an informed consent that was approved by the Ethic Committee of University of Porto. Information on some biometric characteristics (age, gender, weight, height), smoking habits of the close relatives, consumption of boiled, roasted and grilled foods in the two days before urine sampling was collected for each participant (children/firefighter). Parents of preschool children and firefighters were asked to collect spot-urine samples in sterilized polycarbonate containers, which were taken to the laboratory and immediately frozen at -20 ºC until analysis.

Analysis of airborne PAHs and urinary OHPAHs

The extractions of airborne PAHs (filters and PUF foams) were realized according to previously validated methodology (Castro et al, 2009, 2011). Briefly, PAHs were extracted in a microwave (MAE; MARS-X, CEM, Mathews, USA) with 30 (filters) and 45 mL (foams) of acetonitrile at 110 ºC during 20 min.

An aliquot of 10 mL of urine was buffered with acetate buffer (pH 5.0) and incubated for 120 min with 80 µL of β-glucuronidase/arylsulfatase (Helix pomatia; EC3.2.1.31/EC3.1.6.1; 5.5/2.6 U/ml; Roche Diagnostics - Indianapolis, USA). Then incubated urine samples were loaded into Sep-Pak®Light Plus C18 (Waters; Sigma-Aldrich, Steinheim, Germany), being OHPAHs extracts eluted with 20.0 mL of methanol/ethyl acetate (10:90; v/v). PAHs and OHPAHs extracts were evaporated to dryness using a rotary evaporator (Buchi Rotavapor, R-200) at 20 °C; redissolved in 250-500 µL of acetonitrile (PAHs) or methanol (OHPAHs) and filtered with a PTFE filter (0.45 µm) before analysis.

Chromatographic analysis of airborne and urinary extracts was performed in a Shimadzu LC system (Shimadzu Corporation, Kyoto, Japan) equipped with an LC-20AD pump, DGU-20AS degasser, and photodiode array SPD-M20A (PAD) and fluorescence RF-10AXL (FLD) detectors on line according to previously validated studies (Castro et al, 2009, 2011; Chetiyanukornkul et al, 2006). Chromatographic separation of the 18 PAHs and 6 OHPAHs compounds were made in a C18 column (CC 150/4 Nucleosil 100-5 C18 PAH, 150×4.0 mm; 5 µm particle size; Macherey-Nagel, Duren, Germany) that was kept at room temperature (20±1 °C). Each analyte was detected at the respective optimized chromatographic conditions (Castro et al, 2009, 2011; Oliveira et al. 2016a).

The levels of urinary OHPAHs were normalized with the concentrations of creatinine (µmol/mol) determined by the Jaffe colorimetric method (Kanagasabapathy and Kumari, 2000) in the urine of each preschool children and firefighter. Analytical blanks and standards were daily analysed; analysis was made in triplicate.

RESULTS AND DISCUSSION

Children environmental exposure

The concentrations of total PAHs (∑PAHs) in the indoor total air of preschools ranged from 26.1-150.5 ng/m^3 at A1 and between 52.6-85.3 ng/m^3 at A2, being these levels much higher than the respective outdoor total air values (2.79-46.9 ng/m^3 at A1 and 6.20-19.2 ng/m^3 at A2). The predominant sources of PAHs in the indoor air of classrooms may be the infiltration of outdoor air (i.e. light-duty gasoline fuelled vehicle exhausts, emissions from local industries since those compounds are used in the production of dyes, plastics, pigments, pharmaceuticals and pesticides) (Oliveira et al, 2015b; Ravindra et al, 2008). Gaseous and particulated-bound PAHs represented 95-97% and 3-5% of indoor total air ∑PAHs and 77-91% and 9-22% of outdoor total air ∑PAHs, respectively. Among the 18 PAHs considered, dibenz(a,h)anthracene was the predominant compound in the indoor air particulate phase of both preschools, followed by benzo(b+j)fluoranthene, benzo(ghi)perylene, and acenaphthene. Altogether, these compounds accounted with approximately 50% of particulate PAHs. Naphthalene was one of the most predominant compounds in the gas phase of classrooms (13.6-62.7 ng/m^3 for A1 and 13.1-20.8 ng/m^3 for A2) for both preschools; still those levels were always well below the recommended annual guideline of 10 µg/m^3 (WHO, 2010). At A2, the concentrations of phenanthrene were 2 times higher than naphthalene ($p < 0.001$) and accounted for 55% of total gaseous PAHs. The major indoor sources of naphthalene and phenanthrene include the use of pest repellents and deodorants as well as vapour vehicle emissions (ATSDR, 1995; Batterman et al, 2012). Median concentrations of total carcinogenic (including probable/possible) PAHs ($\sum PAHs_{car}$) ranged from 15.5-16.3 ng/m^3 in indoor total air and from 4.80-10.5 ng/m^3 for ambient total air at both preschools. $PM_{2.5}$-benzo(a)pyrene concentrations at both preschools (3.96×10^{-2} to 0.853 ng/m^3 indoors *versus* 3.69×10^{-2} to 0.972 ng/m^3 outdoors) were always below the guideline of 1 ng/m^3 defined for PM_{10} content (Directive 2004/107/EC). Since naphthalene, a possible carcinogen to human (group 2B; IARC, 2002) has a strong contribution in the gas phase and consequently to the total air, the levels of $\sum PAHs_{car}$ may be overestimated. At both preschools, total air ΣPAHs were higher indoors than outdoors; however, the PAH profiles in indoor and ambient air were similar for both particulate and gaseous phases, thus suggesting that penetration of outdoor emissions was the dominant source to indoors. Particulate PAHs were principally associated with PM_1 (54-76%). Indeed PAHs with 5-6 rings (benzo(b+j)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(a,h)anthracene, benzo(ghi)perylene and indeno(1,2,3-cd)pyrene) were predominantly found in particulate fractions, while 2-3 ring compounds (naphthalene, fluorene and phenanthrene) were principally present in the gas phase (76-94% indoors and 42-79% outdoors).

Detection rate of OHPAHs ranged between 82% for 1OHNaph + 1OHAce to 94% for 2OHFlu and 1OHPhen. Urinary 3OHB(a)P, the PAH biomarker of carcinogenicity, was never found in the urine of preschool children,

which is in line with the low concentrations found in preschools air and with the results reported by other authors (Fan et al, 2012; Miller et al, 2010; Wilson et al, 2000). Moreover, it has been reported that PAHs with low molecular weights are mostly eliminated through the urine with high molecular weights are predominantly eliminated through feces (Li et al, 2012; Marie et al, 2010). In fact, it was observed that the higher the molecular weight of the PAH the lower the concentration of the respective metabolite. Urinary 1OHNaph and 1OHAce was the most predominant metabolites (78-84% of ∑OHPAHs), followed by 2OHFlu (8-11%), 1OHPy (3-7%), and 1OHPhen (3-5%) at both preschools. Therefore, a similar distribution profile was observed between airborne levels of PAHs at A1 and A2 and children' urinary OH-PAH concentrations, with the 2-3-ring compounds being the most predominant. Since children spent majority of their school daily time indoors (6.75-h indoors *versus* 1.25-h outdoors) spearman correlation coefficients were determined between the concentrations of individual and ∑PAHs in school indoor total air and children urinary levels of OHPAHs. The strongest correlations were found between ∑PAHs in preschool indoor air and the urinary levels of ∑OHPAHs ($r = 0.218$ to $r = 0.700$), followed by the positive correlation between airborne naphthalene and acenaphthene with urinary 1OHNaph + 1OHAce ($r = 0.264$ to $r = 0.533$). These findings revealed the impact of school indoor levels of 2-3 ring PAHs on preschool children total exposure to PAHs.

Firefighters' exposure

The concentrations of PAHs in the breathing air zone of Portuguese firemen attending at eight fire corporations during a regular work shift varied between 46.4 to 428 ng/m^3. This wide range of values was attributed to the fire stations local specificity (urban/rural) and its building characteristics (age and layout). Among the 18 compounds under study, acenaphthylene contributed the most for ΣPAHs (46.4-61.5%) in the breathing air zone of firefighters attending Portuguese fire corporations, except for the individuals working in two rural fire stations where acenaphthylene was not detected. Acenaphthylene is frequently found in crude oil, coal tar, and tobacco smoke and also as a product of combustion, which justifies its abundance in fire station (micro)environments (Kirk and Logan, 2015a, 2015b; Lin et al, 2002; Perwak et al, 1982). Acenaphthene, naphthalene, and phenanthrene were the other predominant PAHs with contributions ranging from 2.65 to 38.6% of ∑PAHs. Alltogether, these compounds represented 84.6-95.0% of $PM_{2.5}$-bound PAHs in the breathing air zone of firefighters. Thus, naphthalene, acenaphthylene, acenaphthene, and phenanthrene (2-3 ring compounds) accounted with 63.9 to 95.7% of ΣPAHs; 4-ring PAHs represented 0.79 to 2.05% of ΣPAHs and compounds with more than 5-rings contributed with 2.74 to 34.7% of ΣPAHs. Concentrations of $\Sigma PAHs_{carc}$ ranged from 8.24 to 150 ng/m^3, with naphthalene and dibenz(a,h)anthracene being the compounds that contributed the most for $\Sigma PAHs_{carc}$ (39.4-78.1% and 4.1-33.8%, respectively). Benzo(a)pyrene concentrations in the breathing air zone of firefighters accounted with 1.5 to 10% of $\Sigma PAHs_{carc}$ and in one fire station its levels were 10-20 times higher than the existent limit of 1 ng/m^3 (an annual mean total content in PM_{10} fraction) for ambient air (Directive 2004/107/EC). However, firefighters' personal exposure to PAHs were always well below the existent PAHs occupational exposure limits proposed by the American Conference of Governmental Industrial Hygienists, the National Institute for Occupational Safety and Health and the US Occupational Safety and Health Organization (ACGIH, 2012; EHME, 2017; Fent et al, 2013; NIOSH, 2007).

Overall, the concentrations of urinary ∑OHPAHs among non-smoking and non-exposed firefighters ranged from 0.259-3.71 µmol/mol creatinine. Moreover, consistent evidences were found that excretion of main individual and total urinary OH-PAHs was significantly increased (1.7-35 times) in firefighters that were directly involved in firefighting activities comparatively with non-exposed firefighters. The profile of urinary OHPAHs distribution is in line with airborne PAH distribution, with urinary 1OHNaph and 1OHAce being the most predominant metabolites (64-96% of ∑OHPAHs), followed by 2OHFlu (1-16%), 1OHPhen (1-11%), and 1OHPy (1-7%). Biomonitorization of urinary 1OHPy has been used to control occupational exposure to PAHs in some health-relevant professional workers such as coke ovens, primary aluminium production among other individuals that handle coal tar derived products (Jongeneelen, 2014). Despite no reference standard guidelines are defined for urinay OHPAHs, the levels of urinary 1OHPy in non-exposed and exposed firefighters were well below the benchmark level of 0.5 µmol/mol creatinine recommended by the American Conference of Governmental Industrial Hygienists (ACGIH, 2010). Positive and moderate to strong spearman correlation coefficients ($r = 0.367$ to $r = 0.886$) were found between airborne ∑PAHs and the urinary ∑OHPAHs for firefighters attending at Portuguese fire stations, proving the contribution of fire stations indoor air to the firefighters' total exposure to PAHs.

CONCLUSIONS

The major findings of this study reveal the need to consider the gas phase for an adequate assessment of environmental and occupational exposure to PAHs. Despite urinary 1OHPy being considered as a biomarker of exposure to PAHs, the reviewed studies indicated that it was one of the less abundant metabolites in the urine of both preschool children and firefighters, thus suggesting that 1OHPy may be a non-sensitive marker of environmental inhalation exposure to pyrene. As a consequence, the use of different urinary OHPAHs is strongly recommended in the assessment of individual's recent total exposure to PAHs. Spearman correlation coefficients revealed to be a crucial tool to identify and estimate the major emission sources that contribute the most to the total exposure to PAHs. The collected data also highlight the need to establish more specific air quality international limits for environmental and occupational exposure to PAHs and the implementation of international guidelines for urinary OHPAHs, principally in the most susceptible groups of the population.

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2.4. LEAVES OF COMMON URBAN TREE SPECIES AS A MEASURE OF PARTICLE POLLUTION

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ABSTRACT

Magnetic biomonitoring has been proven as a reliable proxy for deposited airborne particles (PM). However, the leaf entrapment of PM is species-specific and it should be a matter of investigation. In this study, four tree species common in urban areas of Europe and beyond (*Acer platanoides*, *Aesculus hippocastanum*, *Betula pendula* and *Tilia cordata*) were studied for their PM-entrapment capacities. In two urban parks of Belgrade (Serbia), the tree leaves were sampled in May and September of four consecutive years (2011–2014). Saturated Isothermal Remanent Magnetization (SIRM) quantified the magnetic PM fraction in the leaf samples. The magnetic measurements were considered regarding the regulatory PM_{10} measurements. The median leaf SIRM values of *T. cordata*, *A. hippocastanum* and *A. platanoides* (174, 140, and 123 × 10^{-5} × A m^2 kg^{-1}, respectively) indicated the more prominent capacity of these species for capturing magnetic particles compared with to *B. pendula* (68 × 10^{-5} × A m^2 kg^{-1}). However, *B. pendula* leaves showed statistically significant correlation of the SIRM and PM_{10} values (r = 0.75), and spatio-temporal differences in the leaf SIRM between the studied parks/years. These results recommend *B. pendula* as a valuable biomonitor of particles. 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.

INTRODUCTION

Particulate matter (PM) pollution is nowadays one of the key problems in cities due to its adverse health and environmental effects. The urban environment is under heavy impact of airborne PM emitted mostly from traffic, which often carries other pollutants – toxic elements, PAHs, etc. (Pacyna, 2007). Although emissions of the main air pollutants in Europe have declined, reductions do not always produce a corresponding drop in their atmospheric concentrations, especially PM_{10} and $PM_{2.5}$. In 24 of the 26 mega-cities, annual average PM_{10} concentrations exceeded air quality standards (Zhu et al, 2013). Considering the large spatial and temporal variations of pollution phenomena, current instrumental monitoring of PM is quite scarce and limited predominantly due to a high costs and maintenance of instruments. Therefore, in the last few decades, plant biomonitoring has been developed as a powerful tool for assessing environmental pollution. Complementary with conventional instrumental monitoring, plant biomonitoring may provide a high density of sampling sites for assessment and mapping of pollution levels over wide areas and with high resolution of sampling sites (Markert et al, 2003; Aničić Urošević et al, 2017). The leaves of urban trees are of vital importance for the quality of life in urban environments by capturing atmospheric particulates (Beckett et al, 2000; Nowak et al, 2006; Dzierżanowski and Gawroński, 2011). As reported in the annual urban air quality assessment within the Environmental Area in Rome, street trees are able to remove about 60% of the total particulate emission (Ortolani and Vitale, 2016).

Specifically, magnetic biomonitoring may be applied for the characterisation of leaf-deposited particles and their class-sizes (Hofman et al, 2014a). The studies on the leaf magnetic properties have shown that different species have specific capacities for particle capture and accumulation (Mitchell et al, 2010; Kardel et al, 2011) with the distinct possibility of PM removal from air. In the Belgrade urban area, since 2002, leaves of deciduous trees have been used for biomonitoring of trace elements testing several species (*Aesculus hippocastanum*, *Tilia tomentosa*, *Tilia cordata*, *Acer platanoides*, and *Betula pendula*) and different methodological steps (Aničić et al, 2011; Tomašević et al, 2011; Deljanin et al, 2014). However, these biomonitoring data have never been considered in the context of the regulatory PM_{10} or magnetic particle measurements.

In this study, the leaves of deciduous trees were investigated in a multi-annual period (2011–2014) with the aims: 1) to select the most consistent biomonitor of magnetic particles among four deciduous tree species (*A.*

hippocastanum, *T. cordata*, *A. platanoides*, and *B. pendula*); and 2) to investigate correlations between the leaf Saturation Isothermal Remanent Magnetization (SIRM) values and the collocated PM_{10} measurements.

METHODOLOGY

The study was conducted in Belgrade (44°50' - 44°44'N and 20°22' - 20°32'E at 70-250 m altitude), Serbia, with about 1.6 million inhabitants. Belgrade represents the second largest urban centre in the Balkans and an important regional traffic core of connections between Eastern and Western Europe. Two urban parks were selected as sampling sites: the central urban (CU), and the central suburban (CS) (Figure 1). Both parks are situated in the old city cores surrounded with heavy traffic occupied streets with public transportation lines. The Air Quality (AQ) monitoring stations are positioned close to the parks.

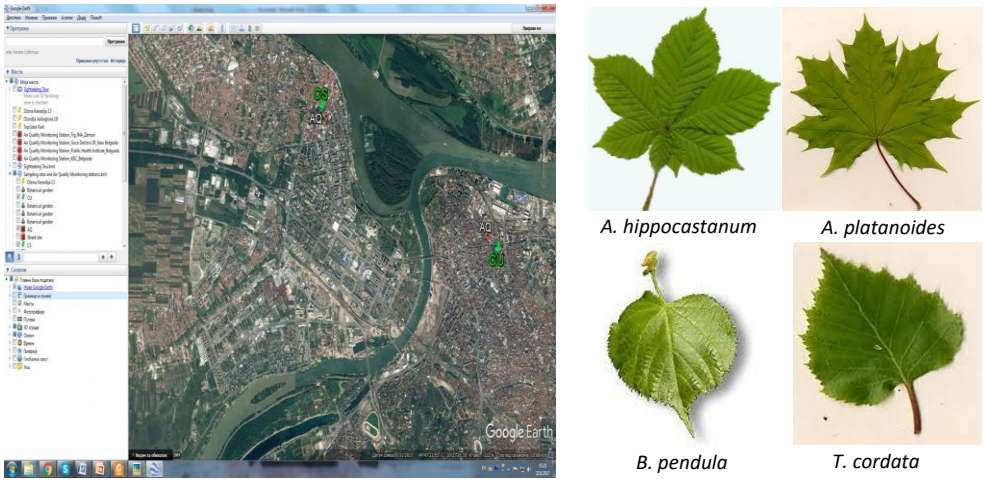

Figure 1. *Map of the Belgrade urban area with the studied parks: central suburban (CS) and central urban (CU) parks; and the nearest Air Quality Monitoring stations (AQ); leaves of the studied tree species*

Leaves of four deciduous tree species were sampled in the parks: *Aesculus hippocastanum* L. (horse chestnut), *Tilia cordata* Mill. (linden), *Acer platanoides* L. (Norway maple) and *Betula pendula* Roth (birch). The species are frequently occurring urban trees in the study area and in Europe, and have different leaf morphology. The leaf sampling was conducted at the beginning (May) and at the end (September) of the vegetation season from 2011 until 2014. The leaves were taken from five individual trees of approximately the same age, at ≈ 2 m height above ground. Five sub-samples (each consisting of 10-30 fully developed leaves) were collected per species per site. Unwashed leaf sub-samples were dried in an oven at 45ºC for 24 h, packed in polyethylene bags, and kept under stable laboratory conditions until analyses.

Three leaf sub-samples of about 500 mg were taken for magnetic analysis (n = 3 sub-samples per species × 4 species per park × 2 parks × 2 sampling time × 4 years = 192). The sub-samples were tightly packed by clingfilm™, avoiding movement of any sample parts, and pressed into a 10 cm^3 plastic container. The sub-samples were individually magnetised in a direct current (DC) field of 1 T with a pulse magnetiser (Molspin Ltd, UK) (Kardel et al, 2011; Hofman et al, 2014a). The isothermal remanent magnetisation (IRM) of the samples (A m^2) was measured twice using a spin magnetometer with high sensitivity (~0.1×10^{-8} A m^2, Molspin Ltd, UK). The instrument was calibrated before and after every ten measurements by means of a magnetically stable rock specimen. The IRM at 1 T is taken to be the Saturation IRM (SIRM) of each measured sample. The SIRM was normalised for leaf dry mass (10^{-5} A m^2 kg^{-1}).

Data of the ambient daily PM_{10} concentrations were obtained from two AQ monitoring stations positioned close to the leaf sampling parks. The monitored dataset includes PM_{10} mass concentrations (µg m^{-3}), five measurements per month per monitoring station.

RESULTS AND DISCUSSION

The results of the leaf SIRM obtained for the studied multi-annual period (2011–2014) are shown in Figure 2. For all tree species, the leaf SIRM increased significantly ($p<0.05$) from the beginning (May) to the end of vegetation season (September). Further, due to evident atmospheric deposition during the vegetation season, only the SIRM values obtained for the leaves sampled in September are compared with the relevant median PM_{10} concentrations measured during the same month (Table 1).

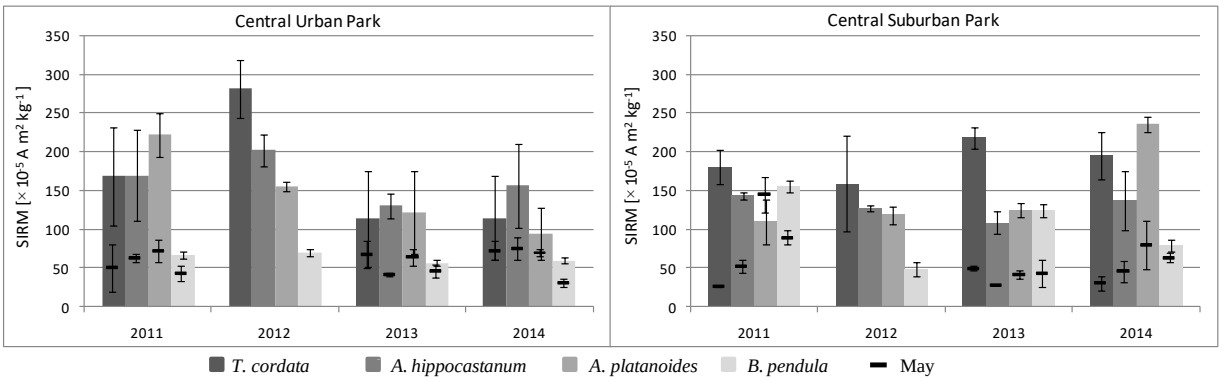

Figure 2. *Median SIRM values (× 10^{-5}A m^2 kg^{-1}) in the leaves of four tree species sampled in the central urban (CU) and the central suburban (CS) parks, at the beginning (May) and at the end (September) of the vegetation seasons from 2011 to 2014*

The magnetic analysis showed the following order of the leaf particle enrichment: *T. cordata* ≥*A. hippocastanum* ≥*A. platanoides* >*B. pendula*. Among the studied tree species, the leaf SIRM was significantly different ($p<0.05$) only between *T. cordata* and *B. pendula* at both studied sites, CU and CS, ranged between 113.90 – 281.20 × 10^{-5} × A m^2 kg^{-1} and 48.69 – 155.15 × 10^{-5} × A m^2 kg^{-1}, respectively (Figure 2). Statistically significant correlation coefficients ($p < 0.05$) were obtained between the PM_{10} and the SIRM values of *B. pendula* and *A. platanoides* leaves, $r = 0.75$ and $r = 0.71$, respectively. No correlation was observed for the other studied species (Table 1).

Table 1. *Spearman's correlation coefficients between SIRM values (× 10^{-5}A m^2 kg^{-1}) in the leaves sampled in two Belgrade`s parks, and PM_{10} concentrations (μg/m^3) at the nearest air quality monitoring station; the data are related to the period 2011-2014; significant correlations ($p < 0.05$) are marked in bold.*

	A. hippocastanum	***A. platanoides***	***B. pendula***	***T. cordata***	**PM10**
A. hippocastanum	1.00				
A. platanoides	0.29	1.00			
B. pendula	0.00	**0.64**	1.00		
T. cordata	-0.64	-0.39	-0.57	1.00	
PM10	-0.11	**0.71**	**0.75**	-0.50	1.00

According to the leaf SIRM values, *B. pendula* was the only tree species sensitive to both spatial and temporal differences within both CU and CS parks throughout the multi-annual period at a statistically significant level ($p < 0.05$) (Figure 2). Regardless the lowest leaf SIRM values obtained for *B. pendula* leaves, the highest correlation coefficient ($r = 0.75$, $p<0.05$) was obtained between these values and the PM_{10} concentrations (Table 1). Dzierżanowski et al. (2011) found that leaf wax layer of *B. pendula* retains predominantly the particles smaller than 10 μm, while Mitchell et al. (2010) pointed out that a tree species from genus *Betula* has the highest deposition velocity among other studied tree species, and may provide better compliance of the result with co-located PM samples. In the extensive study investigating a large number of common urban tree/bush species, *B. pendula* exhibited the highest particle entrapment capability for anthropogenically emitted PM_{10}, $PM_{2.5}$, $PM_{0.2}$, followed by *T. cordata*, *A. platanoides* and *A. hippocastanum* (Sæbø et al, 2012). All these findings recommended *B. pendula* leaves as a valuable indicator of PM_{10} pollution.

A. platanoides was another studied tree species which leaf SIRM values highly correlated with the PM_{10} concentrations ($r = 0.71$, $p<0.05$) (Table 1). The species of the genus *Acer* are among the top 10 most frequently occurring worldwide (Yang et al, 2015). Species such as *A. platanoides* are the most common in cities across Europe, and becoming increasingly widespread across the planet (McKinney, 2006; Grote et al, 2016). Although, in the past, *A. platanoides* was mainly selected for their aesthetic values and "urban-adaptable" features (Saebo et al, 2003; McKinney, 2006), it was not often studied for magnetic biomonitoring. Moreover, considering the vitality of tree species influenced by different anthropogenic factors, *A. platanoides* seems to be the most appropriate for city parks (Krzyżaniak et al, 2015).

The leaf SIRM values of *T. cordata* were among the highest between the studied species (Figure 2), which demonstrates its prominent capacity for capturing magnetic particles. However, the SIRM values of this species were not correlated with the available PM_{10} measurements (Table 1). Probably coarse particles were more prevalent on the leaves of *T. cordata*. With respect to the PM removal efficiency from the air, species from the genus *Tilia* spp. are between moderate and high (Yang et al, 2015; Grote et al, 2016).

Although a high loading of magnetic particles was observed for *A. hippocastanum* leaves (Figure 2), the SIRM values were not correlated with the PM_{10} measurements at all (Table 1). Note that the PM removal efficiency of this species is moderate (Grote et al, 2016). The correlation between SIRM and PM_{10} does not necessarily reflect the amount of magnetic particles captured by leaves. For example, it was reported that the majority of the SIRM signal (62%) originated from the size fraction >10 μm (Hofman et al, 2014) while the recent research specified that the majority of the magnetic particles were in the range of 0.3-0.6 μm.

In general, particles gradually accumulate on the leaf surfaces until a dynamic equilibrium between particle deposition and particle loss is reached. Particulates may be encapsulated, i.e., immobilized within the wax layer during the growing season (Hofman et al, 2014b). Due to the waxy leaf surface of *B. pendula*, this species keeps the fine particles tightly after deposition. Given the high correlation of the magnetic measurements with the regulatory PM_{10} measurements, and sensitivity to the spatio-temporal variations of the particles, *B. pendula* could be an appropriate biomonitor species for assessment of particle pollution. However, a high capacity for capturing magnetic particles comparable with the PM measurements, along with the aspect of high adaptability to urban ambient, also recommends *A. platanoides* for magnetic biomonitoring of PM (Table 2).

Table 2. *Biomonitoring parameters of the studied tree species*

Parameter	*A. hippocastanum*	*A. platanoides*	*B. pendula*	*T. cordata*	Reference
SIRM signal	+ + +	+ + +	+	+ + + +	**this study**
PM10 (*r*)	**0**	+ + + +	+ + + +	**0**	**this study**
Elements (*r*)	+	+ + +	+ + + +	+ + + +	**this study**
"Urban-adaptable"	+ + +	+ + + +	+	+ + + +	**McKinney, 2006**
Abundance	+ + +	+ + + +	+	+ + + +	**Grote et al, 2016**
PM removal efficiency	+ + +	+ + +	+ +	+ + +	**Grote et al, 2016**

CONCLUSION

Magnetic biomonitoring of tree leaves has enabled establishment of an extensive and dense network of sampling sites for assessment of particles and particle-bound air pollutants in urban areas. In this study, the leaves of four deciduous tree species (*A. hippocastanum*, *A. platanoides*, *B. pendula*, and *T. cordata*) were investigated to select the most consistent biomonitors of magnetic PM in comparison with the regulatory PM_{10} measurements for a 4-year period. For all tree species, significantly higher SIRM and element values were observed in September than in May (the beginning of the season). *T. cordata* leaves exhibited the highest SIRM values followed by *A. platanoides* and *A. hippocastanum* while the lowest SIRM was obtained for *B. pendula*. However, the highest

correlation coefficients between the PM_{10} concentrations and SIRM values was obtained for the *B. pendula* leaves ($r = 0.75$, $p < 0.05$). In addition, only *B. pendula* showed statistically significant spatio-temporal variations of the SIRM values, but due to the lowest SIRM load this species is probably not the best choice for PM removal within urban ambient. Otherwise, *A. platanoides* showed high capability for capturing magnetic particles and the SIRM values significantly correlated with the regulatory PM_{10} measurements ($r = 0.71$, $p < 0.05$) that recommends this species for PM removal and biomonitoring purposes. Finally, *B. pendula* may be considered as appropriate for biomonitoring of fine PM fraction while *A. platanoides*, as highly "urban-adaptable" species, could be recommended for both biomonitoring of PM and particle removal.

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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 PM_{10}, SO_2, NO_2, and O_3 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 the aforementioned cities. The analysis revealed that there are up to 38% more 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 HEALTHCARE IN WOMEN

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ABSTRACT

The aim of the research was to determine how exposure to biomass fuel smoke impacts on the degree of use of primary health care in the female population. The survey was conducted on 411 women, from two areas with different levels of sulfur dioxide and black smoke. The control group was women who heat their homes using electricity and the exposed group were women who used wood for heating. The questionnaire is adapted from the American Thoracic Society. Data on use of primary care were collected on the basis of hospital registrations. The number of women who have used primary health care and are absent from work is statistically significantly higher in the group exposed to biomass fuel smoke ($\chi 2=89.02$; $p< 0.001$). The results show that biomass fuel smoke is a significant form of indoor air pollution and affects the health of women and also increases the cost of healthcare.

Keywords: biomass fuel smoke, women, primary health care, absence of work, air pollution.

INTRODUCTION

Indoor air pollution is usually quite different from outdoor air pollution. There is a difference in the type of pollutants, as well as their concentration. Persons who spend most of the day in their home are usually the most sensitive part of the population (children, women, chronic patients, elderly) (Sallsten et al, 2006; Liu et al, 2005). The ways of heating the home, especially if they are based to the use of coal and wood, releases toxic and noxious gases, which affect the health, such as carbon monoxide, carbon dioxide, sulfur dioxide, particles, oxides of nitrogen and others. Exposure to hazardous pollutants may have an immediate or a long-term effect, which may not show up for many years. The significance of the exposure depends upon the source, how much is emitted from the source, how harmful the pollutants are, and how much of the pollutants have accumulated within the home. Pollutants which are well-soluble in water are almost totally extracted inside of the upper respiratory tract, whereas poorly soluble pollutants are removed in the smaller airways and alveoli (Sehlstedt et al, 2010; Boman et al, 2006). Inhaled pollutants reduce the movement of cilia in the trachea so they do not perform their very important function of cleaning, which affects the increase in the risk of respiratory symptoms and diseases (Simoni et al, 1998; Bruce et al; 2000).

The objective of the research was to determine how exposure to biomass fuel smoke impacts on the prevalence of respiratory symptoms and the degree of use primary health care and lost work time in the female population.

METHODOLOGY

In this study we evaluated data from a sample of 401 women, ages 30-50, who lived in part of the town with low concentrations of outdoor air pollutants. Women of both groups were non-smokers and they were not occupationally exposed to air pollution, and they have lived for at least five years in those locations. The control group (n=214) were women who heat their homes using electricity and the exposed group (n=197) were women who were used wood and coal for heating.

The survey was conducted by a physician, through interviews in the period from May to June 2008. Data of the women's prevalence of respiratory symptoms (cough, phlegm, blocked-runny nose, wheezing and shortness of breath) in the last 12-month period of life and lifetime prevalence of respiratory illnesses (asthma, allergic rhinitis, sinusitis, pneumonia and bronchitis, as diagnosed by their doctors) were obtained through questionnaires. Trained physicians filled out questionnaires during the interview with women.

The questionnaire was adapted from the American Thoracic Society questionnaires validated for Serbian language (Ferris, 1978). Respiratory symptoms were defined based on yes/no responses to the symptoms questions in the questionnaire. The questions about respiratory symptoms were as follows: Have you had daily coughs for > 3 weeks in the last 12 months? Did you have phlegm in your nose or throat in the last 12 months when you did not have a flu? Did you have wheezing in your chest in the last 12 months when you did not have a flu? Have you ever had attacks of shortness of breath in the last 12 months? In the past 12 months, have you had a problem with a runny

or a blocked nose when you did not have a flu? The data collected are divided into: symptoms of upper respiratory tract symptoms and the lower respiratory tract. Symptoms of the upper respiratory system were recorded as stuffy nose, secretion from the nose, breathing difficulty, nose, dry throat, sore throat, hoarseness, and expectoration. Chest tightness, wheezing, shortness of breath and dry cough lengthy recorded as symptoms of the lower respiratory tract

Our questionnaire also included items about socioeconomic status, indoor environmental determinants (ETS - environmental tobacco smoke at home, use of biomass fuels, home dampness and the keeping of pets) and family history of respiratory illnesses.

Data on use of primary care and absence from work are collected on the basis of hospital registrations, in order to determine statistically significant differences using the Student T-test and $\chi 2$ -test.

RESULTS AND DISCUSSION

The highest percentage of the patients (57.15%) who live in apartments had individual heating systems or storage ovens. The exposed group of subjects for home heating used wood most commonly (28.21%) and coal (17.11%). The average age of exposed women was 35.331 ± 6:03 years and the average age of the non-exposed women subjects was 35.44 ± 3.12. The homogeneity of the group is satisfactory because there is no statistical significance ($t = 0.567$, $p > 0.05$) in the average age of groups. Between two groups of women, there was a statistically significant difference in the incidence of respiratory symptoms, decreasing from the upper to the lower respiratory tract (Table 1).

Table 1. *The statistical significance of the difference in the prevalence of respiratory symptoms*

Group	Respiratory symptoms	
	Upper	Lower
exposed	217 (8.11%)	124 (4.49%)
nonexposed	65 (3.82%)	52 (2.02%)
χ^2	$\chi^2 = 32.57$	$\chi^2 = 21.29$
p	$p < 0.01$*	$p < 0.01$*
Odds Ratio	2.89 (1.33 < OR < 2.1)	3.17 (1.61 < OR < 6.30)

* *Statistically significant*

The exposed group of women were significantly more likely to use primary healthcare (Table 2) due to problems with respiratory organs. Absence from work due to problems with respiratory organs was also significantly higher in the group of women exposed to smoke-producing fuel material (Table 3).

The extended number of days absent from work for the exposed group of women compared to the control group is statistically significant (Table 4).

Table 2. *Exposure to biomass smoke and the number of physician visits due to problems with respiratory organs*

Group	Physician visits (n / %)				χ^2	p
	Not even once	1-3	4-6	>6		
Exposed (n=197)	15 (7.61)	142 (72.08)	30 (15.23)	10 (5.07)	89.02	p<0.001*
Nonexposed (n=214)	107 (50.00)	79 (36.91)	22 (10.28)	6 (2.80)		

* *Statistically significant*

Table 3. *Exposure to biomass smoke and absence from work due to problems with respiratory organs*

Group	Absence from work (n / %)				χ^2	p
	Not even once	1-3	4-6	>6		
Exposed (n=197)	12 (6.09)	111 (56.34)	54 (27.41)	20 (10.15)	82.56	p<0.001*
Nonexposed (n=214)	91 (42.52)	75 (35.05)	21 (9.81)	27 (12.61)		

* *Statistically significant*

Table 4. *Exposure to biomass smoke and the length of absences from work due to problems with respiratory organs*

Group	Absence from work (n / %)				χ^2	p
	0 days	<7days	7-30 days	>30 days		
Exposed (n=197)	12 (6.09)	149 (75.63)	28 (14.21)	8 (4.06)	73.03	p<0.001*
Nonexposed(n=214)	91 (42.52)	103 (48.13)	15 (7.00)	5 (2.33)		

* *Statistically significant*

In our study, it has been found that the women who had wood and coal heating at home and were exposed to pollutants from fuel material had a greater prevalence of respiratory symptoms in comparison to women in the control group. The frequent occurrence of respiratory problems due to exposure to biomass smoke causes the increased use of primary healthcare. Also, absenteeism was significantly observed in the exposed group of women.

Today, developed countries generally use wood and coal as an energy source. Smoke from household solid fuels is a complex mixture which contains many potentially relevant components from a toxicological point of view. Coal usually contains of 0.5 to 5% of sulfur and wood about of 3% of sulfur. Exposure to sulfur dioxide leads to non-specific effects in the form of irritation and inflammation due to the ease of dissolution in the mucus of the respiratory tract. Other pollutants are also involved in the development of pathological changes in pulmonary function which are manifested as an increase in respiratory frequency, inspiratory and expiratory reduction in flow rate and frequent occurrence of respiratory symptoms and diseases (Bennett et al, 2010). Particles which are formed during the combustion of fossil fuels are proven to be toxic to the respiratory tract and induce a reduction of pulmonary function These increase the incidence and duration of serious respiratory symptoms, resulting in an increased hospitalization rate due to respiratory illnesses and increased cardiopulmonary morbidity (Bolling et al, 2009; Russell et al, 2009). Exposure to nitrogen oxides leads to inflammatory changes in the airways and increased

serum IgE, IgA and IgG. Air pollution due to the use of biomass fuel has been shown to be associated with chronic obstructive lung disease, especially in females (**Romieu** et al, 2009; Regalado et al, 2006; Torres-Duque et al, 2008). Carbon monoxide acts on the respiratory tract and reduces the capacity of the blood for oxygen transport, damaging the red blood cells (Barregard et al, 2008). It has been found that exposure to pollutants from the biomass smoke leads not only changes on the respiratory system, but also changes can occur in the cardiovascular, reproductive and hematopoietic system (Naehe et al, 2007).

Ekici et al. (2005) compared the presence of chronic airway diseases (CAD) in two groups of nonsmoking women older than 40 years with (exposed group) and without a history of exposure to biomass cooking (control group). The prevalence of CAD in the exposed group was found to be higher than that in the control group (28.5% vs. 13.6%, crude odds ratios (ORs) 2.5 (1.5-4.0), P=0.0001). Kiraz et al.(2003), found that rural women exposed to biomass fumes are more likely to suffer from CB and COPD than urban women even though the prevalence of smoking is higher among the latter group.

There is a clear need for more studies on indoor pollution and health in adults, and especially for women. Future studies should address both short-term and long-term health effects related to indoor air pollutants

CONCLUSION

We conclude that there is a statistically significant difference in the expression of respiratory symptoms in women exposed to biomass smoke relative to nonexposed women. Women exposed to biomass smoke had a statistically significant greater use of primary healthcare and longer absences from work.

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

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ABSTRACT

Diesel and Biomass combustion-derived particles (CDPs) largely contribute to air pollution and likely to adverse health effects. This study aims to investigate the cytotoxic and genotoxic properties of particles collected during the combustion of different diesel and biomass sources. Diesel Exhaust ultrafine Particles (DEP) were from a standard reference (SMR 2975) and directly sampled from a Euro IV vehicle run over a chassis dyno. Biomass particles were collected from the emission of a heating system operating with certified pellets. Human lung cells were used to study the CDP-induced inflammatory and antioxidant response and the potential genotoxic effects. The strongest cytotoxic action was achieved after exposure to DEP Euro IV, which induced the release of the pro-inflammatory cytokine IL-6 and the oxidative stress response activation, which lead to DNA strand breaks, confirming the oxidative-mediated genotoxicity as a shared mechanism of action.

INTRODUCTION

Air pollutant is a risk factor for human health, and many epidemiological studies have clearly demonstrated the strong association between air pollution exposure and increased morbidity and mortality (Pope and Dockery, 2006; Simoni et al, 2015). A recent study, has showed that the increased risk of natural-cause mortality is associated with long-term exposure to fine particulate, even at concentration ranges well below the present European annual mean limit value (<25 μg/m^3) (Beelenet al, 2014); but the physiopathological effects of the different particles that constitute the PM are still poorly understood. In the contemporary era, the level of exposure to combustion-derived particles (CDPs) increased dramatically in urban centers with the consequent presence of fine (aerodynamic diameter <2.5 μm, $PM_{2.5}$) and ultrafine (aerodynamic diameter <0.1 μm, UFP) particles in the near surface atmosphere. The aerodynamic properties of particulates determine how deep they can get into the respiratory system. The UFP fraction comprises higher numbers of particles, which have higher reactivity and smaller mass compared to larger particulate matter (PM) fractions, resulting in higher lung deposition ability, reduced clearance efficiency and capability to translocate through biological barriers and to penetrate into the systemic circulation in humans (Corsini et al, 2017; Schmid et al, 2009). Toxicological studies have shown the specific reactivity patterns induced by UFP, including the activation of the inflammatory response, enhanced oxidant capacity and the ability to induce oxidative DNA damage (Schwarze et al, 2013; Miller et al, 2012). The physicochemical properties of UFP vary according to the different sources, nature of the substances forming the core of particles and the different chemical compounds that enrich the surface area of the particles. The chemical characterization of UFPs have revealed indeed their highly heterogeneous composition, involving a complex mixture of chemical species, including black carbon (soot), metals, trace elements, aromatic hydrocarbons and heterocyclic organic compounds, thus evidencing the increasing importance of studies focused on the analyses of the relationship between UFP chemical composition and their potential health effect (Longhin et al, 2016; Corsini et al, 2017; Yang et al, 2014). The emissions from anthropogenic combustion sources, like vehicles and biomass combustion, contribute significantly to $PM_{2.5}$ and UFP. Diesel engine exhaust particles (DEP) are a complex mixture of compounds whose physicochemical characteristics are highly dependent on fuel and engine technology. The International Agency for Research on Cancer (IARC) of the World Health Organization (WHO) in 2012 classified DEP as carcinogenic to humans (Group 1). Exposure to DEP does not only induce carcinogenic effects, but also cardiovascular and mutagenic effects (IARC: DIESEL ENGINE EXHAUST CARCINOGENIC, 2012). During the last decade, the use of biomass burning for residential heating has largely increased in Europe. The adverse effects on health from biomass combustion have been demonstrated by the occurrence of respiratory disease among the population living in areas with a high wood smoke contribution to PM (Kocbach Bølling et al, 2009). Wood smoke may cause health effects similar to particulate matter from other sources and in particular to traffic-emitted particles (Barregard et al, 2006). A recent study shows that UFP derived from biomass combustion induced significant genotoxic effect on human lung epithelial cells and the related DNA damage was caused by the alteration of the cellular redox status (Marabini et al, 2017). The aim of this study is to investigate the comparative cytotoxic and genotoxic properties of particles collected during the combustion of different diesel and biomass

sources, in order to correlate the different biological effects of particulate matter generated from different combustion technologies on the respiratory system. Here different DEPs and biomass particles have been characterized and their biological effects evaluated. The biological responses to CDPs have been evaluated in lung cells cultured in vitro. A low dose was chosen to mimic as much as possible a realistic exposure scenario to the selected CDP sources. Different biological endpoints were evaluated: the inflammatory and oxidative stress responses and the induction of genotoxic damage. The obtained results suggest that CDPs from different emission sources may affect respiratory health to different extents and can activate different toxicological pathways, pointing out the importance of developing new strategies focused on lowering the health hazard coming from the emission of diesel vehicles and biomass-propelled heating systems.

METHODOLOGY

CDPs Sampling and Chemical Characterization. Different ultrafine CDPs were used to investigate and compare their cytotoxic potential on *in vitro* lung cell systems. Two different types of DEPs were analysed: one standard reference material (SMR) 2975 (Sigma Aldrich) provided by the National Institute of Standards and Technology (NIST), which derived from the combustion of a light engine, and DEP sampled by a light duty Euro IV vehicle run over a chassis dyno without Diesel Particulate Filter (DPF). Finally, biomass CDPs were collected from a modern automatic 25 kW pellet boiler propelled by prime quality spruce pellet, under a standardized combustion process. CDPs were sampled and extracted for biological investigations as previously described (Longhin et al., 2016) and the morphological analysis performed by transmission electron microscopy (TEM) and Dynamic Light Scattering (DLS).

Cell Culture and Treatments. Studies on DEP exposure, were performed on the SV40 hybrid (Ad12SV40) transformed human bronchial epithelial cell line BEAS-2B (ATCC® CRL9609™, American Type Culture Collection, Manassas, USA) maintained in LHC-9 medium (Gibco, Life Technologies, Monza, Italy). For biomass studies, a human alveolar epithelial cells line was used, A549 (ATCC® CCL185™) routinely maintained in OptiMEM medium (Gibco), supplemented with 10% inactivated fetal bovine serum (FBS, Gibco) and 1% penicillin/streptomycin (100 X, Euroclone, Pero, Italy). For CDP exposure experiments, cells were cultured in OptiMEM medium with 1% FBS. The concentration of 5μg/cm^2 was selected as the lowest tested dose able to induce significant effects in the *in vitro* system here described after a single acute exposure. After exposure for 20h and 24h respectively for DEP and biomass particles, the media were collected and the cellular responses analysed.

Oxidative stress: ROS production. BEAS-2B cells were incubated for 20 minutes in Hank's Balanced Salt Solution (Thermo Fisher Scientific; Monza, Italy), and successively, exposed to DEPs *for 90 minutes* to Carboxy-DCFDA probe. *At the end of the incubation, cells were detached and re-suspended in PBS and analyzed at the flow cytometer* (CytoFLEX 13/3, Beckman Coulter, USA). *Fluorescence of 10,000 events was detected using 525 nm band pass filter (FITC). Data were analysed as mean percentage of positive cells for the staining.*

Antioxidant response: HO-1 expression. After exposure to CDPs, cells were scraped and lysed on ice with lysis buffer (RIPA buffer and 0.1 % of proteases inhibitor). Equal amounts of proteins (25μg) were loaded onto 12 % SDS-PAGE gels, separated and transferred on nitrocellulose membranes. After blocking for 1h with Tris-Buffered Saline (TBS) supplemented with 0.1% Tween20 in 5% (w/v) BSA solution membranes were incubated overnight at 4 °C with the primary polyclonal antibody rabbit anti HO-1 (HO-1 P249 Antibody, 1:1000, Cell Signaling Technology, Danvers, USA). The day after, membranes were incubated with the specific HRP-linked secondary antibody in blocking buffer for 1h at RT (anti-rabbit IgG, 1:2000, Cell Signaling). Finally, membranes exposed to Chemiluminescent Substrate (Euroclone). Digital images were taken by a luminescence reader (Biospectrum-UVP, LLC, Upland, CA, United States) and densitometry analysis performed with dedicated software (VisionWorks LS).

Release of the pro-infiammatory mediator: Interleukin 6. After incubation with DEPs or biomass, the supernatants of BEAS-2B and A549 cells were collected and used to detect IL-6 cytokine levels by sandwich ELISA according to the manufacturer's guidelines (Life Technologies). The absorbance of each sample was measured by Multiplate Reader Ascent (Thermo) at 450 nm and 630 nm. *Standard curves* were used to determine the concentration of proteins in pg/ml.

DNA Damage. The phosphorylated form of the histone H_2AX (γH2AX) was used as marker of DNA damage and measurements were performed by flow cytometry. At the end of the exposure, cells were fixed with 1% paraformaldehyde in PBS at 4°C, re-suspended in 90% cold methanol and stored overnight at -80 °C prior to analysis. For the analysis, after discharging the methanol, cells were incubated with the Alexafluor-488 conjugated

γH2AX antibody (1:100 dilution, Cell Signaling Technology, Danvers, USA) in PBS 0.5% BSA, 0.2% Triton X-100 for 4h at R.T. After the incubation, cells were analyzed on the CytoFLEX 13/3using 525 nm band pass filters.

Cell Cycle. Cell cycle analysis was performed by flow cytometry. At the end of the exposure, cells were harvested, fixed in 90% ethanol and stored at -20°C. For the analysis, ethanol was discharged by centrifugation, cells resuspended in PBS containing of RNAse DNAse-free (1 mg/ml, Sigma-Aldrich, Italy) and incubated for 30 min at 37 °C. Finally, the fluorescent dye PI (1 mg/ml) was added to stain cells DNA. The cytochemical analysis was performed using a 617 nm band pass filters.

Statistical Analyses. The data are reported as mean values of independent experiments ± SEM. Statistical differences between samples were tested with unpaired t-test or one-way ANOVA and post hoc comparisons performed with Dunnett's method, by GraphPad Prism 6 software. Statistical differences were considered significant at the 95% level ($p < 0.05$).

RESULTS AND DISCUSSION

Chemical Characterization. The morphological analysis of DEP particles (performed by TEM and DLS techniques) allowed their characterization in terms of form and aggregation state. The DEP samples were very similar to each other and the single particles, that were smaller than 50 nm, were presented as aggregates, typical of soot particles. Specifically, the Euro IV sample was characterized by larger aggregates than SMR 2975 (data not shown). Biomass samples also showed aggregates of soot particles and the presence of ash particles, with dimensions comparable to DEPs, as previously reported (Longhin et al, 2016). The CDP chemical composition has been previously investigated (Comparing Certificate of Analysis of DEP SMR and our previous study (Longhin et al, 2016)) and it was reported that Euro IV was the material with the greater presence of polycyclic aromatic compounds (PAHs), in particular phenanthrene and pyrene. Even the metal content was higher in Euro IV samples, except for Mn and K, which were higher in biomass sample.

Biological investigations. In order to investigate the biological effect of CDPs derived from different emission sources on human BEAS-2B (bronchial) and A549 (alveolar) cells, we first examined the particles' capability to affect cellular metabolic activity and viability after 20 and 24h of exposure respectively. The exposure to 5 μg/cm^2 of CDPs was not able to induce any significant cytotoxic effect (data not shown). A reduction in the relative number of normal viable cells was only observed. The modulation of the inflammatory response after the exposure to the different CDPs was investigated by measuring the release of the pro-inflammatory interleukin 6 (IL-6) from BEAS-2B and A549 cells. The results showed that IL-6 levels were significantly increased by BEAS-2B as previously reported (Bengalli et al., 2017), while no significant results were obtained after exposure to SMR material. In contrast to the effects observed on BEAS-2B cells, biomass particles were not able to induce any significant inflammatory response (Figure 1A), in agreement with our previous study reporting that traffic-derived particles induce a higher cytokine release with respect to wood smoke particles in the *in vitro* systems used (Longhin et al, 2016).

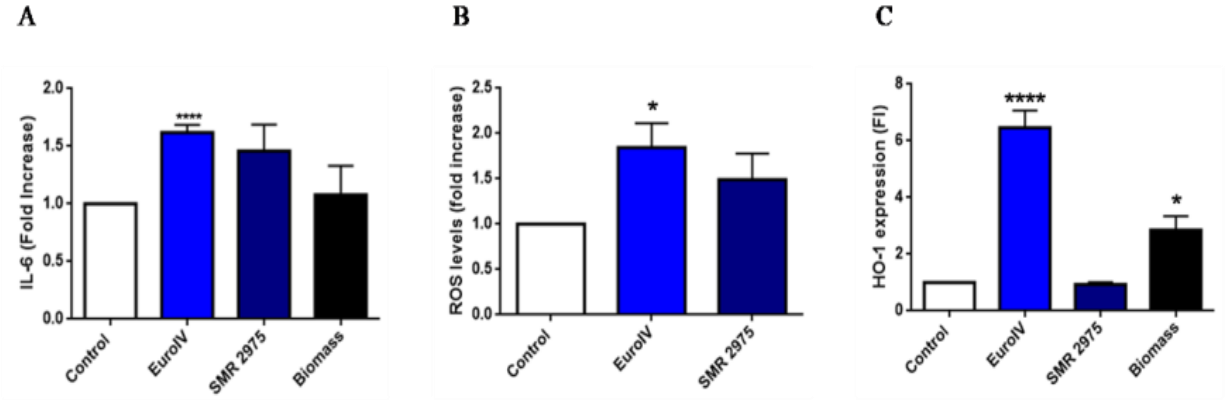

Figure 1. *A) Release of the pro-inflammatory cytokine IL-6. The release of IL-6 has been evaluated in BEAS-2B and A549 cells exposed for 20 and 24h respectively to CDPs from different sources (5μg/cm^2). B) Intracellular ROS production by BEAS-2B exposed to DEPs. C) Expression of HO-1 protein in BEAS-2B and A549 cells exposed*

*to 5μg/cm² CDPs. Data are presented as fold increase over control values. ****p<0,0001 and * p < 0.05 vs control cells.*

Oxidative stress (Crobeddu et al, 2017; Deng et al, 2013) and inflammation (Noël et al, 2016), are reported to be important mechanisms involved in the development of health effects deriving from $PM_{2.5}$ (Deng et al, 2013) and CDP exposure (Tseng et al, 2016). The oxidative stress response after exposure to DEPs was investigated and the cytometric analyses confirm statistically significant ROS production only after BEAS-2B exposure to DEP Euro IV (Figure 1B). The activation of the anti-oxidant response was also evaluated by measuring the expression of the oxidative stress marker HO-1 following exposure to CDPs. Data obtained by Western blot showed that HO-1 expression increased significantly after exposure to Euro IV and Biomass particles compared to control cells (Figure 1C). DEP SMR 2975, on the other hand, did not induce an intracellular protein increase, indicating that at this dose, and in our experimental conditions, these particles do not induce oxidative stress. The exposure to CDPs can also lead to genotoxic effects, such as alterations of DNA integrity and function, and they can be analysed by looking for DNA double-strand breaks (DSBs) or following the progression of the cell cycle. Cell cycle analysis was carried out in order to investigate the possible genotoxicity of CDP particles. Results revealed that both DEPs were not able to affect BEAS-2B cell cycle progression (data not shown). The same result was observed after exposure to biomass, that is known to have a lower toxic potential, also in respect to DEP Euro IV (Longhin et al, 2016). The genotoxic effect produced by CDPs was also assessed by evaluating the phosphorylation of the histone-2AX (γH2AX), marker of DNA DSBs. Preliminary data on DEPs showed that both of the particles seems to induce DNA damage in exposed BEAS-2B (Figure 2A). Biomass CDPs instead, did not affect the expression of γH2AX on A549 cells (Figure 2B). The DEP genotoxic potential observed is in agreement with literature data, in which CDP-induced oxidative stress and inflammation are reported to give rise to oxygenic and mutagenic DNA lesions (Danielsen et al, 2009; Marabini et al, 2017).

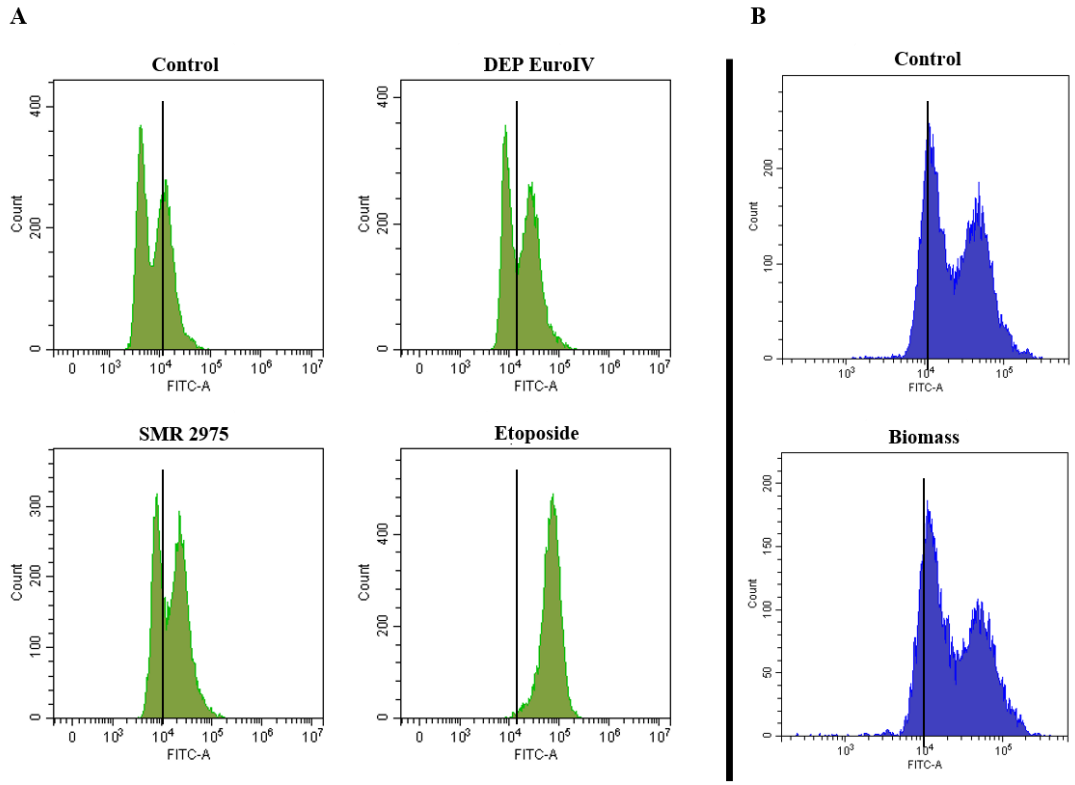

Figure 2. *γH2AX expression measured by flow cytometry in exposed BEAS-2S and A549 cells using 525 nm band pass filters (FITC). Data are presented as X-mean of the fluorescence intensity. Preliminary data suggest that the exposure to DEPs (panel A) seems to induce an increase in γH2AX expression, while biomass CDPs (panel B) are not genotoxic.*

CONCLUSIONS

In recent years, great attention has been dedicated to the ultrafine fractions of PM, since several studies have reported their involvement in the onset of pulmonary and cardiovascular diseases. The results from our study evidenced that DEP Euro IV, which is the material with the higher concentration of polycyclic aromatic compounds (PAHs), activates both oxidative and inflammatory responses in lung epithelial cells, with consequent oxidative lesions observed at the DNA level. SMR2975 instead is not able to affect the biological endpoints investigated in our experimental conditions. Moreover, the lower toxic properties observed after biomass CDP exposure could be explained by the source of these combustion particles, which derived from a certified pellet with a low content of PAHs and metals. CDPs obtained from other biomass sources were instead able to induce genotoxic effects on A549 cells (data not shown). From our results it is arguable that different CDPs may activate different toxicological pathways in the lung. The role of CDPs on human health is still under investigation and further studies are necessary to assess the CDP-induced molecular mechanisms responsible for the toxic effects observed at the lung and cardiovascular levels.

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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 $PM_{2.5}$ 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 ($PM_{2.5}$), associated with health effects, both for long-term and short-term exposure. $PM_{2.5}$ 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 $PM_{2.5}$, PM_{10}, 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 pollution, 2013) 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 - TURNING SCHOOL'S SCIENCE PROJECTS FUN

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ABSTRACT

Increasingly available low-cost environmental sensing technologies provide an opportunity for citizens to learn about their environment. This contribution summarizes students' activities in primary school in Ljubljana which participated in CITI-SENSE project. The school was provided with indoor and outdoor low-cost air quality sensor systems enabling the students to conduct research work with the support of researchers and teachers. In addition, other educational awareness-raising activities were used for engagement and empowerment of pupils during the project, aligned with their curriculum. These activities created win-win situations, awareness at the school, increased the individual students' and teachers knowledge about air quality, and also led to mitigation measures at school such as changing the ventilation practices. One example of research work conducted by fourth graders was to investigate characteristics and behaviour of dust in their classroom. The students presented their research work at a national school competition and among others were rewarded with a trip to Gardaland.

INTRODUCTION AND SUMMARY

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 examines and summarises the experience on integrating such technologies in a school setting.

We demonstrate a case study where low-cost air quality sensor systems were deployed in a primary school in Ljubljana, Slovenia as part of the CITI-SENSE project. The overall objective of the project was to develop technology-enabled "Citizens' Observatories" to empower citizens and various citizens' groups to (i) contribute to and participate in environmental governance, (ii) to support and influence community and policy priorities and the associated decision making, and (iii) to contribute to European and global monitoring initiatives (CITI-SENSE, 2016b). The school case studies aimed at enabling the school stakeholders to examine their school's environment with help of sensor technology and support from researchers.

More specifically, this contribution focuses on student activities carried out in a primary school participating in the project and where low-cost air quality sensors and other means were used for the engagement and empowerment purposes. The 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 the primary school 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 while providing an affordable means to examine the school environment (CITI-SENSE, 2016a; Robinson et al., 2015; Robinson et al., 2016).

SETTING THE SCENE FOR THE ACTIVITIES

The presented case study primary school was one of the three schools in Ljubljana participating in the CITI-SENSE project. Previous activities had been established with the school prior to inviting them to participate in the project. Initial meetings at the school were set up to identify what kind of activities they wanted to carry out. Teachers were given an overview of air quality sensor devices and the teachers could identify the relevance of the project activities for diverse parts of curricular activities aiming for meaningful research planning. Some teachers saw this as an opportunity to conduct individual student-led research, while others planned to integrate them into everyday teaching. Many wished the researchers could organize additional activities.

The project lasted four years (2012-2016), during which some of the sensor devices were being developed. Due to delays in supply during the first years, the school was initially provided with an off-the-shelf easy to use indoor sensor device set (Netatmo, Figure 1a). Later on, the project supplied an outdoor air quality unit (AQMesh, Figure

1b), three indoor air quality units (Atmospheric sensors, Figure 1c), and one radon sensor unit (Obeo Liessem, Figure 1d). All of the air quality units worked autonomously sending data online either through WiFi (Netatmo) or GPRS connection (CITI-SENSE sensor units). The indoor units worked on mains supply, while the outdoor unit, which was installed at the playground in front of the school, had an inbuilt battery. Also, the Netatmo, which consisted of two units, had a smaller unit working on 2 AAA batteries which the teachers and students could move more freely. The Table 1 gives an overview of the sensor devices and individual sensors. The CITI-SENSE data were accessible through a dedicated downloading webpage, while the Netatmo data could be accessed in real time both on the web and on the Netatmo App.

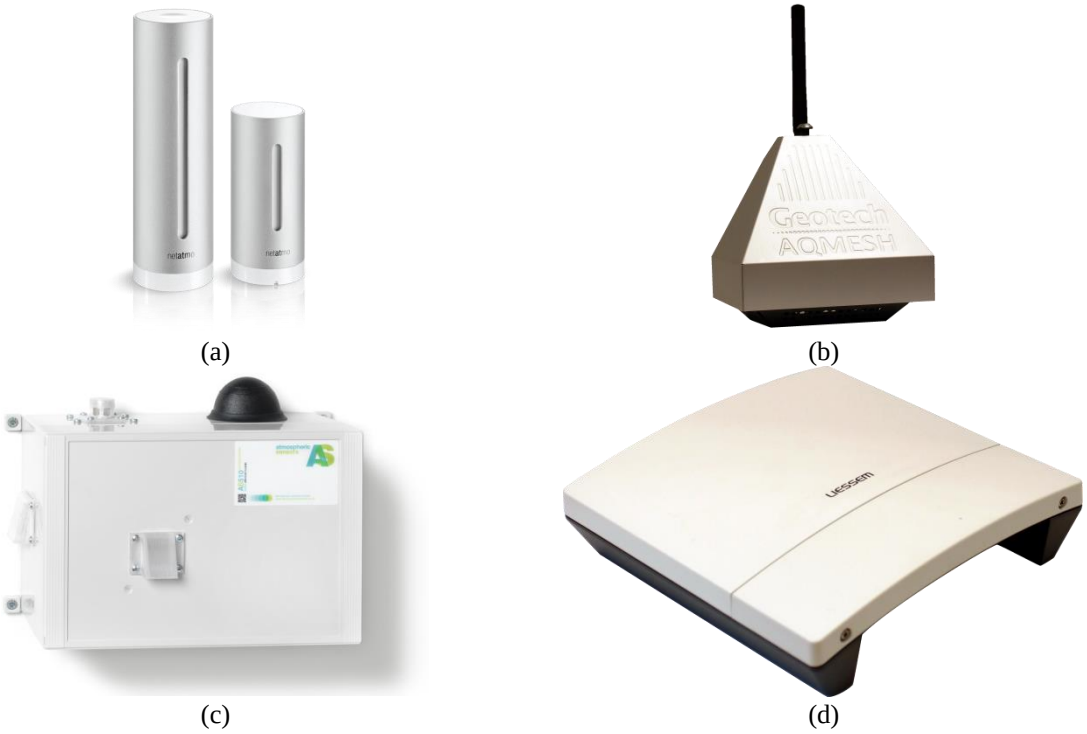

Figure 1. *(a) Netatmo (https://www.netatmo.com/en-us), (b) AQMesh (https://www.aqmesh.com/), (c) Atmospheric sensors (http://atmosphericsensors.com) (d) Obeo Liessem (*www.obeo.no/*)*

Table 1. *Sensor devices individual sensors overview.*

	Netatmo	AQMesh	Atmospheric sensors	Obeo Liessem
Temperature	**x**	**x**	**x**	
Humidity	**x**	**x**	**x**	
Atmospheric Pressure	**x**	**x**	**x**	
CO_2	**x**		**x**	
CO		**x**	**x**	
NO		**x**	**x**	
NO_2		**x**	**x**	
Total VOC			**x**	
O_3		**x**	**x**	
PM		**x**	**x**	
Noise	**x**	**x**	**x**	
Radon				**x**

FACILITATING SCHOOLS' SCIENCE ACTIVITIES

Various teachers actively participated in the project with their students. This did not only include science teachers, but also for example the air quality theme was integrated in language classes. A Slovene language teacher for example took the opportunity to teach about the subject by introducing key words in the field. The topic was integrated also during art classes, which resulted the students drawing posters with an environmental theme, and which were also on display in a cultural centre in Ljubljana. Most of the activities at the school however fall under a class called "Ecology with environmental protection". Sensors were actively moved between classrooms by interested students and teachers, and they were also for example moved to the library, gym and computer classroom. The teachers and students accessed the CITI-SENSE data on demand through dedicated online platforms, while the Netatmo also had an instant colour-coded air quality indication in the unit once pressed. This feature was used frequently everyday in a classroom of the youngest primary school children. Pressing the button also popped up a notification in the researchers' and teachers' smartphones while a pop-up message was also received if, for example, the CO_2 concentration exceeded a pre-defined limit value.

The researchers gave two thematic lectures on air quality, where the school children could actively participate. During one of these lectures, the children could pin air quality according to their feelings in various parts of Ljubljana using colour codes (green=good air quality, yellow=moderate air quality, red=bad air quality) in a large printed map of Ljubljana. See Figure 2a.

Figure 2. *a) Activity at school to mark students' subjective opinion on air quality in their city b) Snowflake poster in an open day event.*

Dust particles and carbon dioxide were the research topics of most interest as well as the comparison of pollution in a city and greener areas. The researchers facilitated the students' interest to research these areas by providing scientific knowledge and support, giving examples of research methods and organising additional activities in addition to technical support with the sensor devices. Another thematic meeting was arranged on dust and particulate matter, where, for example, the role of the nose was discussed, a demonstration with a vacuum cleaner and a filter to point out the dust in the classroom was carried out, followed by a demonstration on how vaseline could be used to collect dust particles and finally discussion on how to collect snow samples from outside and examine them indoors once melted. In addition, a poster featuring the formation of snowflakes was drawn by one of the researchers, which was presented at the school's open day event and later hung and used in a classroom teaching (Figure 2b).

The research interests mentioned earlier also resulted in student-led research projects. A group of eighth graders studied the concentration of CO_2 in a classroom in relation to classroom size, ventilation and amount of pupils while a group of fifth-graders studied the difference between the concentrations of air pollutants in a city area compared to a rural area using CITI-SENSE outdoor sensor units. A group of fourth graders studied dust in their classroom using the provided indoor sensor units while extending the research to also examine the knowledge of their classmates about particulate matter using questionaires. One of their hypotheses was whether cleaning the classroom would result a lower concentration of dust in the classroom which prompted a cleaning activity to test the hypothesis. The researchers were invited to join the cleaning activity (Figure 3a) as well as to help to draw and interpret graphs. The research work was later presented at the schools open day event (Figure 3b) as well as at a national school competition and were rewarded with a trip to Gardaland.

(a) (b)

Figure 3. *a) Cleaning activity as part of the dust experiment b) Science project poster at the school's open day event*

NATURE DAYS

During the four years of the CITI-SENSE project, altogether 12 classes of primary school children (1st-4th graders) participated in Nature days. The Nature day concept involved various activities in a nearby forest. Two types of activities were carried out aimed at two different age groups. The youngest ones were 6-8 years old, and the oldest ones 9-10. In a Nature day for the youngest elementary school kids, the concept was tied around an introduction to the concept of measurements and uncertainty which researchers tackle in their daily tasks. The storyline for the activities was based on explaining and experimenting how there are things around us that we can measure ourselves based on our observations and tools, but for some we need special devices, e.g. for air quality (Figure 4a). The children got to learn about it through various measurement techniques, where instruments (e.g. CO_2 meter, portable air quality unit, infrared camera, 1 m stick and a laser distance measurer) were used together with or by the children and coupled with gaming exercises. In one exercise for example kids could pipet and measure water (Figure 4b).

Nature days for higher classes i.e. 3rd and 4th graders included a treasure hunt. A treasure map was prepared, which the children used for orientating into and in an urban forest near the school (Figure 4c). Several activity locations were marked with dots on the map. The children had to find their way to these locations where centrifuge tubes were hidden (Figure 4d). Once found, the tubes included instructions for activities, as well as a hint to find the next location. On each location, children were asked to colour the air quality in their maps either green=good, orange=moderate, red=bad. Educational effort was also made by comparing air quality in the urban and traffic areas with green areas with the help of portable CITI-SENSE air quality sensor units. At the final dot of the treasure map, a complementary treasure was waiting to be found.

At the end of the Nature days, the classes were provided with group images taken with an infrared camera, as well as a printed map of air pollution measured in the location covered during that day's activities. The teachers wanted to repeat the activity every year also after the project had officially ended. One of the teachers showed her enthusiasm for sharing the experience with other teachers in Slovenia by writing an article in *Naravoslovna solnica* - journal for teachers of natural sciences (Jeraj, 2015).

The children were asked to write a feedback letter about the Nature days. The children either wrote what they learned and liked while some drew images and mind maps instead. During the Nature days, some of the children gave their feedback on video. All of the children's feedback was positive, and revealed they like the Nature days, not only subject-wise, but because it enabled them to spend their day in nature amongst their peers and run around freely.

(a) (b)

(c) (d)

Figure 4. *Nature day collage from Ljubljana a) Measuring and displaying air pollution with a mobile device b) Pipetting practice for metrology themed Nature day c) Navigating with the help of the treasure map d) Searching a hidden tube with activity instructions*

CONCLUSIONS

The tools and expertise that the CITI-SENSE project could offer was easily integrated in the school's curriculum extending also beyond typical science classes. The connection between research institution and a local school created win-win situations enabling students to interact with the scientists who could provide them with equipment and support. We observed that teachers and students pay attention to their school's environment which also resulted in improved ventilation practices. We learned how air quality issues are well understood even by the youngest ones. They are already familiar with locations and sources of good and bad air and how one can influence it. Despite the limited deployment of sensors at the beginning of the project as well as their questionable data quality, the various awareness-raising activities and teachers' high motivation and capability to integrate the subject in the curricula lead to science projects where the students demonstrated capability to set up research questions, collect, examine and interpret site-specific data. The younger student groups needed more help in data download and interpretation from the scientists, while the older ones only needed general mentoring. The activities were organized in a fun and meaningful way for all participants, while one of the science project teams also got rewarded with a trip to an amusement park in Gardaland. The Nature days were both a fun and effective way to raise awareness as well as to rehearse previously learned subjects from school. Challenges of sensor data quality were taken as an opportunity to learn about metrology, which was also a theme for the youngest primary school children during the Nature days. Several positive chain reactions occurred during the project. Teachers and students, not originally recruited to participate, heard about the project and wanted to participate. The interactions within the school evolved in the lifetime of the project as well as beyond e.g. connections to other local institutions were made for future projects. The school showed interest to continue with the measurement activities as well with as the Nature days. The low-cost sensors are an affordable way for schools to take steps towards observing and improving the schools

environment while supporting everyday learning. Many off-the-shelf sensors on the market are ready for use with minimal set-up effort, reliable dataflow and easy-to-use interfaces for data management suitable for primary schools, which the recently developed low-cost sensor units are partially still struggling with.

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5. PM COMPOSITION AND MODELING II

5.1. ATMOSPHERIC MINERAL DUST AS THE MOST ABUNDANT AEROSOL: IMPACTS AND MODELLING - A REVIEW

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ABSTRACT

Dust is a global phenomenon, but also with strong regional impacts. When strong turbulent wind blowing over desert soils in deserts, it lifts loose particles from the surface to the atmosphere. This is the beginning of the atmospheric dust process composed of dust emission, transport, deposition and its feedback with the environment.

Dust impacts are numerous. Dust modifies the weather and climate through direct (with radiation) and indirect (with clouds) interactions. Dust is crucial for cloud formation and therefore for precipitation. Dust is also an air pollutant causing various diseases and infections. Furthermore, dust events have a substantial economic impact such as reduced visibility that can affect air traffic and road transportation. Reduced radiation at the surface has negative impact on the output from solar power plants. Mineral aerosol also interacts with continental and maritime ecosystems by being a source of micronutrients, with the fertilising effects which might play an important role in global climate.

Following the increased societal needs to better monitor and predict the dust process, development of numerical dust models and dust-related observations had a rapid growth over the past two decades. Models are used as a tool to investigate and forecast dust at large and regional scales. Although the atmospheric dust is a critical societal and environmental hazard to arid and semi-arid areas, it has been also recognized that dust effects cannot be ignored in other regions like Southern Europe.

This article reviews different dust impacts. It also reports on modelling efforts to better predict/assess the dust atmospheric process.

INTRODUCTION

When near-surface winds over bare dry desert soils are strong, large amounts of fine dust particles are lifted into the atmosphere. Dust is further transported downwind, affecting regions hundreds and thousands of kilometres away. The most important dust sources are located in the North Hemisphere (i.e. North Africa, Middle East, East Asia and North America). North African and Arabian deserts are the most dust-productive sources. Being the most abundant aerosol, mineral dust accounts for one third to one half of the mass of the total aerosol budget. E.g. between 1000 and 3000 Tg of dust is uplifted into the atmosphere annually from the Saharan desert; Figure i illustrates the scales of the dust process. The complex process of dust emission starts over the dry bare or sparsely vegetated desert surfaces when the near-surface wind exceeds a threshold value above which soil particles begin to move. Through the vertical turbulent flux it elevates becoming available for the free-atmosphere long-range transport. Through gravitational sedimentation and wet and dry settling, dust deposits far away from its sources. The schematic picture of the atmospheric process is shown in Figure 2.

Just three decades before, there was not very clear idea about dust impacts to the climate, environment, human health and economy (such as agriculture, solar energy and transportation). The development of numerical dust models and the refinement of satellite retrievals and in-situ observations in the end of 1980-ies have led to a rapid growth of the scientific interest in atmospheric dust over the past decades reflected among others to explosive increase in the number of published scientific papers (Figure 3). These numbers are a demonstration of the dynamic development of dust as a research topic of international relevance (Knippertz, P. and Stuut, Eds 2014). This interest was a reaction to the concept introduced in 1990-tes advocating that the Earth system requires a full understanding of interactions and feedbacks of different Earth ‘spheres' (the atmosphere, ocean, land, vegetation, aerosols) and their integrative consideration in numerical models. Dust appeared as a par excellence topic for this evolving research area, since it depends on and interacts with several spheres of the Earth system (Knippertz, P. and Stuut, Eds, 2014).

DUST MODELLING

Westphal and Toon (1988) was the first group used a 2D, size-resolving, full physics numerical dust transport model, and demonstrating the possibility to numerically simulate dust process. Soon after, in the period 1991-1993, the predecessor version of the current DREAM dust model (Nickovic 1996; Nickovic and Dobricic 1996) was

developed as the first regional model in which dust concentration was embedded as the prognostic equations of an numerical weather prediction atmospheric model. By now, tens of new advanced dust models has been developed providing operational forecasts. Many of these daily forecasts are now delivered to the community through the WMO Sand and Dust Storm Warning Advisory and Assessment System programme (WMO SDS-WAS; http://www.wmo.int/sdswas) (Benedetti at al., in Knippertz, P. and Stuut, Eds, 2014). Not only research but there is also interest from diverse users ranging from solar energy plant managers to health and aviation authorities, from policymakers to climate scientists. All this pushed further developments in dust modelling to develop new user-oriented products.

***Figure 1**. Saharan dust over the Mediterranean sea on July 16, 2003 as observed by the NASA MODIS satellite (https://www.visibleearth.nasa.gov/view.php?id=67401)*

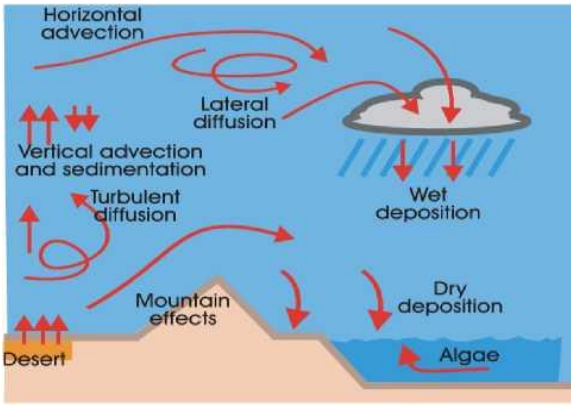


***Figure 2.** Schematic picture of the atmospheric dust process*

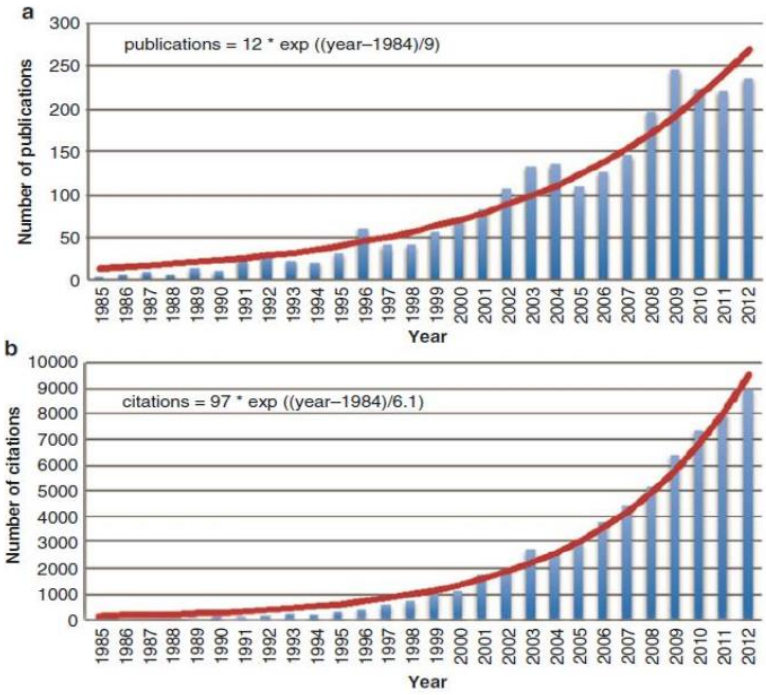


***Figure 3.** Increase in (a) publications and (b) citations of papers on Saharan dust Thompson Reuters web of knowledge the term 'dust and Sahara'. blue bars give actual numbers and red lines best-fit exponential growths. Source: Knippertz, p. and Stuut, Eds., (2014).*

DREAM: DESIGN AND MODELLING APPLICATIONS FOR IMPACTS

Model design

We here present modelling results preformed by the Dust Regional Atmospheric Model (DREAM) addressed to various dust impacts.

DREAM is driven on-line by the one of the NOAA/NCEP (US National Centers for Environmental Prediction) atmospheric numerical weather prediction models (ETA or NMME). It is designed to simulate the atmospheric cycle of mineral dust aerosol (Nickovic et al., 2001; Nickovic, 2005; Perez et al., 2006; Pejanovic et al., 2010). DREAM solves the Euler-type partial differential nonlinear equation for dust mass continuity. The concentration equation simulates all major processes of the atmospheric dust cycle: dust emission, turbulent diffusion, vertical and horizontal advection,

lateral diffusion, and wet and dry deposition. Dust particle size distribution is described by eight bins with effective radii of 0.15, 0.25, 0.45, 0.78, 1.3, 2.2, 3.8, and 7.1 gm. Within each transport bin, dust is assumed to have time-invariant, sub-bin lognormal distribution (Zender et al., 2003) employing the transport mode with mass median diameter of 2.524 mm (Shettle, 1984) and the geometric standard deviation of 2.0 (Schulz et al., 1998). The submicron particles correspond to the clay-originated aerosol (bins 1-4) and the particles from silt soils (bins 5-8).

The specifics of DREAM in terms of the emission parameterization, when compared with the other dust models, is that it includes a thin viscous sublayer between the surface and the lowest model layer (Janjic, 1994) to regulate the intensity of the emission dust flux. Namely, there is a physical similarity between mass, heat and momentum exchanges over mobile surfaces (such as ocean waves) with that of the mobilized dust particles over desert surfaces; we exploited the similarity and introduced the viscous sublayer model in DREAM. Following such concept, the turbulent transfer of dust into the lowest model layer is accounting for different turbulent regimes (laminar, transient and turbulent mixing), using the simulated surface dust concentration as the lower boundary (Figure 4). At sources, the clay/silt content is specified according to soil type characteristics evaluated from the Staub and Rosenzweig-Zobler near-surface soil texture data, and the UNEP/GRID Gridded FAO/UNESCO soil units (Nickovic et al., 2001). Grid points acting as desert dust sources are specified using arid and semiarid categories of the global USGS 1-km vegetation data. Source particle size distribution was derived according to d'Almeida (1987), combined with the Total Ozone Mapping Spectrometer Aerosol Index (TOMS AI) satellite retrieval (Prospero et al., 2002; Ginoux et al., 2012), providing so information on dust sources where enclosed basins containing former lake beds or riverine sediment deposits has an abundance of small clay-sized particles that are loosely bound; these sources happened to dominate the global dust emission.

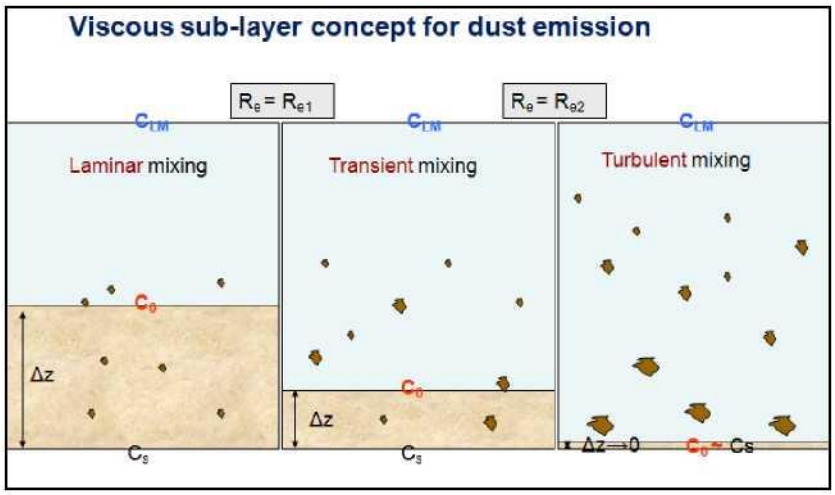


Figure 4. *Viscous sub-layer structure for dust emission in DREAM*

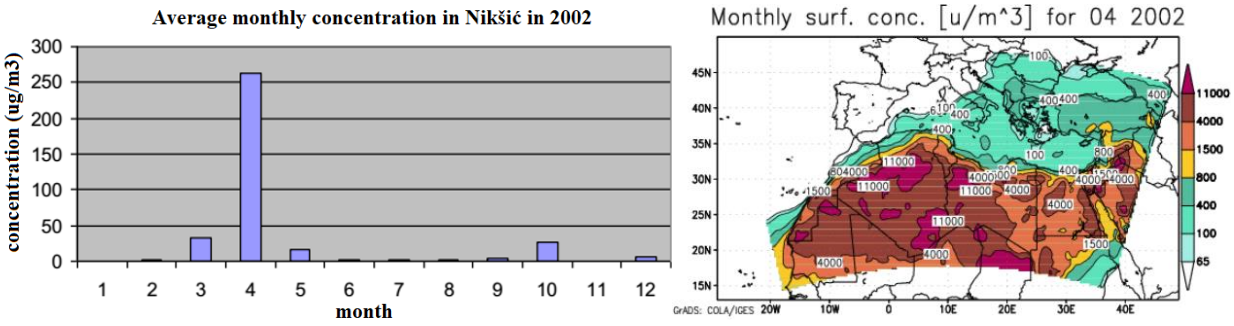
Parameterization of the wet removal is done using a parameterization method for wet deposition involving rainfall rate and washout ratio. The dry deposition scheme follows Georgi (1986) which calculates dry deposition velocity relative to the surface as a function of particle size and on surface types. This scheme includes processes of deposition by turbulent and Brownian diffusion, gravitational settling, interception and impaction on the surface roughness elements.

DREAM has demonstrated its capabilities in a number of validations against data from observation networks such as the European Lidar Network EARLINET, the NASA and METEOSAT data, and the AERONET/PHOTONS sun photometer network (e.g. Perez et al., 2006; Nickovic et al., 2016; model intercomparison at https://sds-was.aemet.es/forecast-products/dust-forecasts/forecast-comparison).

Health-related applications

UNEP, WMO, UNCCD (2016) in their 'Global Assessment of Sand and Dust Storms' strongly advocates the connection between mineral dust and health. Dust causes numerous human health problems, in arid and semi-arid regions, but also elsewhere. Inhalation of fine particles can cause diseases such as asthma, bronchitis, and silicosis (lung fibrosis). Chronic exposure to fine dust is associated with premature death due to cardio-vascular and respiratory disease, lung cancer, and acute lower respiratory infections. According to the World Health Organization report in 2016 (http://www.who.int/mediacentre/news/releases/2016/air-pollution-estimates/en/), some 3 million deaths a year are linked to exposure to outdoor air pollution due to non-communicable diseases such as cardiovascular diseases, stroke, pulmonary disease and lung cancer. A part of this number certainly should be linked to the most abundant natural polluter - dust.

In the Mediterranean, Saharan dust events can contribute to exceedances of PM_{10} daily European Union Limit of 50 gg/m^3. Some recent studies, although performed using a limited number of cases in the Mediterranean, observed links between dust and medical problems. In Cyprus, an increased number of hospitalization cases (particularly related to cardiovascular problems) is recorded during dusty days (Middleton et al, 2008). An evidence on adverse health effects of PM_{10} on mortality in Athens linked to desert dust events was also found (Samoli et al, 2011). Furthermore, during Saharan dust intrusion in Madrid it has been observed that there are effects of PM_{10} on mortality due to respiratory causes (Diaz et al, 2012). The Balkan Peninsula has been the focus of a DREAM-based simulation study addressed to the 2002 'annual' dust climatology (Nickovic, 2004). This study has been performed in other to better understand the seasonality of dust in this region and to eventually link it to health impacts. It has been found that the monthly maxima for dust deposition reaches 7000 mg/m^2 and up to 2000gg/m^3 for the surface concentration. The absolute surface max of 7042 gg/m^3 was found at Niksic station during 9 April 2002. April was the month with the highest concentrations - the model monthly average is 263 gg/m^3 in Niksic (Figure 5a) which is about 5 times more than the recommended EU standard. Figure 5b shows the April 2002 mean spatial distribution of the surface dust concentration as simulated by the model.



(a) (b)

Figure 5. *(a) Monthly mean dust concentration for 2002 in Niksic; (b) Monthly mean dust concentration for August 2002 in the Mediterranean*

Another dust-related illness caused by a soil-dwelling coccidioidomycosis (or cocci) fungus typical for the US Southwest and Mexico (Figure 6a) is the valley fever. When cocci is inhaled, it causes shortness of breath, exhaustion or skin rash, being in some cases fatal. To better understand the atmospheric transport of cocci spores travelling together with dust particles, DREAM was modified to simulate the spore emission, transport and deposition (Sprigg et al, 2014). Associated with the dust source data, the mineralogy data base developed for dust modeling was used in this study as well (Figure 6b) to better describe the fact that some dust minerals like quartz are preferential soil environments for cocci (see more details on the dust mineralogy in one of the sections below). An example of the model concentration performed in this study is shown in Figure 6c.

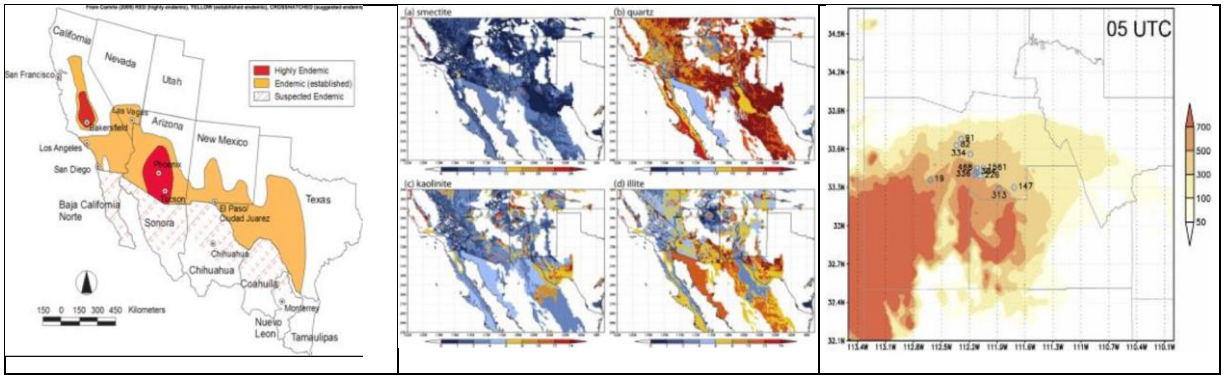


Figure 6. *Valley fever in the US: (a) Estimated Valley Fever endemic zones; (b) Geographic distribution of minerals smectite, quartz, kaolinite and illite (favorable for the cocci growth) used as input data in the model; (c) simulated dust concentration carrying cocci spores in the Phoenix region (Arizona).*

Another DREAM application over the USA performed within the health-related NASA-supported study Public Health Applications in Remote Sensing (PHAiRS) has been addressed to dust sources and dust transport. In the project, the NASA remote-sensing and the DREAM products has been integrated into the New Mexico public health decisionsupport system (Figure 7). To characterize model behavior, a point-by-point comparison between in-situ observations and DREAM model output has been performed across reporting stations from north-central New Mexico to the Texas Gulf (Yin et al., 2005).

Direct dust-atmosphere impacts

The direct effect is the mechanism by which dust aerosol scatter and absorb shortwave and longwave radiation. As a result, this process alters the radiative balance of the Earth-atmosphere system. Key parameters for determining the direct radiation forcing are the aerosol optical properties (the single scattering albedo, specific extinction coefficient, and the scattering phase function), which vary as a function of wavelength and the atmospheric loading and geographic distribution of dust in the horizontal and vertical, which vary in time as well. Comparisons between weather prediction model results with ssatellite measurements of the outgoing longwave radiation (OLR) demonstrated a significant difference is found over desert regions of northern Africa where the model emits too much OLR by up to 35 Wm^{-2} because current models do not consider dust-atmosphere feedback mechanisms. As a consequence, in the cloud-free areas, there are, among others, errors in the model surface temperature.

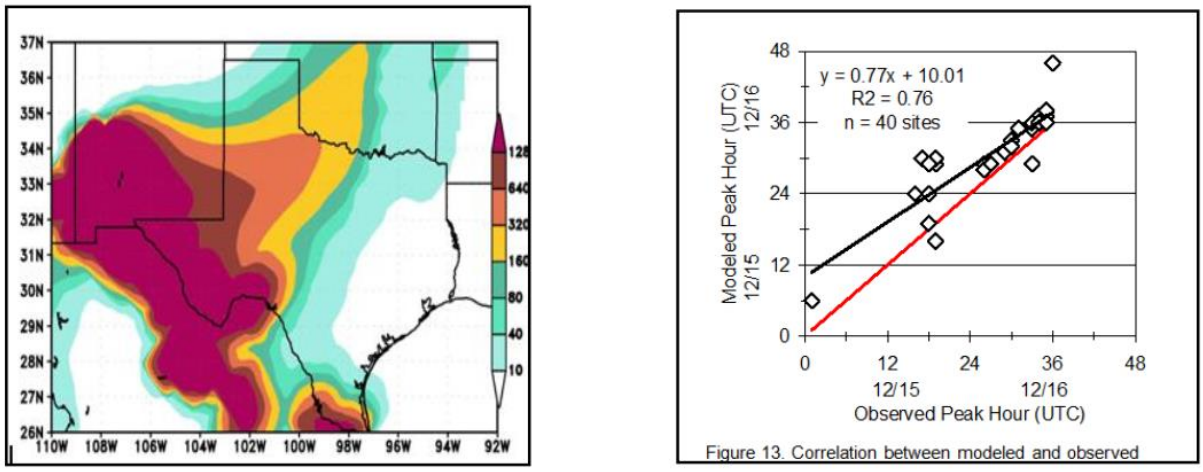


Figure 7. *(a) Model surface concentration valid for 02UTC December 2003; (b) Model vs. observation surface correlation for north-central New Mexico locations*

The question how large are these errors was examined in studies of Nickovic (2005) and Perez et al. (2006) which was the first attempt to link dust and radiation within the same modelling system. A major dust outbreak over the Mediterranean region has been selected to assess the radiative dust effects on the atmosphere at a regional level.

Over land, the studies showed there is a negative radiative forcing at the surface which significantly reduces the sensible heat flux to the atmosphere, which in turn reduces the surface temperature; differences in 2m temperature has reached 6K in some areas of the model domain, as shown in Figure 8.

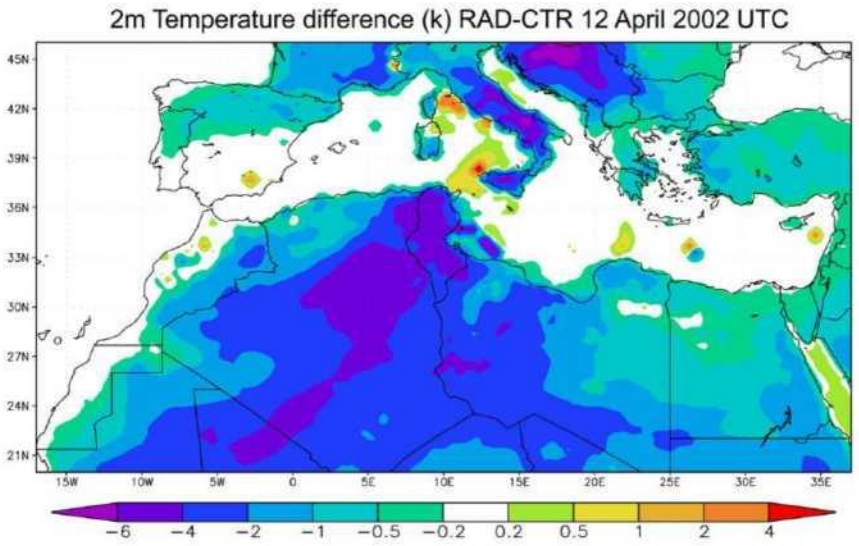


Figure 8. *2m temperature difference (with - without feedback) in DREAM simulations*

Although the use of interactive dust-radiation parameterization could be a step forward in improving the accuracy of numerical weather prediction and climate radiative impact assessments, there is no yet an operational numerical weather prediction system established, mainly because of the complexity of the problem.

Indirect dust-atmosphere impacts

The indirect dust effect is the process by which dust modifies the microphysical properties, amount and lifetime of clouds. Key parameters for determining the indirect effect are the effectiveness of a dust particle to act as a nucleus for cloud generation process, in which the particle size, dust mineralogical composition and the ambient temperature and moisture play the major roles. Aerosols in general, acting as ice nucleating particles (n_{IN}) enhances the heterogeneous glaciation of cloud water making it freeze earlier and at higher temperatures than otherwise. Dust is known as the best ice nuclei agent. Cziczo et al (2013) showed that mineral dust found as residues in the ice crystals are prevailing (61%).

Mineral dust as a significant contributor in the ice nucleating process is associated with the cloud formation and precipitation (e.g. DeMott et al., 2003; Yakobi-Hancock et al, 2013). Measurements suggest that dust enhances both ice formation in mid-level clouds and precipitation (Creamean et al, 2013). A new generation of n_{IN} parameterizations where dust is recognized the major contributor has been recently developed (Niemand et al, 2012; DeMott et al, 2015). Exploiting these findings, Nickovic et al (2016) have developed a coupled (atmospheric NMME) - (dust DREAM) forecasting system, which for the first time introduces n_{IN} affected by dust as an online model variable. The method has been extensively tested by comparing the model results with different observation types: with the MSG SEVIRI parameters related to cloud ice content; and with the combined in-situ lidar and cloud radar data detecting cold clouds. Figures 9 and 10 demonstrate how the model compares against the observations.

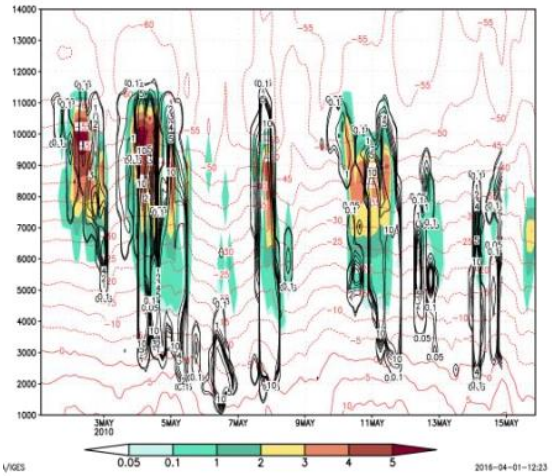


Figure 9. *Comparison of log_{10} (Ice Water) obtained from the Doppler radar reflectivity (solid black line contour plot) versus DREAM log_{10} (n_{IN}) (coloured shaded plot) in the period 1-15 May 2010*

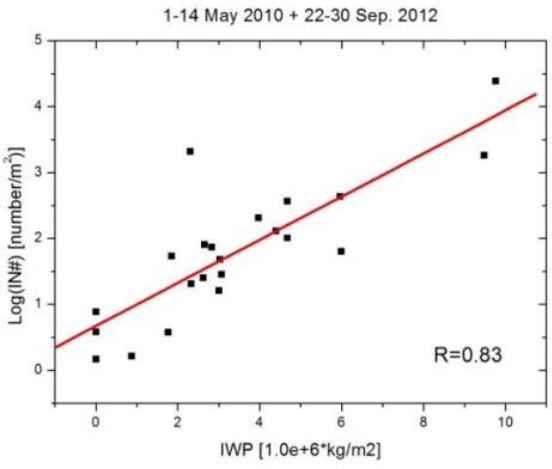


Figure 10. *Correlation between observed Ice Water and DREAM log_{10} (n_{IN}) during 1-15 May 2010*

Introducing the indirect effects in numerical weather prediction systems would be a step towards potential improvement of the operational prediction of cold clouds and precipitation. For the moment, current operational numerical weather prediction systems do not include aerosol effects in cloud formation or consider aerosols in a simplistic way.

Dust mineralogy and impacts

The mineral composition of dust affects various processes, such as processes in atmospheric, ocean and terrestrial environments, and it also affects human health. Including mineral dust transport interacting with the atmosphere in numerical models can improve the accuracy of weather forecasts and climate simulations and contribute to a better understanding of the environmental processes caused by mineral dust. Motivated by the interest of the modelling community to study impacts of dust mineralogy, a high-resolution (global 30 arc-seconds ~1km) gridded database GMINER30 for eight minerals in dust-productive soils (quartz, feldspar, calcite, gypsum, illite, kaolinite, smectite and hematite) has been developed (Nickovic et al, 2012), public available at http://www.seevccc.rs/?p=623.

Minerals and radiation. The response of solar radiation to dust depends on the dust mineral composition. The mineral composition substantially changes the amplitude of the radiative forcing of dust in both solar and infrared spectra (e.g. Balkanski et al., 2007). In this process the solar component is strongly related to the presence of iron oxides in dust, making it darker than other dusts.

Minerals and cloud formation. As mentioned above, is considered as an important source of ice nuclei in mixed-phase clouds. Atkinson et al (2013) discovered that the feldspars represent the dominant ice-nucleating minerals, several orders more efficient than the other clay and silt minerals, opening with this spectacular finding a new promising direction of research.

Minerals and health. Iron-catalyzed free radicals are known to be an important factor that enhances acute lung inflammation (Prospero, 1999); it is also a major carcinogenic factor (Fubini and Arean, 1999). Iron in lungs can support microbial growth, resulting in more virulent infections. The rate of reaction between oxygen and ferrous iron in the goethite dust mineral is particularly high (Schoonen et al., 2006). In the case of meningitis seasonally occurring in the Sahel belt, it is hypothesized that the activation of the meningococcal bacteria is fostered with high iron content in Fe-rich minerals in dust (Thomson et al. 2009). The mechanism by which dust may cause meningitis epidemics is assumed to be the physical damage to the nose and throat epithelial cells by dust particles permitting invasion of bacteria into the blood stream.

Minerals and marine productivity. Minerals carried by dust particles and deposited over remote ocean regions after long atmospheric transport can provide important nutrients for marine life. Iron embedded in dust is considered as

one of the major micronutrients for ecosystems in remote oceans. Although the iron input into the ocean by rivers is large, it affects only the biota of the coastal zones. However, the deposition of mineral dust in remote oceans after long-range dust transport is considered as a likely source of iron in these regions. The availability of iron to photosynthetic marine microorganisms depends on the iron aerosol solubility. Iron in desert soils is essentially non-soluble, but cruise-based observations indicate that the solubility increases during aerosol transport (Baker and Jickells, 2006). The iron solubility depends: on mineralogy of desert soils; on Fe cloud processing (clouds are more acid than their environment); on Fe photo-reduction by radiation; on chemical processing by pollution; and on particle size segregation happening during the transport (smaller particles are more efficient in the Fe processing) (Figure 11a).

All these factors are incorporated in a DREAM version (Nickovic et al, 2013) developed el for simulating the atmospheric processing of iron-containing mineral dust. The high-resolution soil mineralogy GMINER30 was used to calculate the emitted iron fraction in the dust (Figure 11b). A transport equations for the total iron (Fe-rich goethite and hematite dust minerals) and for the chemically processed iron has been introduced as additional model governing equations to parameterize the soluble iron chemical reaction as a function of the mineralogy at dust sources. The model results were validated against field data collected during several Atlantic cruises (Figure 11c).

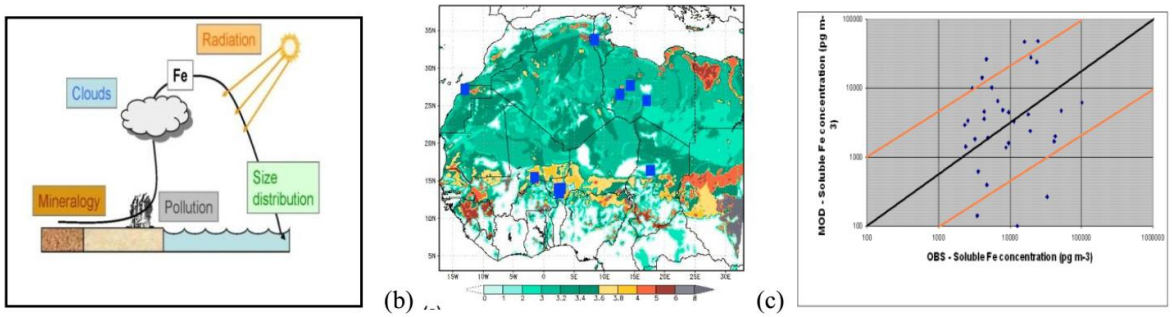


Figure 11. *Fe in dust: (a) Schematic picture on the Fe solubility chemistry process in the atmosphere; (b) Geographic distribution of iron in soils over northern Africa; (c)Model vs. observed soluble Fe concentrations*

CONCLUSIONS

Dust was for a long time considered more as a subject of scientific curiosity, in both observational and modelling studies. The first idea on the large-scale character of the atmospheric dust process was gained through aerosol measurements begun on Barbados in 1965; see Figure 12a (Prospero and Nees, 1977) and continued to this day. In 1979, another aerosol observational network was established in central North Pacific, where dust was detected to everyone's great surprise, when the analysis showed that the samples contained high concentrations of Al which was attributed to dust transported from Asian sources; see Figure 12b (Duce et al., 1980). These first lessons on dust process behaviour were an important guidance for modellers who developed first dust models and introduced them to run them operationally in early 1990-ties (see Figure 13).

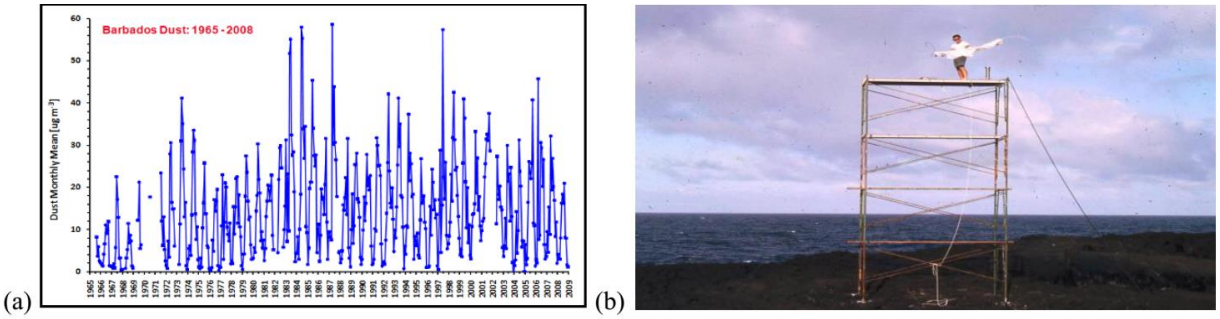


Figure 12. *First dust measurements: (a) Barbados dust measurements starting 1965; (b) Air/sea chemistry sampling tower in Hawaii in 70-ties*

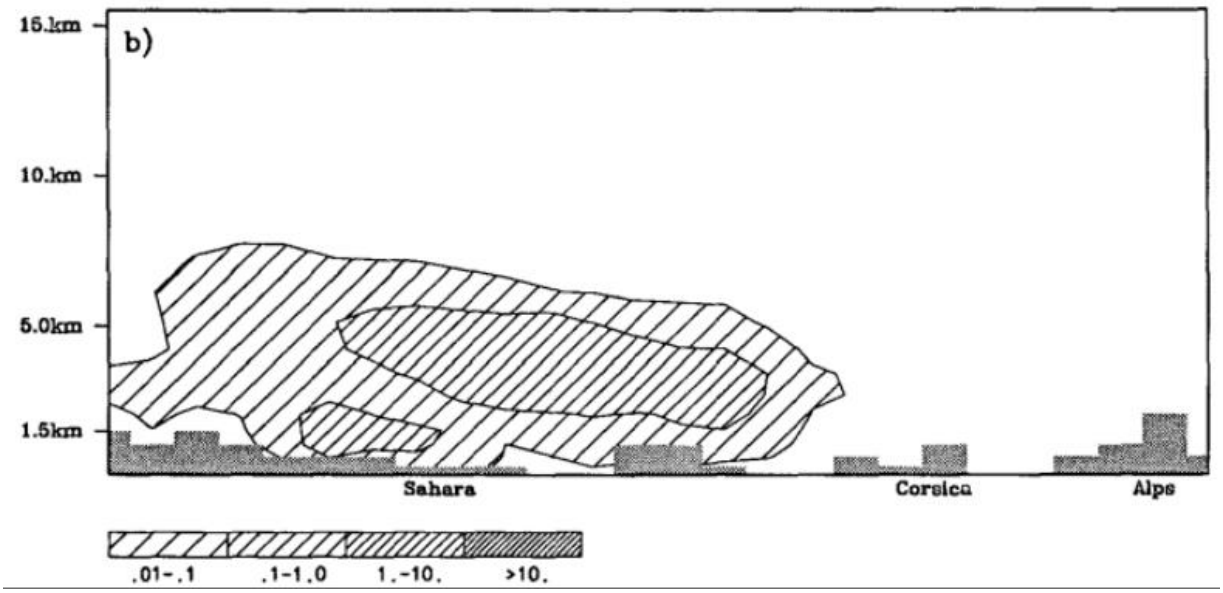


Figure 13. *An example of early dust forecasts, showing a cross section of concentration*

Today, both monitoring and modelling of the dust process which substantially advanced meanwhile, are the scientific and technical tools unavoidable in better understanding the process and in dealing with numerous dust impacts to weather, climate and to the societal activities in general.

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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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ABSTRACT

Elevated levels of surface ozone adversely affect human health and ecosystems including forest and vegetation. The aim of the study is to describe the atmospheric conditions leading to ozone episodes in the north-western side of the Biga Peninsula of Turkey which covers mountainous and forested areas. To understand the identification, the possible sources of the ozone episodes, rural and semi urban ozone measurements from the Biga Peninsula during a 3-year period (2013-2015) have been analysed. The NOAA HYSPLIT model driven by the WRF model is used to identify transportation of ozone and its precursor.

INTRODUCTION

Surface ozone is a major constituent of photochemical smog. Its elevated concentrations can cause serious damage to human health and natural ecosystems. Most of the human health impacts are associated with the respiratory system and lung irritation. Its damage on ecosystems were found on sensitive plant species and reduced yield of crops. Moreover, surface ozone is important greenhouse gas with radiative forcing which can have an impact on climate change by enhancing the greenhouse effect. Surface ozone is a secondary pollutant formed under intense solar radiation-driven chemical reactions involving ozone precursors as carbon monoxide (CO), non-methane volatile organic compounds (VOCs), and nitrogen oxides (NOx). These precursors result from both human activities and biogenic sources. According to the EU Directive 1-h standard, the level for surface ozone is 120 $\mu g/m^3$ at maximum 8-hr daily average and not exceeding 25 days in a calendar year.

Atmospheric conditions also have a role on the formation of ozone as well as its dispersion, transport and accumulation at the surface. Numerous studies have shown that elevated ozone levels are often associated with intense solar radiation and high temperatures, under anti-cyclonic pressure conditions and stagnant atmospheres, which are favourable for photochemical production and accumulation of ozone (e.g., Thompson et al., 2001; Vukovich and Sherwell, 2003; Duenas et al., 2002). Besides, *surface ozone* in non-urban areas can be strongly influenced by transported regional air pollutants from distant urban emissions. Long-range transport of air pollutants from highly polluted areas could bring high concentrations of ozone and its precursors in surrounding areas. Due to the impacts of atmospheric conditions on ozone levels and the nonlinear relationships between ozone and its precursors, it is usually difficult to recognize the sources of ozone at a particular location (Tong et al. 2018).

Numerous studies worldwide have been performed on surface ozone and its precursors over the past several decades. However, the majority of the studies were conducted in urban areas. Only a small number of ozone studies were carried out for rural areas. This situation is similar for the studies performed in Turkey. For example, Im et al. (2013) examined the elevated ozone levels at an island in Istanbul by using HYSPLIT model. Kasparoglu et al. (2015) examined back trajectories and showed the impacts of European air pollutants on the ozone levels in the Şile province of Istanbul. Sarı et al. (2016) investigated the surface ozone levels in the forest and vegetation areas of the Biga Peninsula, Turkey and showed the transportation of air pollutants to the area using back trajectories. Kasparoglu et al. (2018) examined elevated levels of ozone and its precursors over the Marmara region in northwestern Turkey. They showed the impacts of transport of air pollutants over the urban and rural areas in Marmara region. The back trajectories from the Eastern Europe and Ukraine support the results by findings of Freiwan and Incecik (2006).

The Biga peninsula is located in the northwest part of Anatolia. It is also known by its ancient name Troy (Figure 1). The region is covered with agricultural and forest areas with limited settlement areas. There is no intensive industry in the region, but there are several power plants.

In this study, in order to identify the reasons for elevated ozone concentrations, ozone measurements from the rural and semi-urban areas in the Biga Peninsula of Turkey recorded during the 3-year period (2013-2015) have been analysed. Surface ozone concentrations in the study region tend to follow a seasonal cycle; generally reaching maximum levels in spring-summer, especially during July-August and minimum values in the October-December

period. 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 μg/m^3 while monthly average ozone concentrations were between 78 and 187 μg/m^3 for summer periods (June, July and August) in the Biga Peninsula. Moreover, the maximum O_3 concentration appears at around 16:00-17:00 in rural and 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).

METHODOLOGY

The surface ozone data over the 3-year period (2013-2015) were taken from 10 passive samplers and two continuous air quality stations, while the meteorological data came from the meteorological stations in the region (Figure 1). The Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model is a useful tool for the study of long-range transport of air mass (Camalier et al., 2007). *HYSPLIT* has been developed at the NOAA Air Resources Laboratory (ARL). In the present study, HYSPLIT 4 model was performed to follow the long-range transport sources leading to the high ozone levels in the region. HYSPLIT usually run by using the Global Data Assimilation System (GDAS) meteorological dataset. However, HYSPLIT model was integrated with meteorological fields derived from the WRF model to identify the source locations using backward trajectory analysis in this study. The HYSPLIT model driven by the WRF model is used to identify the ozone and its precursor transportation.

The WRF model which generates atmospheric field simulations at a high resolution is suitable for use in a broad range of applications across scales ranging from metres to thousands of kilometres. The WRF uses fully compressible, non-hydrostatic equations, terrain following vertical coordinates, and staggered horizontal grids (Skamarock et al., 2008). The model has several options for spatial discretization, diffusion, nesting, lateral boundary conditions, and parameterization schemes for sub-grid scale physical processes. The physics used consists of microphysics, cumulus convection, planetary boundary layer turbulence, land surface, and longwave and shortwave radiation. The WRF simulations for the five episodes were run using a set of 9, 3 and 1 km horizontal resolution and one-way nested grids (Figure 2). A total 30 vertical levels from the surface to the 100 hPa level are considered in the model. The outermost domain (D01) covers the most areas of East Europe and Russia, with the horizontal grids of 287×273 and the grid spacing of 9 km. The nested domain (D02) covers the Balkans and the western side of Turkey, with the horizontal grids of 346×298 and the grid spacing of 3 km while D03 which is the finest domain covers the Northwestern part of Anatolia including Biga Peninsula, with the grid system of 526×448 and 1 km resolution.

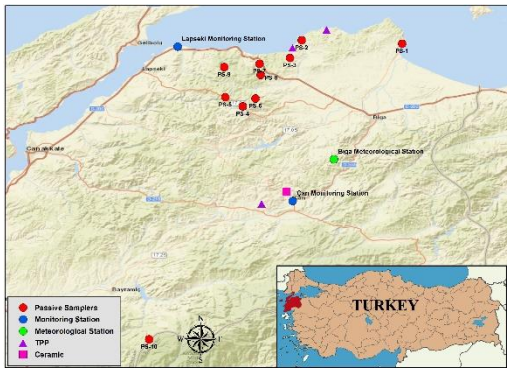

Figure 1. *A map of the study region*

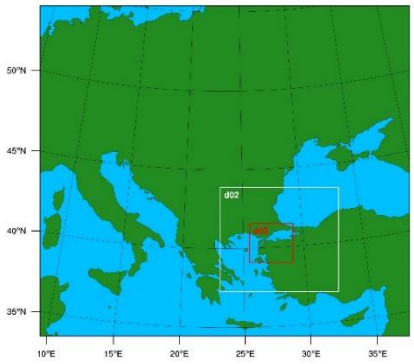

Figure 2. *WRF model domain*

In the presented study, the HYSPLIT 4 model was used to compute the advection of a single pollutant particle, or simply its trajectory. The dispersion of a pollutant is calculated by assuming either puff or particle dispersion. In the puff approach, puffs expand until they exceed the size of the meteorological grid cell (either horizontally or vertically) and then split into several new puffs, each with its share of the pollutant mass. In the particle approach, a fixed number of initial particles are advected about the model domain by the mean wind field and a turbulent component. The turbulent component of particle motion is computed by an autocorrelation function based on Lagrangian time scale and a computer-generated random number (Draxler and Hess, 1998). The backward trajectories for a 72-h period were plotted at 3-h intervals starting from two observation locations to identify

probable sources. Using meteorological files with higher spatial resolution in the computation of back trajectories give better results.

RESULTS AND DISCUSSION

Characteristics of Ozone Episodes

The time series of the daily 8-hour mean ozone concentrations in episodes are shown in Figure 3. The daily maximum 8-h ozone concentrations reaching 120 µg/m^3 or above (which is the 8-h European standard threshold) are considered (Table 1), and 5 different ozone episodes were selected in the period of 2013 and 2015. Episode periods are a few days up to 2-3 weeks with high concentrations, characterized by exceedances of the thresholds set to protect human health. Ozone concentration is dependent on emissions of precursors and on the amount and intensity of sunlight. Therefore, ozone episodes will mainly occur during periods of warm sunny weather.

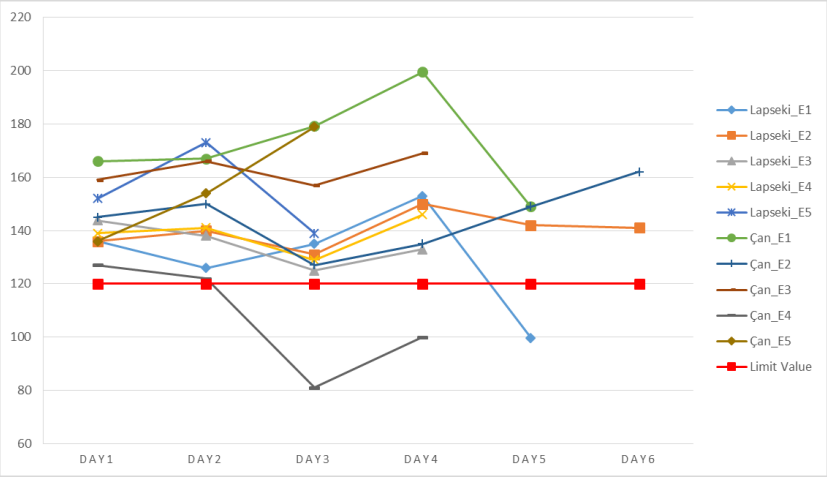

Figure 3. *Time series of the daily 8 hour mean ozone concentrations in episodes in the Biga Peninsula (µg/m^3)*

Table 1. *Ozon levels in the 5 episodes*

AQ Stations	E1- (22-26/06/13)			E2- (09-14/08/13)			E3- (10-13/08/14)			E4- (01-04/09/14)			E5- (27-29/07/15)		
	Av	T-1	T-2	Av	T-1	T-2	Av	T-1	T-2	Av	T-1	T-2	Av	T-1	T-2
Lapseki (rural)	99.7	4	-	117	6	-	91.6	4	-	99.3	4	-	109	3	2
Çan (semi urban)	131	5	8	97.7	6	2	99.1	4	3	68.1	2	-	94.7	3	5

Av.: Hourly average ozone level in episode µg/m^3

T1: Number of days when maximum daily 8 hour mean greater than 120 µg/m^3

T2: Number of hours greater than 180 µg/m^3

Validation

To validate the WRF model predictions, the model outputs were compared with the meteorological measurements during the five episodes. Temperature, relative humidity, wind speed and pressure data from meteorological stations were used. In order to evaluate the model performance, four statistical metrics are used: correlation, index of agreement, mean absolute error and root mean square error. The results indicate that prediction of the temperature and wind speed is quite successful.

LRT of Ozone and Its Precursors

The HYSPLIT model was used to compute hourly 3D backward trajectories at 500m above ground level (agl): 500m agl for model runs was chosen to represent the well-mixed conditions in atmospheric boundary layer and likely to affect the surface air quality in Biga peninsula. The 72-hour period can be well suited to capture the long-

range transport of air pollutants since most pollutants will be deposited within two days (Im et al., 2013). The HYSPLIT back trajectory analysis driven by the WRF simulated fields with 1 km resolution are shown in Fig.4.

This analysis was completed with 3-day backward air mass trajectories to assess the contribution of long-range transport of the 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 (Figure 4).

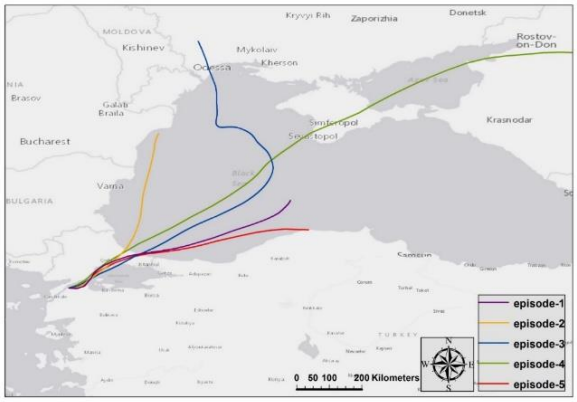

Figure 4. *HYSPLIT model outputs*

CONCLUSIONS

The WRF model was used to generate meteorological fields at high resolution over the Biga Peninsula region. Then the HYSPLIT4 driven by the WRF simulations was used to identify the possible emission source locations and transportation routes. The results from the 5 different ozone episodes selected between 2013 and 2015 indicate that İstanbul, Eastern Europe, and Western Russia are possible source locations affecting the elevated ozone levels in the Biga Peninsula. Furthermore, meteorological conditions and synoptic weather patterns leading to low wind speeds are associated with high ozone levels in the study region. 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 the north, including İstanbul.

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

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ABSTRACT

This paper is to present the results of aerosol measurements from a dust intrusion episode in Belgrade during the period of July 5-7, 2014. A vertical profile of the aerosol backscattering coefficient, obtained from ground-based LIDAR measurements in Belgrade, showed a distinct elevated dust layer at altitudes of 2-5 km on July 5, 2014. The altitude of the layer decreased later in the episode, with its centre of mass decreasing from approximately 4 km to below 3 km. On the last day of the episode, an entrainment of the dust layer into the planetary boundary layer was observed, consistent with the observed change of PM_{10} concentration at the surface level. The PM_{10} concentration increased by 15-17 μg m^{-3} at three monitoring sites in Belgrade, as the dust plume was settling down during the episode. The DREAM model simulations reproduced well the observed dust layer altitude. Dust surface concentrations from the model showed an increase of 11 μg m^{-3} during the episode. The difference from observed PM_{10} increase was attributed to contributions of other aerosol types to observations.

INTRODUCTION

Mineral dust is one of the most abundant components of the global aerosol burden (Kinne et al., 2006). Saharan dust originates from the world's primary dust source region, and can be transported over long distances (Prospero, 1999; Ansmann et al., 2003). It mixes with other aerosol types along the transport path, affecting their physical, optical and radiative properties. Mineral dust affects the Earth's radiative budget by scattering and absorbing solar and terrestrial radiation (direct effect), by modifying cloud properties due to their role in cloud formation (indirect effect) or by changing the thermal structure of the atmosphere (semi-direct effect). However, there is significant uncertainty in estimating role of dust in the Earth's climate system (IPCC, 2013). Dust impacts air quality, even at locations distant from the source region (Prospero, 1999), and has harmful effects on human health (Giannadaki et al., 2014). To address these problems, it is important to improve the understanding of dust properties on temporal and spatial scales. This requires the synergistic use of ground-based and satellite measurements, along with a regional dust model, for the analysis of dust spatial and temporal variability.

Here we present a case study of a dust intrusion episode observed in Belgrade from July 5-7, 2014. The analysis of the temporal variability of the dust layer was based on ground-based LIDAR measurements in Belgrade, while satellite measurements were used in the discussion of the spatial distribution of dust. Furthermore, the impact of the dust intrusion episode on PM_{10} concentrations in Belgrade was analysed. The measurement results were compared with results of Dust REgional Atmospheric Model DREAM (Ničković et al., 2001).

METHODOLOGY

The aerosol backscattering coefficient at 355 nm was derived from LIDAR measurements in Belgrade. A combined Raman elastic backscatter LIDAR has been operating at the Institute of Physics Belgrade since February 2014. It is based on the Nd:YAG laser operating at a fundamental wavelength of 1064 nm, and second and third harmonics at 532 and 355 nm. The laser pulses of 5 nm duration are transmitted at repetition rate of 20 Hz, with the output energies of 105, 45 and 65 mJ at these three wavelengths. The receiver is based on a 250 mm Cassegrain telescope in a biaxial arrangement, with adjustable field of view in the range from 0.5 to 3 mrad. Photomultiplier tubes are used to detect the backscatter signal in photon counting and analogue mode. The signals are detected at 355 and 387 nm, with a vertical resolution of 7.5 m and a temporal resolution of 1 minute. In this work we analysed the elastic backscatter signal at 355 nm. The analysis of the LIDAR signal to obtain the aerosol backscattering coefficient was performed using Fernald-Klett retrieval method (Fernald, 1984; Klett, 1985), assuming a LIDAR ratio value of 50 sr. Due to incomplete overlap of the laser and telescope fields of view, the LIDAR signal registering below 500 m was not considered in the analysis.

Daily PM_{10} mass concentrations at surface level, at three stations in Belgrade, were obtained from the State network for automatic monitoring of air quality (https://data.gov.rs/sr/datasets/kvalitet-vazdukha-u-republitsi-srbiji/).

Dust REgional Atmospheric Model DREAM (Ničković et al., 2001) embedded into the NCEP/NMME non-hydrostatic atmospheric model (Janjić et al., 2011) was used to provide horizontal and vertical distribution of dust concentration. The model domain covers Northern Africa, the Middle East and a large part of the European

continent, with a horizontal resolution of 1/5° (~ 30 km) and 28 vertical levels. It uses 8 particle size bins within the 0.1-10 μm radius range.

Additionally, we used an aerosol optical depth (AOD) at 550 nm from combined Deep Blue and Dark Target algorithms and the Deep Blue Ångström exponent (AE) at 412-470 nm products from the MODIS (Moderate Resolution Imaging Spetroradiometer) instrument aboard the NASA Aqua satellite. We used Collection 6, Level 3 data products. It should be noted, that the increase in AOD indicates an increase in aerosol load, while the AE parameter is used as a qualitative measure of particle size (the smaller AE values indicate predominantly coarse particles).

CALIOP (Cloud-Aerosol Lidar with Orthogonal Polarization) on board the CALIPSO satellite, was used to obtain vertical profiles of aerosols and clouds. It is an elastic backscatter LIDAR operating at two wavelengths: 532 nm and 1064 nm, with a depolarization channel at 532 nm. Here we used Level 2 Vertical Feature Mask product, which provides information on the aerosol types present in the detected layers (Omar et al., 2009).

Air-mass back trajectories ending at different altitudes over the LIDAR measurement site were calculated using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Draxler and Hess, 1998; http://ready.arl.noaa.gov/HYSPLIT.php), with meteorological input from the Global Data Assimilation System (GDAS). The backtrajectories were used to provide an indication of the origin and pathways of air-masses arriving at altitudes of interest over Belgrade.

RESULTS AND DISCUSSION

We present an analysis of a dust episode that was observed over Belgrade from July 5-7, 2014. The beginning of the episode can be seen in MODIS data shown in Figure 1. MODIS values of AOD and AE indicate an increase of aerosol load and an increased contribution of coarse particles on July 5th compared to the previous day; this is typical for dust episodes.

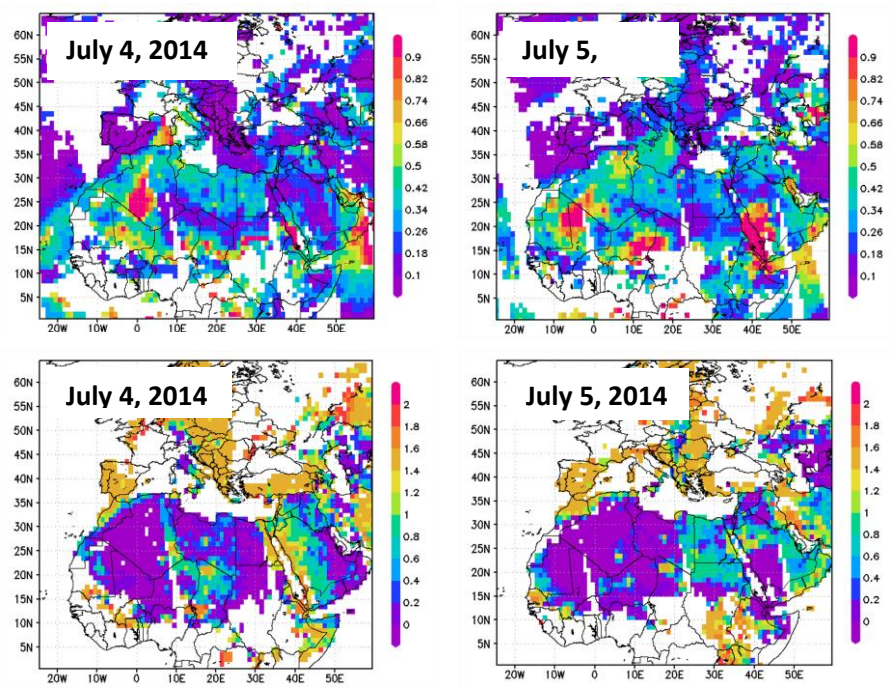

Figure 1. *MODIS aerosol data for July 4-5, 2014: (upper panels) MODIS aerosol optical depth (AOD) at 550 nm from combined Deep Blue and Dark Target algorithms; (lower panels) Deep Blue Angström exponent (AE) at 412-470 nm.*

The observed AOD at 550 nm over Belgrade increased from below 0.1 on July 4th, to about 0.3 on July 5th (the first day of the dust episode), with a decrease in the AE value from 1.4 to 0.4. Moderate AOD values were observed

over Belgrade during the dust episode. MODIS data also showed that the dust event affected parts of western and central Europe.

A close CALIPSO overpass over Belgrade occurred during the peak of the dust episode, on July 6th, at approximately 12 UTC. The CALIOP Vertical Feature Mask data, along the satellite ground track, is presented in Figure 2. We also showed the dust load over the area of interest and a vertical profile of the dust concentration along the CALIPSO ground track, resulting from DREAM model simulations. Both CALIOP data and the DREAM model results indicated that the dust plume extended north to Poland. The concentrations resulting from the model were largest around 40°N, at altitudes between 2 and 3 km, and decreased towards the north. At the part of the track within a 100 km distance from Belgrade, the DREAM model dust concentrations showeda maximum at a similar altitude range. CALIOP data suggested the presence of polluted dust (a mixture of pure dust with smoke or anthropogenic pollution) in this layer.

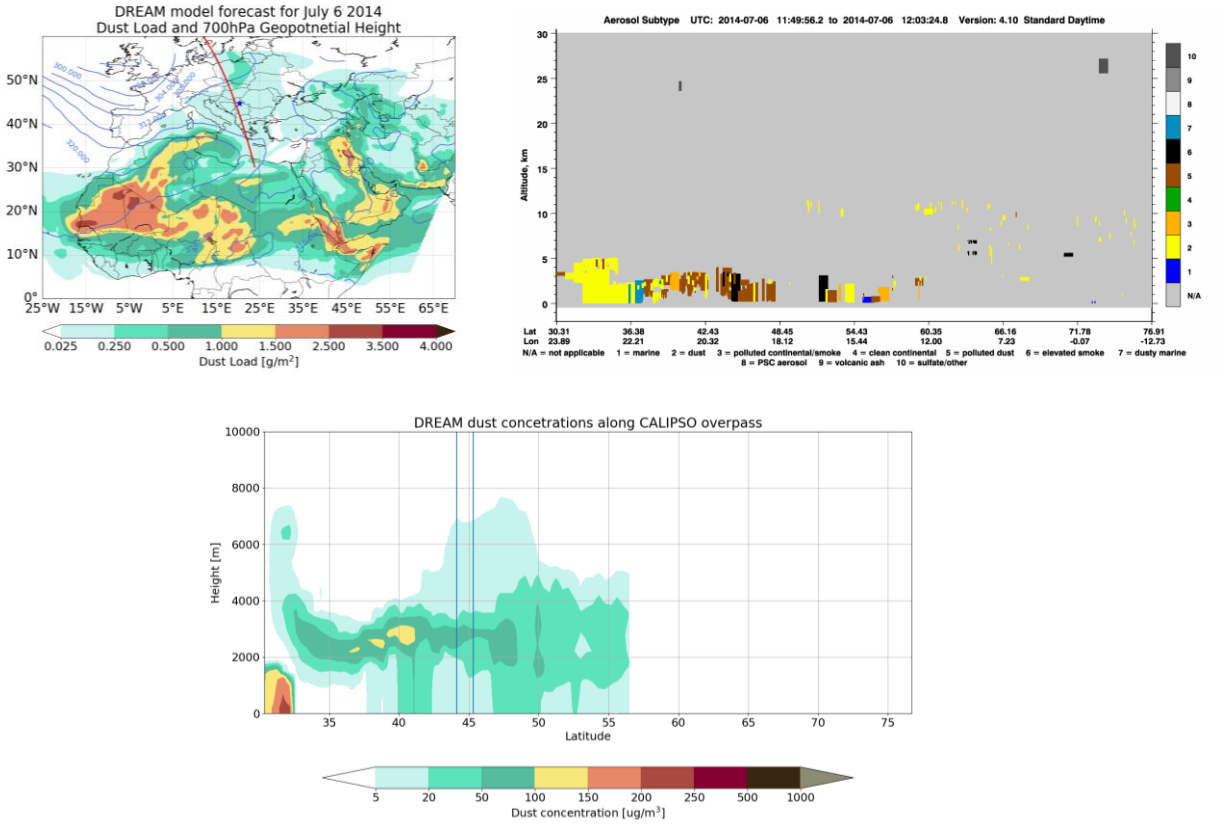

Figure 2. *(upper panels) Map of dust load calculated from DREAM model on July 6, 2014 at 12 UTC, with CALIPSO ground track and Belgrade LIDAR station marked; and the corresponding results of CALIOP aerosol classification. (lower panel) Dust concentration vertical profiles along the CALIPSO ground track obtained from DREAM model. Data between the two vertical lines corresponds to the part of the track within 100 km distance from Belgrade LIDAR station.*

Ground-based LIDAR measurements in Belgrade were analyzed to characterize the aerosol vertical profile during the dust episode. The profile of the aerosol backscattering coefficient showed a distinctly elevated aerosol layer on July 5th, at altitudes between approximately 2 and 5 km, with a maximum at about 4.5 km. It was identified as a dust layer, based on the air-mass backtrajectory was calculated to find the corresponding aerosol source region. Selected vertical profiles of the aerosol backscattering coefficient, and of the corresponding profiles of dust mass concentration obtained from DREAM model simulations, are presented in Figure 3. It should be noted that their comparison is only qualitative as we did not attempt to calculate the backscattering coefficient from the DREAM model results due to its high sensitivity to aerosol chemistry. The averaging of LIDAR signals for the analysis of the presented data was performed in 30minute intervals centered at the time of the model result. The dust layer boundaries were determined following the procedure described by Mona et al. (2006). The backscattering

coefficients showed that the layer descended during the course of the dust episode, and indicated an entrainment of dust into the PBL on July 7th. Dust mass concentrations resulting from the DREAM model showed a similar vertical pattern as the LIDAR measurements and a notable increase of dust concentration at altitudes below 2 km on July 7th.

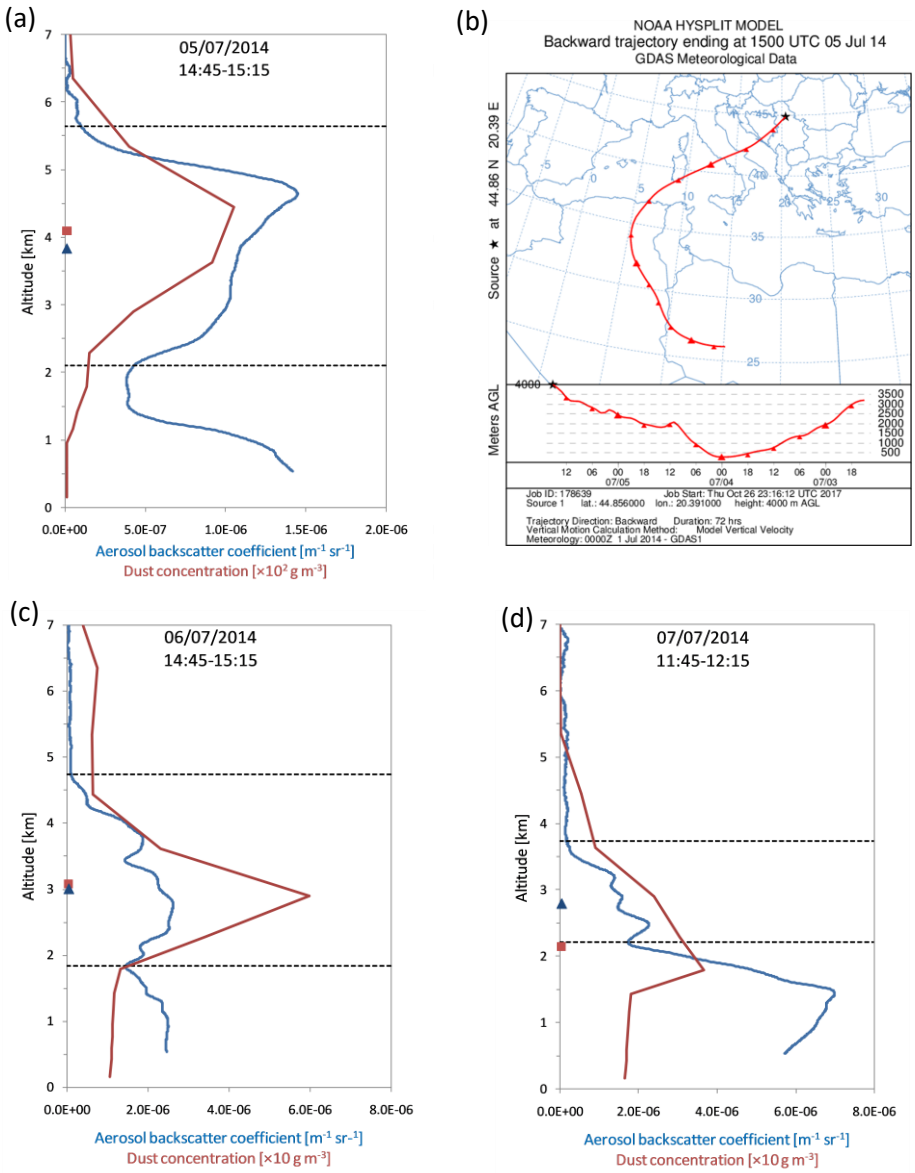

Figure 3. *(a, c, d) Vertical profile of aerosol backscattering coefficient from LIDAR measurements in Belgrade (blue line) and the corresponding profile of dust concentration from the DREAM model (red line); horizontal lines indicate dust layer base and top, while symbols show the positions of the dust layer's center of mass as calculated from LIDAR measurements and the DREAM model (b) 72hour airmass backtrajectory arriving at a 4 km altitude over Belgrade on July 5, 2014, at 15 UTC (corresponding to profile (a)).*

Figure 3 also shows altitudes of the dust layer center of mass, based on LIDAR measurements and the DREAM model. In the case of LIDAR measurements, it was calculated as a backscattering-coefficient-weighted altitude, according to:

$$z_c = \frac{\int_{z_b}^{z_t} z \cdot \beta(z) dz}{\int_{z_b}^{z_t} \beta(z) dz}$$

where z_b and z_t are the altitudes of the base and the top of the dust layer and $\beta(z)$ is the aerosol backscattering coefficient at altitude z. To minimize the effect of anthropogenic pollution, the center of mass from the LIDAR measurements was calculated only for the elevated layer. The dust's centre of mass from the DREAM model was calculated taking into account the entire dust profile.

Daily mass concentration of PM_{10} at ground level showed a similar trend at three air quality monitoring stations in Belgrade, with an increase during the dust episode (Figure 4). The increase started on July 6th, and the maximum was reached on July 7th, exceeding the 95th percentile of the summer (June, July and August) 2014 values. However, the daily limit value of 50 μg m^{-3}, set by the EU Air Quality Directive 2008/50/EC, was not exceeded. The increase of PM_{10} concentration is in agreement with the results of the LIDAR measurements, and the DREAM model, which indicated a settling of the dust plume (as shown in Figure 3). For comparison, daily average dust mass concentrations at the surface, obtained from the DREAM model, are also shown in Figure 4. They showed a similar trend as measured PM_{10} concentrations, increasing by 11 μg m^{-3} during the dust episode, while measured PM_{10} increased by 15 to 17 μg m^{-3} at the three monitoring stations. Larger measured PM_{10} concentrations, compared to surface dust concentrations from the model, were attributed to sources other than mineral dust.

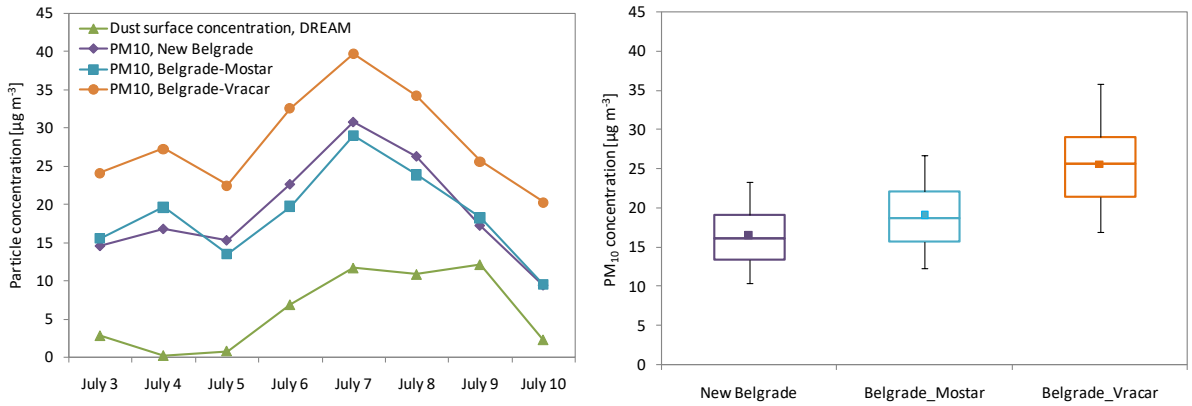

Figure 4. *(left panel) Daily average dust surface concentration values from the DREAM model and PM_{10} concentrations from three air quality monitoring stations in Belgrade. (right panel) Boxplot of PM_{10} concentrations during summer (June, July, August) of 2014 at three monitoring stations in Belgrade; the extent of the box indicates the 25th and 75th percentiles, the central line represents the median value, while the whiskers indicate the 5th and 95th percentiles; the points represent the mean values.*

CONCLUSION

We present analysis of a dust intrusion episode that was observed over Belgrade on July 5-7, 2014. The satellite measurements showed that the dust plume extended to western and central Europe. A distinctly elevated dust layer, extending at altitudes of approximately 2-5 km, was observed on July 5th using ground-based LIDAR in Belgrade. The layer altitude decreased during the dust episode, with the centre of mass altitude decreasing from approximately 4 km to below 3 km. The LIDAR measurements indicated entrainment of dust into the PBL on July 7th, the last day of the episode. The vertical distribution of dust and its temporal evolution over Belgrade was reproduced well by the DREAM model. The observed daily PM_{10} concentrations at three monitoring stations in Belgrade showed an increase of 15-17 μg m^{-3}, while dust was settling down during the episode as indicated by LIDAR measurements. Dust surface concentrations obtained from the DREAM model showed the same trend as measured PM_{10} concentrations, with a smaller increase (11 μg m^{-3}), during the episode: This difference was attributed to the contribution of other aerosol types to the observed PM_{10} concentrations.

ACKNOWLEDGEMENTS

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model and READY website (http://www.ready.noaa.gov), used in this publication. Analyses and visualizations of MODIS data used in this study were produced with the Giovanni online data system, developed and maintained by the NASA GES DISC. CALIPSO data were obtained from the NASA Langley Research Center Atmospheric Science Data Center.

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5.4. RELATIVE IMPORTANCE OF GASEOUS POLLUTANTS AND AEROSOL CONSTITUENTS FOR IDENTIFICATION OF PM_{10} SOURCES OF VARIABILITY

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ABSTRACT

This study combines advanced statistical methods including time series decomposition, source apportionment and supervised learning algorithms, to identify the main sources of particulate matter (PM_{10}) variability in an urban area within Belgrade. The analyses indicated that the season, (i.e., meteorological conditions) strongly influenced daily and annual PM_{10} variations particularly during the colder part of the year. A guided regularized random forest model estimated that As, Cd, BaP, CO, and benzene have the highest relative importance for the prediction of PM_{10}. Polar plot source apportionment revealed common sources of pollution at specific directions. Specifically, emissions of PM_{10}, CO and benzene could be attributed to heating and gasification processes, while processes in oil refineries and chemical industries produced PM_{10} and toluene.

INTRODUCTION

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 worldwide air quality regulation (Fuzzi et al, 2015, Stanišić Stojić et al, 2016). Even though significant progress has been made through the integration of different scientific approaches, modelling of air pollution data remains a challenge due to the complexity and non-linear nature of atmospheric phenomena and processes (Pai et al, 2013). During the last decade, poor air quality in Belgrade, with many PM_{10} limit value exceedances (Directive 2008/50/EC), has been identified as an important environmental risk factor (Perišić et al, 2015, 2017). Identification of factors affecting PM_{10} concentration variability could provide better insight into the aerosol spatiotemporal distribution and source composition, revealing their dominant sources in an urban area (Stojić et al, 2016).

Apart from the commonly used methods for data analysis, this study adopts the advanced statistical classifier, guided regularized random forest (GRRF), widely applied in many fields for feature selection. Moreover, the study demonstrates the possibilities of source apportionment analysis, which combines correlation and regression statistics with the bivariate polar plot analysis, to offer considerably more insight into air pollution sources.

METHODOLOGY

The analysed dataset, comprised of daily PM_{10} and its constituent concentrations (As, Cd, Cr, Mn, Ni, Pb, BaP, Cl^-, NO_3^-, NH_4^+, SO_4^{2-}, Na^+, K^+, Mg^{2+} and Ca^{2+}), and hourly PM_{10} and gaseous pollutant concentrations (CO, SO_2, NO, NO_2, NO_x, benzene, toluene, o- and m, p xylene) have been obtained from an Institute of Public Health regular monitoring station located within an urban area in Belgrade (Longitude 20.470, Latitude 44.817) from 2011 - 2016. The time series of PM_{10} concentrations was resolved into the additive components of the multi-year and seasonal trends, as well as the remainders using the Loess smoothing decomposition model (LSD) (Li et al, 2014). Daily, weekly and seasonal periodicity was analyzed by the use of Lomb-Scargle periodogram (*Lomb* package within the statistical software environment *R*) (Ruf, 1999; Team, 2014). Bivariate polar plot analysis was used for identification of the main PM_{10} emission sources (Carslaw and Ropkins, 2012), while the advanced bivariate polar plots, coupled with pair-wise statistics, were applied to distinguish specific sources and to gain information about pollutant relationships. The model includes a weighted Pearson correlation, linear regression slope and Gaussian kernel to locally weight the statistical calculations on a wind speed-direction surface together with variable-scaling (Grange et al, 2016). Feature selection was implemented using a GRRF ensemble learning method (Deng and Runger, 2013). GRRF can select compact feature subsets revealing higher order variable interactions, thus moderating the problem of dimensionality and avoiding the effort to analyze irrelevant or redundant features.

RESULTS AND DISCUSSION

Annual concentrations of PM_{10} and BaP exceeded prescribed limit values of 50 μg m^{-3} and 1 ng m^{-3}, respectively (Directive 2000/69/EC, Directive 2008/50/EC) every year of the period examined. The most abundant aerosol constituents were Cr, Pb and Mn (Figure 1), while SO_4^{2-} and NO_3^- were the ions with the highest concentrations.

In an urban area, the dominance of sulfate and nitrate ions is related to fossil fuel burning and traffic exhaust emission of SO_2 and NO_x, which, in the presence of water, transform into these ions. In addition, NH_4^+ and Ca^{2+} cations are usually presented as neutralizing agents for SO_4^{2-} and NO_3^- in heterogeneous atmospheric chemical reactions.

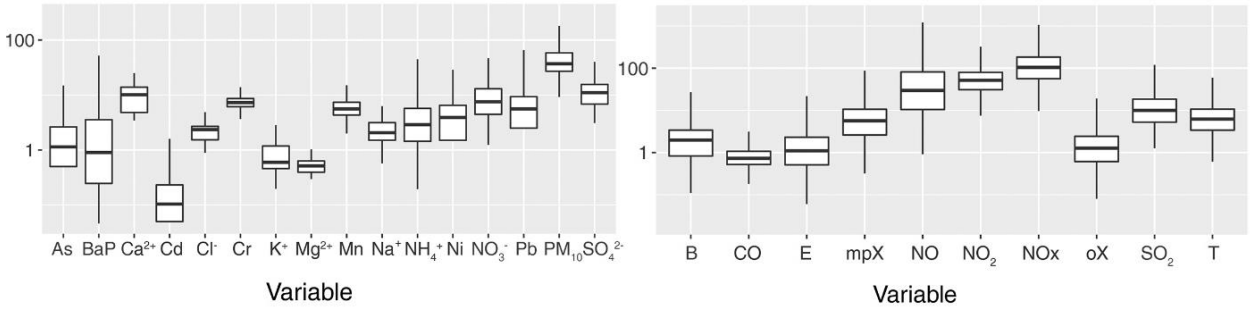

Figure 1. *PM_{10} concentration [µg m^{-3}], its chemical constituent (ions and BaP [µg m^{-3}], metals [ng m^{-3}]) (left) and gaseous pollutant [µg m^{-3}] (right) whisker plots*

Spectral analysis (Figure 2, left) reveals the highest normalized power values are attributed to the periods of 12 and 24 h, 7 days, and 1 and 3 months. This implies that meteorological conditions and anthropogenic emissions are strongly affected by aerosol daily and seasonal variations, and weekly periodicity, respectively (Bigi, 2016).

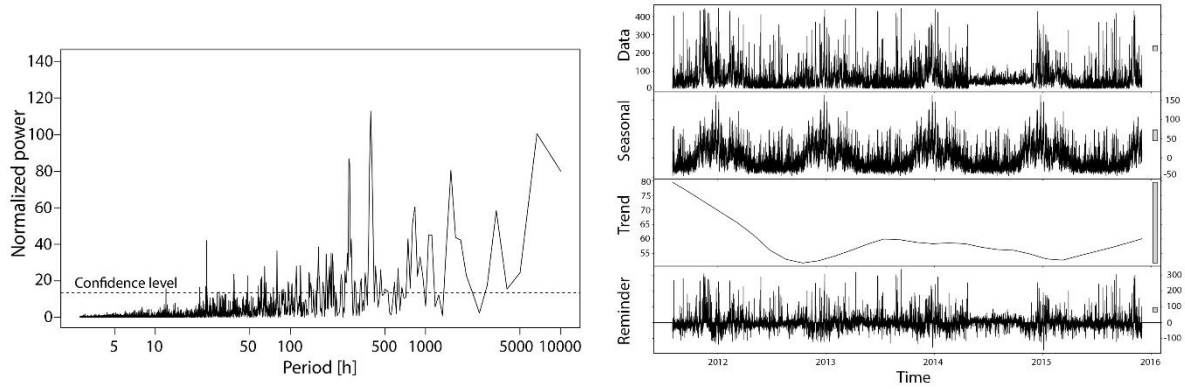

Figure 2. *PM_{10} Lomb-Scargle periodogram (left) and PM_{10} time series decomposition [µg m^{-3}] (right)*

Decomposed PM_{10} time series indicates a decreasing multi-year trend and significant impact of the seasonal component. Large variance of the remainder component possibly occurs as a result of short-term air pollution episodes (Figure 2, right). The conventional bivariate polar plot approach reveals the pronounced influence of both local and remote sources on PM_{10} variability (Figure 3).

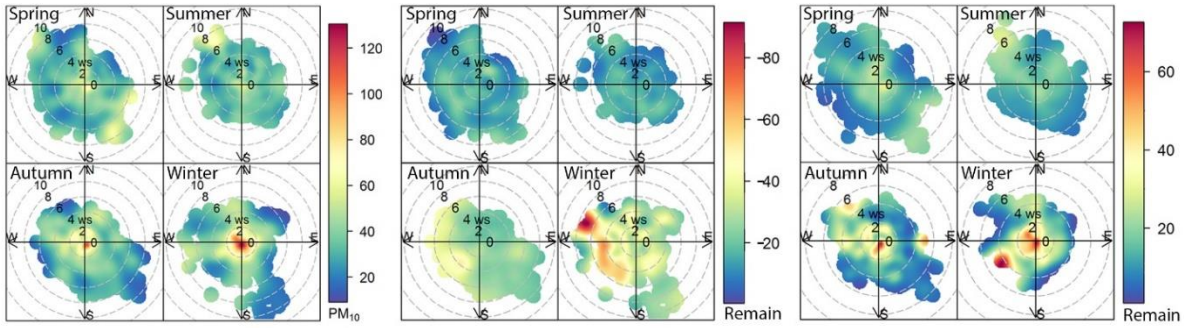

Figure 3. *Bivariate polar plot of PM_{10} concentrations (left) and its remainder components: negative (middle) and positive (right) [µg m^{-3}]*

Bivariate polar plot analysis of the remainder component, separately applied on positive and negative values, confirms that the episodes of the highest variations mainly occur during the colder part of the year. Positive variations related to SW and negative related to NW winds with speeds greater than 6 m s^{-1}.

The highest Pearson's correlation coefficients were obtained between concentrations of PM_{10} and its constituents (BaP (0.83), As (0.81), Cd (0.79) and Pb (0.66)), as well as for the gaseous pollutants: CO (0.56), benzene (0.46), NO (0.35), and NO_x (0.35). Similarly, the GRRF estimated the highest relative importance of As, Cd, BaP, CO and benzene for the prediction of PM_{10}, indicating that the environmental burden is mainly associated with fossil fuel combustion, particularly pronounced during the colder part of the year. An inconsistency between the correlation and GRRF analysis was observed for toluene. This compound had a higher importance for PM_{10} prediction than NO_x, but its correlation coefficient was among the lowest (0.25).

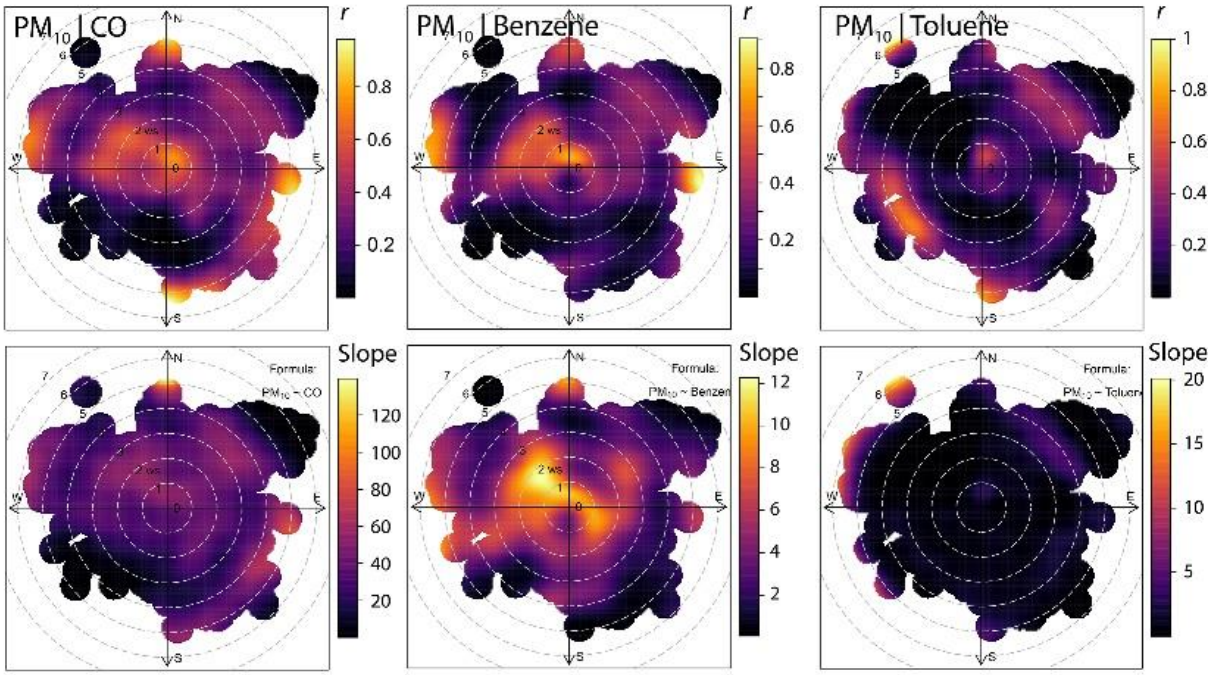

Figure 4. *Bivariate polar source apportionment*

Even though Pearson's coefficients did not indicate a significant correlation between PM_{10} and gaseous pollutants ($r < 0.6$), the bivariate polar source apportionment (Figure 4) showed that during episodes of north-westerly winds, concentrations of PM_{10} and benzene and CO were more correlated ($r \approx 0.7$) probably because of several common sources in the vicinity of the sampling site. Source composition obtained from slope diagrams reveals a 1:0.1 and 1:12 contribution of PM_{10}, CO and benzene, respectively. This could be associated with various biomass combustion processes (traffic activities, heating plants and individual heating units) (Yokelson et al, 2007). Besides the vicinity of the sampling site, particulate matter and toluene shared prominent sources located in the SW, S, NE and SE directions ($r > 0.8$, wind speed > 4 m s-1). Unlike southern and western sources, characterized by PM_{10} to toluene ratio of 1:1 which could be related to mineral oil and gas refineries, the source located on the north-east is characterized by the ratio of 1:6 indicating influences from the chemical industry, and chemical installations for production, on an industrial scale, of basic organic chemicals including aromatic hydrocarbons (European Commission, 2006).

CONCLUSIONS

Due to the pronounced nonlinearity and complexity of atmospheric processes in the troposphere of an urban environment, the application of multivariate and nonlinear methods is required to gain reliable information for a better understanding of the underlying factors which determine the air pollution phenomena. Methods such as feature selection based on advanced supervised learning algorithms, advanced source apportionment techniques and time series decomposition and detailed component analysis, are capable of providing this information, particularly for characterization of variable pollution sources. Summarizing this study, it has been shown that

locally emitted and transported pollution, as well as meteorological factors, have the highest impact on urban air quality.

ACKNOWLEDGMENTS

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6. POSTER SESSION

6.1. MULTISCALE MULTIFRACTAL ANALYSIS OF NONLINEARITY IN PARTICULATE MATTER TIME SERIES

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ABSTRACT

In this study the multiscale multifractal method was used with aim of capturing the fractal behaviour of the particulate matter time series obtained from an urban area in Belgrade, Serbia, as well as investigating their persistence properties and heterogeneity features. As shown, the $PM_{2.5}$ time series exhibited persistency, slightly affected by the concentrations occurring randomly only at the level of small fluctuations and small scales. Compared to $PM_{2.5}$, PM_{10} concentrations were shown to display more stochastic behaviour with more frequent random fluctuations being observed at small scales. The results herein presented contribute to the current understanding of the structural complexity of the temporal evolution of particulate matter and provide a theoretical background for enhanced air pollution modelling.

INTRODUCTION

Comprehensive analyses, conducted over the past few years, of air pollutant emission sources, their subsequent distribution and relationship to mortality caused by circulatory, respiratory and malignant diseases suggest that the exposure to particulate matter (PM) has detrimental effects on human health in the Belgrade area (Stanišić Stojić et al, 2016a, 2016b). Besides the fact that PM levels in Serbia are higher than in most European cities, with a significant number of air quality standard exceedances, our studies have shown that suspended particles also contain high concentrations of carcinogenic contaminants, such as arsenic and benzo(a)pyrene (Stojić et al, 2015a, 2015b, 2016, Perišić et al, 2015, 2017).

Diverse methods have been implemented to provide relevant information for efficient air quality management, including deterministic models, statistical analysis, neural networks, fuzzy models, geographic information system, remote sensing and trend analysis (Yu et al, 2011). Multifractality is one of the inherent properties that can be recognized in physical, chemical, biological, social and other systems, that are described as very complex at different spatial and temporal scale levels (Glushkov et al, 2014). The atmosphere is a complex system that exhibits nonlinear behavior involving both deterministic and stochastic components (Lorenz and Haman, 1996). In previous studies, the multifractal approach has been applied to analyse average ozone concentrations (Kocak et al, 2000), nonlinearity in NO_2 and CO time series (Kumar et al, 2008) and the daily air pollution index (Sivakumar et al, 2007). The aim was to provide information essential to better understand the behaviour of pollution and to forecast the temporal evolution of the species (Dong et al, 2017). The multifractal method was used herein to reveal PM fluctuation properties, *i.e.* to investigate to what extent, and on which time scale, changes in $PM_{2.5}$ and PM_{10} concentration levels can be considered random or persistent.

METHODOLOGY

In this study, multiscale multifractal analysis (MMA) was used to investigate the presence of fractal behaviour in the complex time series of $PM_{2.5}$ and PM_{10} concentrations. Data was obtained during a period of almost three years (2012-2014) of regular pollutant monitoring in Belgrade (suburban site Ovča, Longitude 20.528, Latitude 44.884, Serbia) provided by the Institute of Public Health Belgrade. MMA is a generalization of the standard multifractal detrended fluctuation analysis (MF-DFA), 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).

RESULTS AND DISCUSSION

Measured PM concentrations are presented in Figure 1. According to the results, multiscale multifractal derived Hurst surfaces confirmed the non-linear behavior of PM time series (Figure 2).

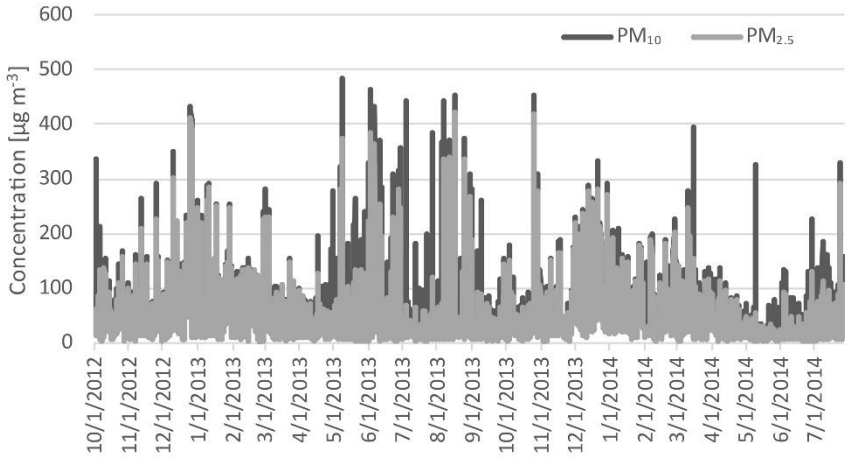

***Figure 1**. Measured $PM_{2.5}$ and PM_{10} concentrations.*

For most of the scale and multifractal parameter values, the local Hurst exponent remains in the interval between 1 and 1.5 indicating persistency of the $PM_{2.5}$ time series, while slightly affected by the concentrations occurring randomly. Such random concentration values occur only at the level of small fluctuations for scales below 44, which corresponds to a period of about 2 days. At this scale, there emerges a clear crossover resulting from the different correlation properties. Given that the sampling site was not directly exposed to intense PM bursts, the occurrence of concentrations in narrow bands (Hurst exponent equals 2) was not recorded. The PM_{10} Hurst surface reveals similar features, except that in the area of small variance and scales below 90, its growth to a maximum of approximately 1.9 is steeper, almost reaching black noise area values of local Hurst exponent. Compared to $PM_{2.5}$, the PM_{10} Hurst structure around its maximum corresponds to visibly more pronounced peaks in the time series (Figure 1). However, unlike $PM_{2.5}$, the PM_{10} Hurst surface shows no crossover.

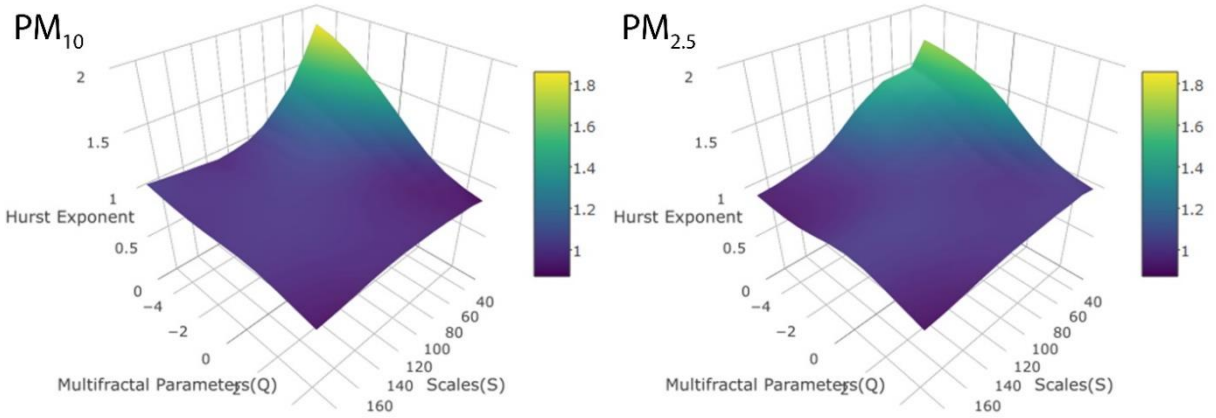

***Figure 2**. MMA derived particulate matter Hurst surfaces.*

In addition, the generalized distance coefficient (0.069) between Hurst surfaces of PM fractions is higher than the threshold value (0.065) and implies that the $PM_{2.5}$ and PM_{10} time series must be considered statistically different. The difference is particularly pronounced in the area of small fluctuations and medium scales (Figure 3).

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 (Figure 4).

The findings of Lalwani (2016) and Liu et al. (2015) confirmed the existence of multifractality in the PM time series and found that daily pollutant concentrations exhibited high persistence in a period of approximately one

year. As argued, the persistence in the air pollutant concentrations over longer period of time may be governed by the impact of background levels, seasonal trend or intrinsic evolution of the system.

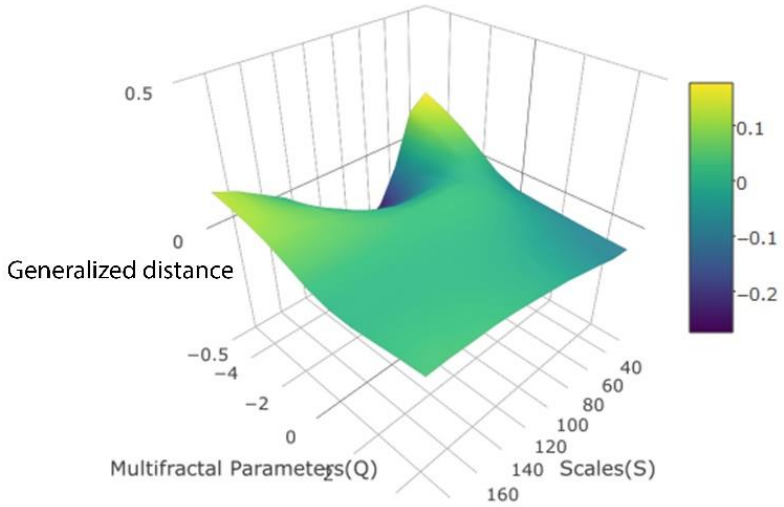

***Figure 3**. Generalized PM_{10}/$PM_{2.5}$ Hurst surface distance.*

The difference in the behavior of the $PM_{2.5}$ and PM_{10} time series was proven by Xue et al. (2015), who employed a multifractal analysis to explore temporal fluctuations and self-similarities within the PM time series and to understand their behaviour associated with diffusion, spreading and coagulation processes. Using the multifractal detrended fluctuation analysis method, the researchers registered the pronounced multifractality and long-term persistence of the $PM_{2.5}$ time-series, whereas the PM_{10} time series were shown to have stochastic behaviour.

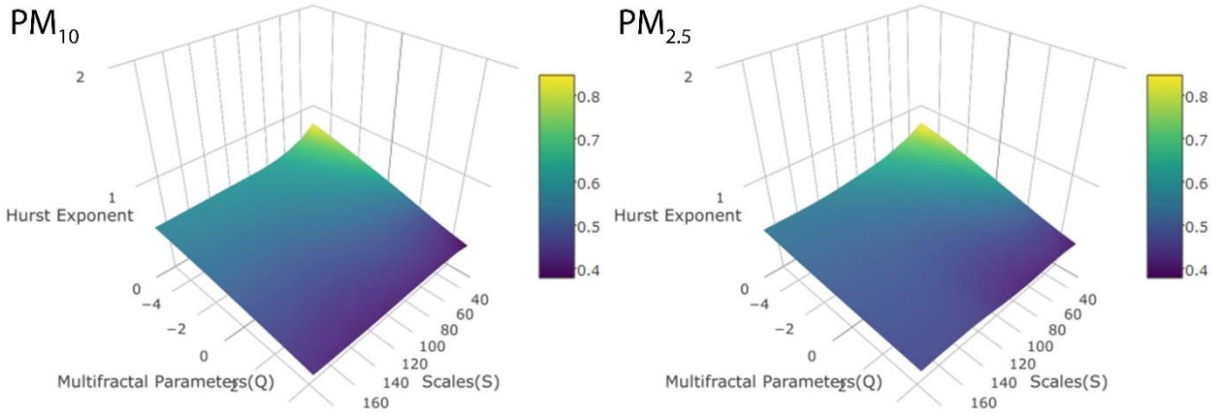

***Figure 4**. MMA derived Hurst surfaces for randomized PM time series.*

CONCLUSIONS

In this study, the multifractal approach was used to analyse the temporal dynamics of $PM_{2.5}$ and PM_{10} concentrations on the basis of a regular monitoring of data over a three-year period. As shown, the particulate matter time series possess a long-term memory of distant past events and require a large number of exponents, the so-called fractal dimensions, to be described. The presented analysis provides essential information for better understanding of the PM behaviour and the underlying factors, as well as for more accurate and reliable pollutant forecasting and efficient mitigation policy.

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6.2. MODELING OF PM_{10} DISPERSION FROM COAL THERMAL POWER PLANTS KOSTOLAC A AND B

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ABSTRACT

Serbian electricity production is predominantly based on coal power plants, which produce large sources of particle matter emissions. Modeling of PM_{10} dispersion from the combustion process of thermal power plants Kostolac A and B (TEKO A and TEKO B) is performed in order to examine the impact of the newly built TEKO B's Flue Gas Desulphurization (FGD) units, and the results are presented in this paper. Two scenarios are discussed within this study, "without FGD" and "with FGD". The AERMOD dispersion model, with hourly meteorological data (five years in row) from a representative measuring station, is used as modeling tool. Despite the large reduction in emission values of TEKO B after installation of the FGD system, the results achieved indicate that the FGD has had no significant impact on air quality in the observed domain, due to dominant influence of TEKO A and characteristics of TEKO B stack/s.

INTRODUCTION

Serbian electricity production is predominantly based on coal power plants, which produce large sources of particle matter emissions. All thermal power plants (TPP) are equipped with electrostatic precipitators (ESP), as a technique to reduce particulate emissions. Total emissions of PM in 2016 from all coal power plants in Serbia were 12.501,978 t (PE EPS, 2016), while TPP Kostolac A and B, with a current total installed capacity of 1000 MWe, had total emissions of 3.197,000 t (PE EPS, 2016). TPP Kostolac A consists of two units A1 (100 MWe) and A2 (210 MWe), while TPP Kostolac B has two equal units B1 and B2 (2x350 MWe). Despite high SO_2 emissions, these TPPs, as well all other TPPs in Serbia, have operated from the very beginning of their operational time without Flue Gas Desulphurization (FGD) systems. According to environmental standards and prescribed domestic and EU legislation, the installation of FGD systems in Serbian TPPs has started, and the first FGD system has been installed at Kostolac B. The term Flue Gas Desulphurization (FGD) system has traditionally referred to wet scrubbers that remove SO_2 emissions from large electric utility boilers. The FGD systems emerged in the industrial field of the coal-fired power plants and in some industrial processes in the early 1970s in the United States (US) and Japan, and expanded rapidly in the 1980s into Europe (Córdoba, 2015). The installed FGD system at TPP Kostolac B is a wet scrubber, limestone-gypsum process (Figure 1.).

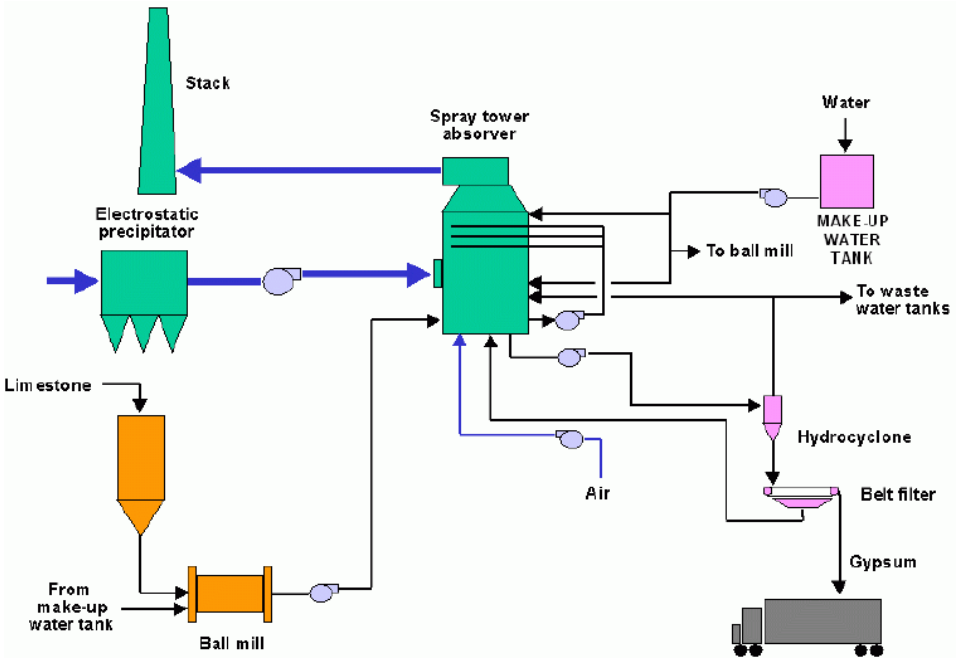

Figure 1. *Schematic flow diagram of a lime/limestone wet scrubber FGD process (BREFs, 2016)*

Wet scrubbers, especially the limestone-gypsum process, are the leading FGD technologies. They have about 80% of the market share and are used in large utility boilers (BREFs, 2016). Despite the high efficiency of electrostatic precipitators (>90%), a small fraction of fly ash escapes and goes into the FGD system. Once in the FGD, fly ash components may be dissolved in the aqueous phase of the absorbent slurry or retained in the solid fraction (gypsum sludge). Fly ash not dissolved in the aqueous phase of the absorbent slurry may be retained in the solid fraction (gypsum sludge) and subsequently extracted from the system by the FGD-gypsum, and/or may firstly be retained in the solid fraction and subsequently entrained with the outgoing flue gas FGD (OUT-FGD) as PM (Córdoba, 2015). After a wet FGD, about 40% of the particulate loadings in the flue gases consist of fly ash, 10% of gypsum particles, while 50% originate from dissolved compounds left over after droplets are evaporated (Meij, 1994). In Europe, experiences with wet FGDs have indicated collection efficiencies of PM by wet FGDs 90%. In the Netherlands, after 1990, wet FGD systems were introduced as a result of which the particulate loads (PLs) were further reduced to <10 mg/m^3 (Córdoba, 2015).

Besides the installed FGD, the old 280 m height common stack for B1 and B2 units is replaced with two 180 m "wet stacks"[1]. Those plant modifications could influence air quality in a closer or wider area and should be examined with adequate tools. Dispersion modelling is a mathematical simulation of emissions as they are transported throughout the atmosphere. Dispersion models replicate atmospheric conditions, (which includes wind speed and direction, air temperature and mixing height), and provide an estimate of the concentration of pollutants as they travel away from an emission source.

In order to analyse the influence of modifications of TPP Kostolac B, the standard model of EPA (US Environmental Protection Agency) AERMOD is used, and modelling results are presented in this study.

METHODOLOGY

AERMOD, which is based on the Gaussian model, includes a wide range of possibilities for modelling the effects of released pollutants on ambient air quality. This model includes modeling of multiple sources of pollution including point, line, area and volume sources. The model contains algorithms for analyzing the aerodynamic flow in the vicinity of, and around, buildings (building downwash) (EPA, 2004). The Gaussian plume model uses a realistic description of dispersion, where it represents an analytical solution to the diffusion equation for idealized circumstances. The model assumes that the atmospheric turbulence is both stationary and homogeneous. In reality, none of these conditions is fully satisfied,however, the Gaussian plume model has been successfully used for rural configurations (Abdel-Rahman, 2008).

The Diffusion Equation and the Gaussian Plume Model

According to (Macdonald, 2003), by performing a mass balance on a small control volume, a simplified diffusion equation, which describes a continuous cloud of material dispersing in a turbulent flow, can be written as:

$$\frac{dC}{dt} + U\frac{dC}{dx} = \frac{d}{dy}\left(K_y \frac{dC}{dy}\right) + \frac{d}{dz}\left(K_z \frac{dC}{dz}\right) + S \qquad (1)$$

where:

x = along-wind coordinate measured in wind direction from the source,

y = crosswind coordinate direction,

z = vertical coordinate measured from the ground,

C (x, y, z) = mean concentration of diffusing substance at a point (x, y, z) [kg/m^3],

K_y, K_z = eddy diffusivities in the direction of the y- and z- axes [m^2/s],

U = mean wind velocity along the x-axis [m/s],

S = source/sink term [kg/m^3-s].

Equation (1) is grossly simplified, since several assumptions are made in its derivation. The Gaussian plume model, which is at the core of almost all regulatory dispersion models, is obtained from the analytical solution to Equation

[1] "Wet stack" implies special construction of the stack used in wet FGD systems, which allows that saturated gases exiting the system's absorber could be directly sent to the stack without reheating and drying.

(1). For a continuous point source released at the origin in a uniform (homogeneous) turbulent flow the solution to Equation (1), for an elevated plume released at z = H_p is:

$$C(\mathrm{x},\mathrm{y},\mathrm{z}) = \frac{Q}{2\pi U_p \sigma_y \sigma_z} \exp\left(\frac{-y^2}{\sigma_y}\right)\left[\exp\left(-\frac{\left(z-H_p\right)^2}{2{\sigma_z}^2}\right)+\exp\left(-\frac{\left(z+H_p\right)^2}{2{\sigma_z}^2}\right)\right] \qquad (2)$$

Schematic representation of the principle of dispersion of pollutants based on the Gaussian model is given in Figure 2.

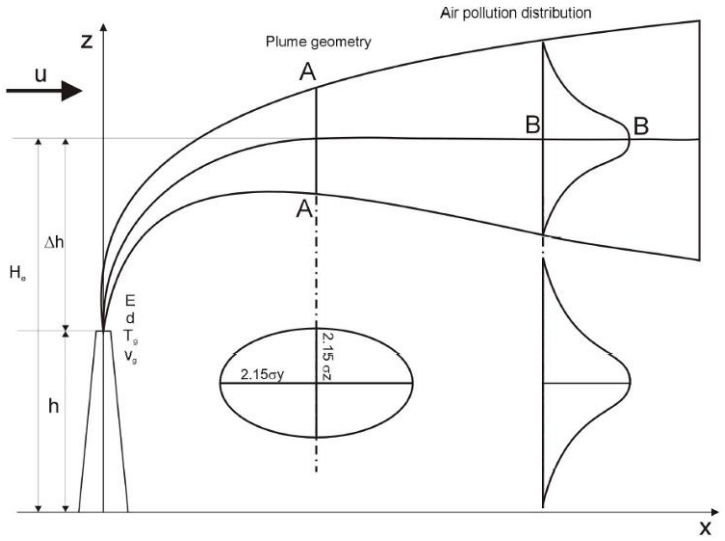

Figure 2. *A scheme of a Gaussian plume model (Markiewicz, 2006)*

Modeling approach

The results presented in this paper were obtained using a model which included the emissions of PM_{10} from the all units of TPP Kostolac A and B. The model included only the stacks of the mentioned units, while neither other sources of emissions, nor background concentrations were included. The focus of modeling presented in this paper is not to evaluate the overall air quality in the project area, but rather to present a representative assessment of the impact of FGD at TPP Kostolac B on air quality in the model domain.

The modeling procedure included the following steps: 1. Preparation of the facility plan, including sources and facilities; 2. Defining the modeling domain and the receptors' locations; 3. Developing source inventories and categorization of all considered sources; 4. Processing of required meteorological data; 5. Terrain data processing; 6. Modeling runs and analysis of the results. Based on the input parameters for all sources, emissions and meteorological data, modeling resulted in the spatial distribution of ground level concentrations of selected pollutants over the selected averaging periods of 24 hours and one-year averages.

Terrain data

A modeling domain of 50 km x 50 km (2500 km^2), with TPPs Kostolac in its centre was selected for this study. A Cartesian coordinate system with the distance of 400 m between adjacent points (receptors) is used, which implies that the models processed 15876 points (receptors). To obtain necessary terrain data, SRTM1 - Shuttle Radar Topography Mission data (resolution: ~ 30m, 1 arc-sec) was used (Figure 3).

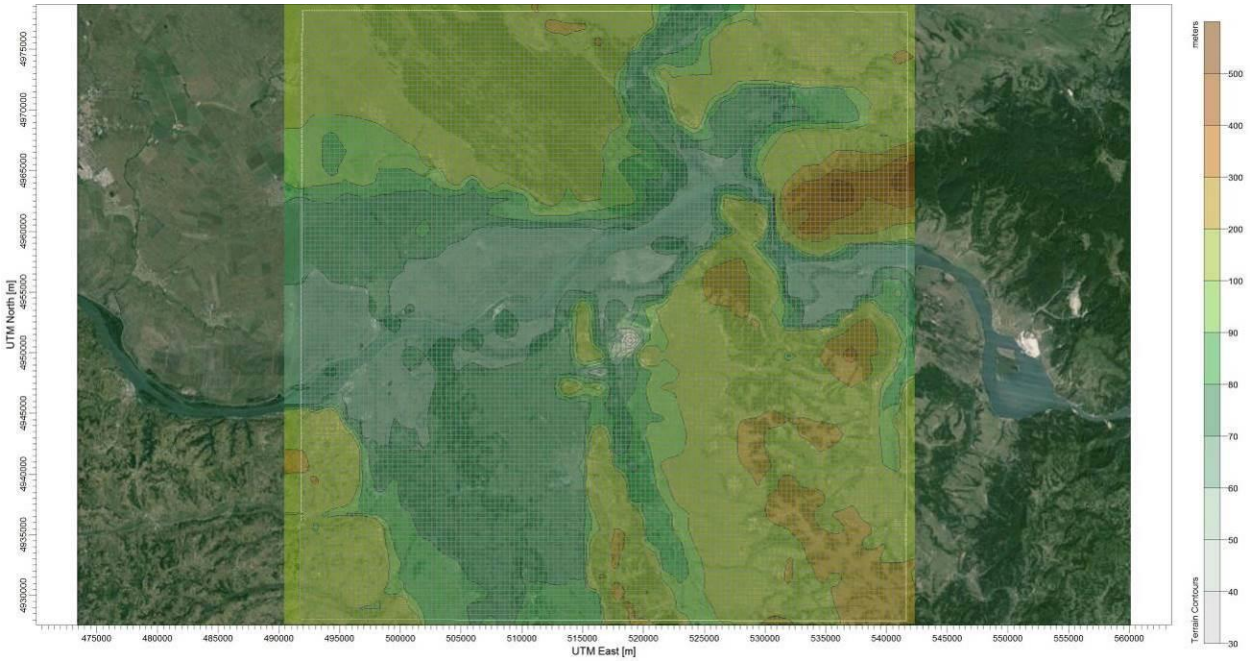

Figure 3. *Processed terrain elevation and Cartesian receptor grid at model domain*

Meteorology data

AERMET, a meteorological preprocessor, prepares hourly surface data and upper air data for use in AERMOD. The surface data are hourly observations of surface level parameters such as wind speed and direction, ambient temperature, and cloud cover that are used by AERMET to generate a surface file for use in AERMOD. The upper air data file provides information on the vertical profiles of atmospheric parameters. This includes the altitude, pressure, dry bulb temperature, and relative humidity (EPA, 2004). Meteorological data that are used for the preparation of model included hourly values of:

wind speed,

wind direction,

ambient temperature,

relative humidity,

atmospheric pressure,

cloud cover - opaque.

Since upper air data were not available, AERMET Upper Air Estimator is used. Hourly meteorological data for the period of 2010-2014 were obtained from the Republic Hydrometeorological Service of Serbia (RHMZ). The closest meteorological station to the power plants was *Veliko Gradište*, and the data from this station were used. Figure 4 demonstrates the wind rose (blowing from) and frequency analysis, based on meteorological data for the period of 2010-2014.

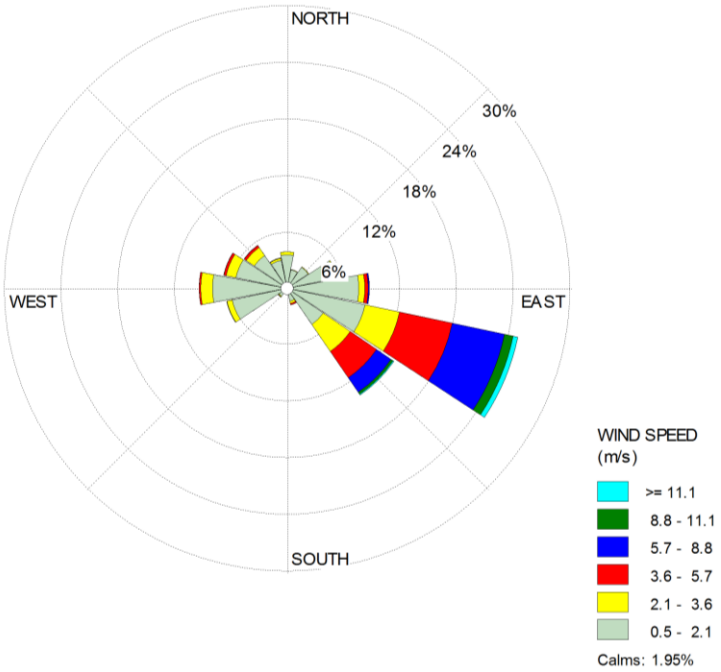

***Figure 4**. Wind rose and frequency analysis 2010-2014*

Based on the presented wind statistics (wind roses), it could be concluded that none of the observed years has shown significant differences and that the prevailing wind direction is from east-southeast followed by the southeast direction. This implies that most of the time, released pollutants will be dispersed towards the west-north-west and north-west from the source.

Sources characteristics

For the modeling process the following parameters have to be obtained either by measurements or by calculations so as to accurately characterize each of the emission sources:

- the type of pollutants,
- physical stack height,
- geographic coordinates of stack,
- diameter of the stack,
- the flow rate of flue gases through the stack,
- the temperature of flue gases exiting the stack,
- pollutant concentrations.

All sources characteristics presented in this paper are calculated.

Scenarios 1 and 2

Scenario 1 considers the current state of TPPs Kostolac A and B. In Scenario 2, work conditions at TPP Kostolac A remain the same as in Scenario 1, while TPP Kostolac B employs FGD and units B1 and B2 are connected to the double inner tube "wet stack" 180 m high, instead of one common 280 m height stack as is the case in Scenario 1. All modelling input data of TPPs Kostolac A and B units within the discussed Scenario 1 and Scenario 2 are presented in the tables below (Table 1 and Table 2).

***Table 1.** Scenario 1 (without FGD) - Work parameters of units*

Parameter	Unit A1	Unit A2	Unit B1-B2	Unit
Chimney Height	**105**	**110**	**250**	**[m]**
Chimney Diameter	**6.5**	**6.5**	**9.9**	**[m]**
Flue Gas Temp. at exit	**186.5**	**182.9**	**178.4**	**[℃]**
Flue Gas Flow (at work condition)	**1,391,690**	**2,079,056**	**6,270,480**	**[m^3/h]**
Mass Flow PM_{10}	**10.07**	**46.2**	**74.7**	**[g/s]**

Table 2. *Scenario 2 (with FGD) - Work parameters of units*

Parameter	Unit A1	Unit A2	Unit B1	Unit B2	Unit
Chimney Height	**105**	**110**	**180**	**180**	**[m]**
Chimney Diameter	**6.5**	**6.5**	**6.7**	**6.7**	**[m]**
Flue Gas Temp. at exit	**186.5**	**182.9**	**66.22**	**66.22**	**[℃]**
Flue Gas Flow (at work condition)	**1,391,690**	**2,079,056**	**2,509,640**	**2,509,640**	**[m^3/h]**
Mass Flow PM_{10}	**10.07**	**46.2**	**10.4**	**10.4**	**[g/s]**

As buildings could radically influence the dispersion of pollutants there is a need for building downwash analysis. Figures 5, 6 and 7, present 3D models, designed using AERMOD, with point sources (red stacks) of TPP Kostolac A and B. Beside point sources, 3D model includes possible significant buildings from the downwash effect perspective.

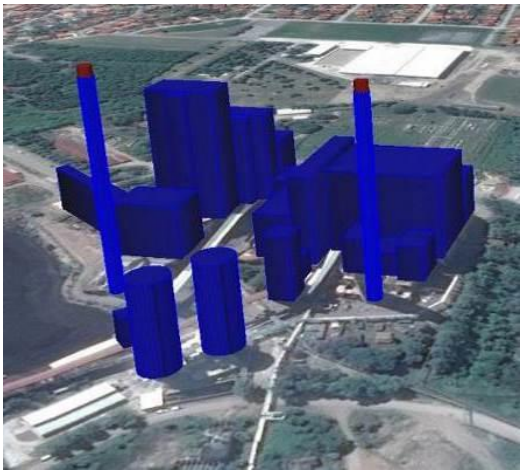

Figure 5. *3D model of TPP Kostolac A*

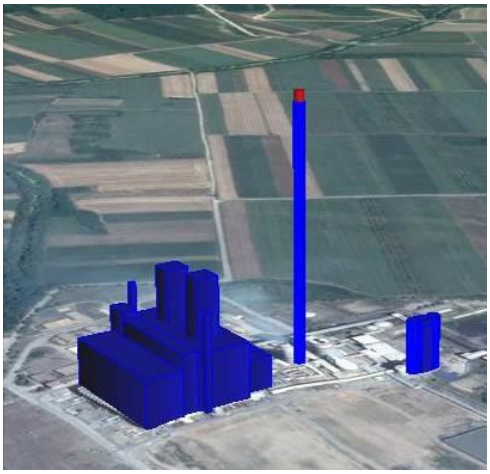

Figure 6. *3D model of TPP Kostolac B (Scenario 1)*

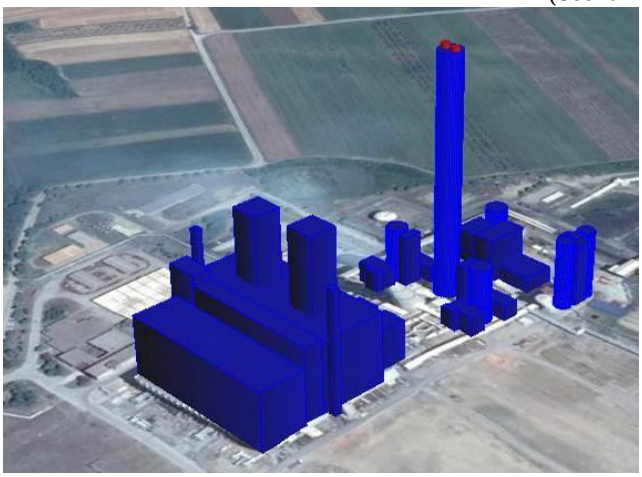

Figure 7. *3D model of TPP Kostolac B* (Scenario 2)

RESULTS AND DISCUSSION

Modeling prepared for this research, did not taken into account background pollution, so presented results (plots) do not represent air quality (PM_{10} concentration) in the model domain, but the contribution of the power plants Kostolac A and B, as a dominate stationary source of PM_{10}, to overall PM concentration at model domain. As well, modeling ha s not taken into consideration emissions of area sources of PM_{10} (ash dump). It is very important to

note that these models represent “the worst case” scenarios, by considering that all pollutant sources emit their maximum emission rate *24 hours* a *day, 365 days a year, which is certainly not the case.*

Besides decreased emissions caused by FGD installations, stack design could be very important for ground level concentration. Namely, stack height (H_s), top inside stack diameter (D), flue gas temperature (Ts), ambient temperature (Ta) and stack exit velocity (vs) define buoyancy flux (Equation (3)):

$$F = g v_s D^2 \frac{T_s - T_a}{4T_s} \ , \tag{3}$$

which directly influence plume rise (Δh) and effective stack height (H) (Equation (4)). So it is very important to set realistic stack and flue gas parameters as much as possible.

$$H = H_s + \Delta h \ . \tag{4}$$

As a result of modelling scenarios, the model provides textual and graphical plots, which include maximum and mean concentrations of PM_{10}, as presented in Figures 8-13. Apart from daily maxima, in accordance with National Air Quality Objectives, PM_{10} concentrations are presented as 90.40th of maximum concentrations for daily means and annual mean concentrations.

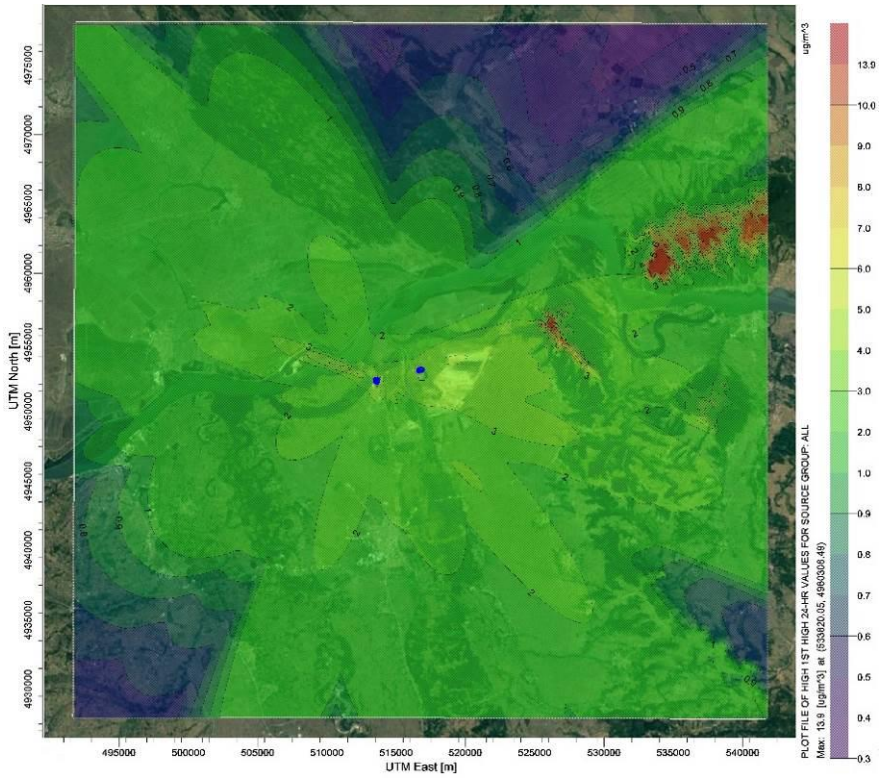

Figure 8. *Scenario 1 - Daily maximum concentration [g m^{-3}]*

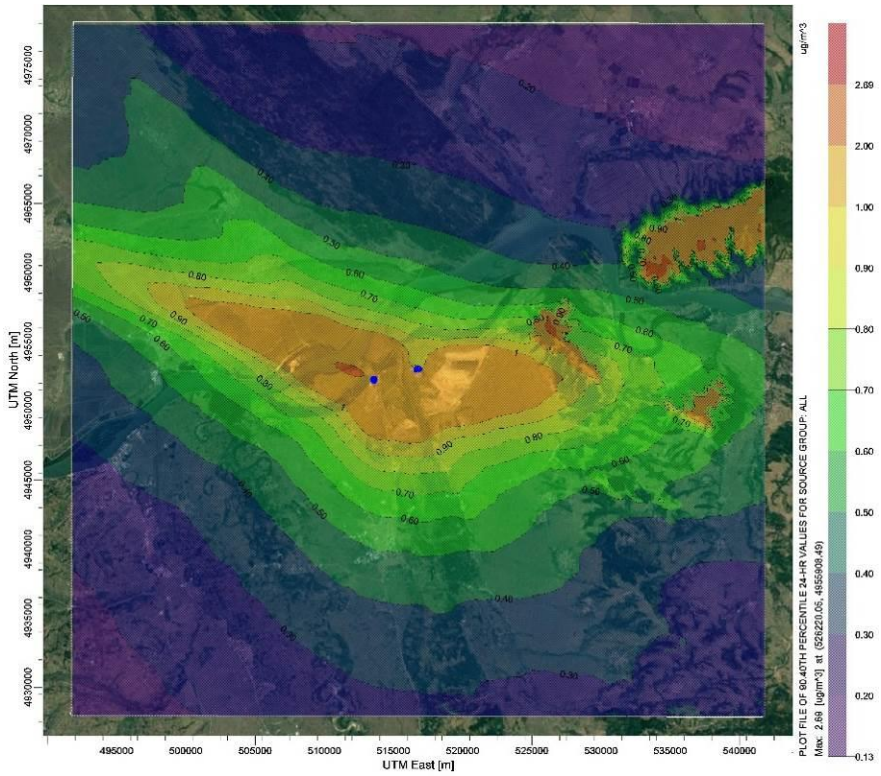

Figure 9. *Scenario 1 - 90.40th percentile of daily mean concentration [g m^{-3}]*

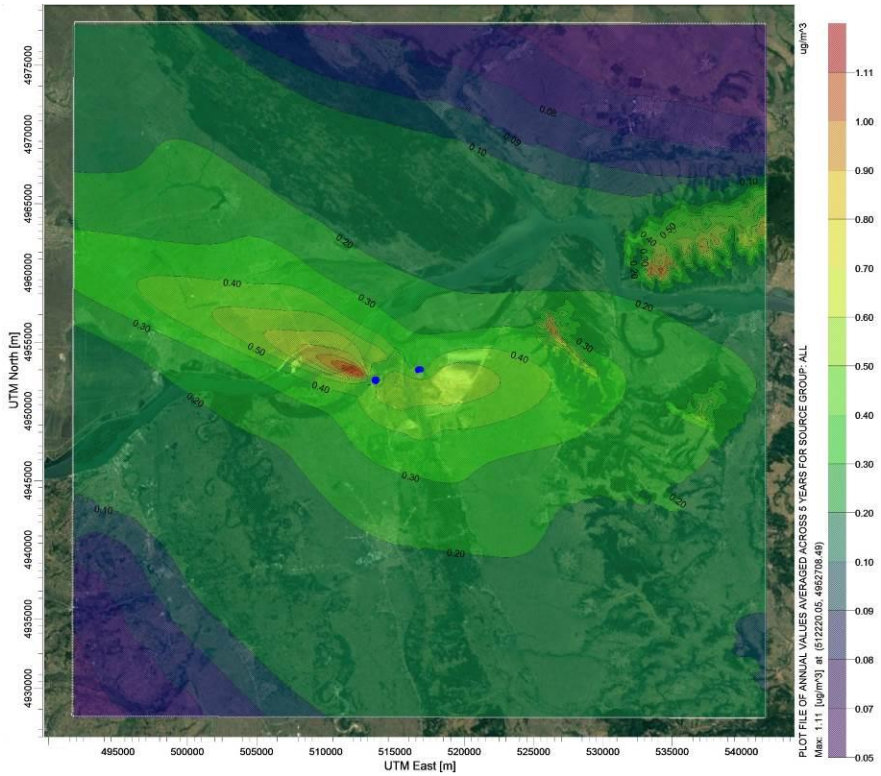

Figure 10. *Scenario 1 - Annual mean concentration [g m^{-3}]*

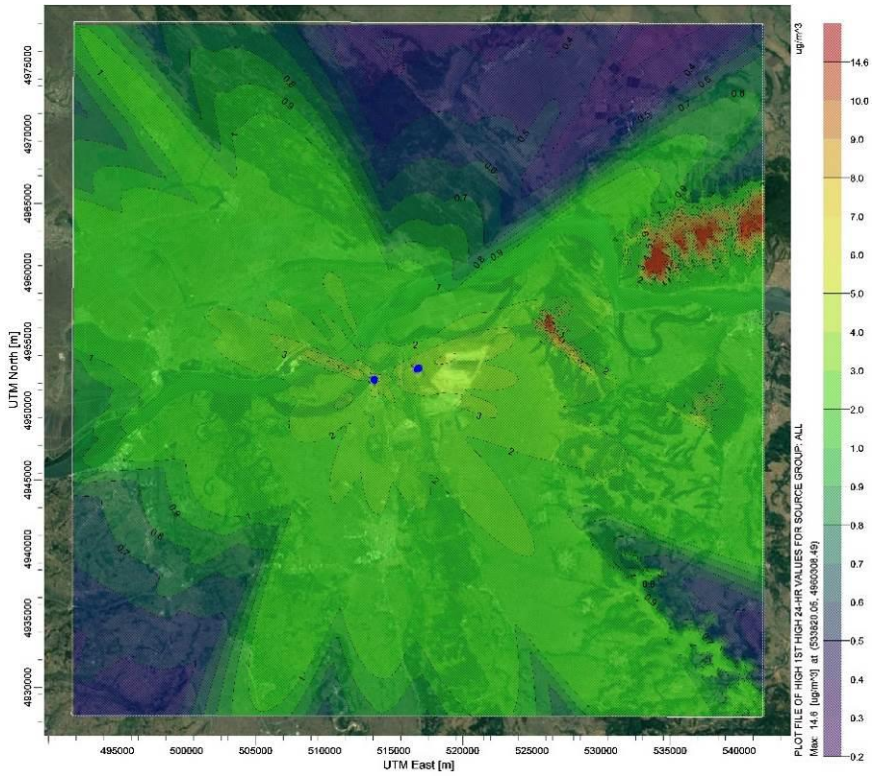

Figure 11. *Scenario 2 - Daily maximum concentration [g m^{-3}]*

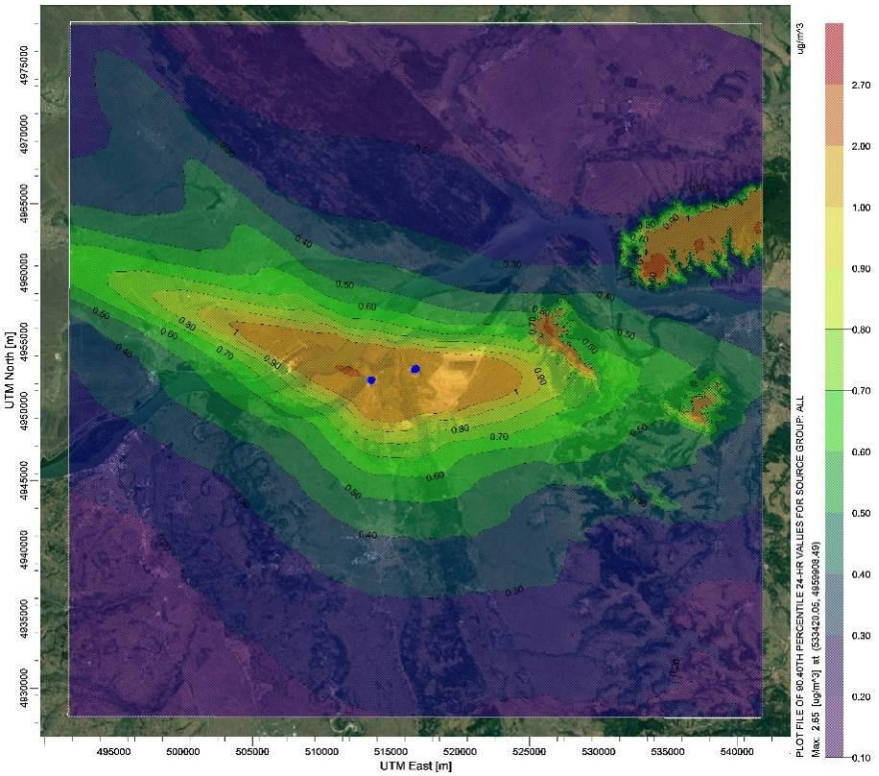

Figure 12. *Scenario 2 - 90.40th percentile of daily mean concentration [g m^{-3}]*

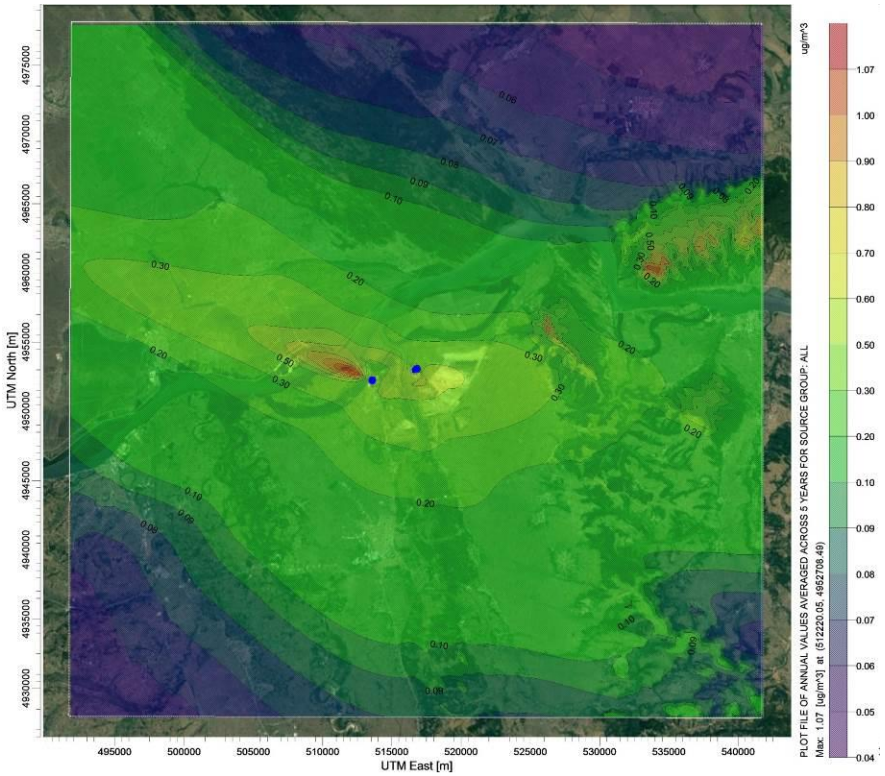

Figure 13. *Scenario 1 - Annual mean concentration [g m^{-3}]*

Modeling results indicate generally 3 locations where the highest concentrations of PM_{10} could be expected. Maximum concentrations at given plots for daily maximum and 90.40th percentile are located at the north-east of model domain. In addition to the source characteristics presented in Table 1 and 2, relief has dominant influence on ground level concentrations at the afore mentioned locations. Deposition of PM_{10} occurs since plume, which is influenced by meteorology conditions, is not able to overcome the complex terrain that is on its path. While annual concentrations are mainly influenced by meteorology (mainly wind direction) and certainly with source characteristics of TPP Kostolac A. Maximum ground level concentrations for both scenarios are presented in table 3.

Table 3. *Maximum ground level concentrations*

Max. concentrations	**Scenario 1 µg/m^3**	**Scenario 2 µg/m^3**
24h max	**13.91**	**14.61**
24h (90.40th percentile)	**2.69**	**2.64**
Annual mean	**1.11**	**1.07**

It is very important to note that maximum concentrations are observed at same locations for both scenarios. Based on the results presented on plots and given in Table 3 for both scenarios, it could be concluded that there is no significant influence of FGD on spatial dispersion of PM_{10}, neither on the expected maximum concentrations. It may indicate that TPP Kostolac A, which has the same characteristics for both scenarios, has a dominant influence on PM_{10} ground level concentration. In order to investigate that assumption, additional modeling is done only for TPP Kostolac A and the results are presented in *Figures 14-16.*

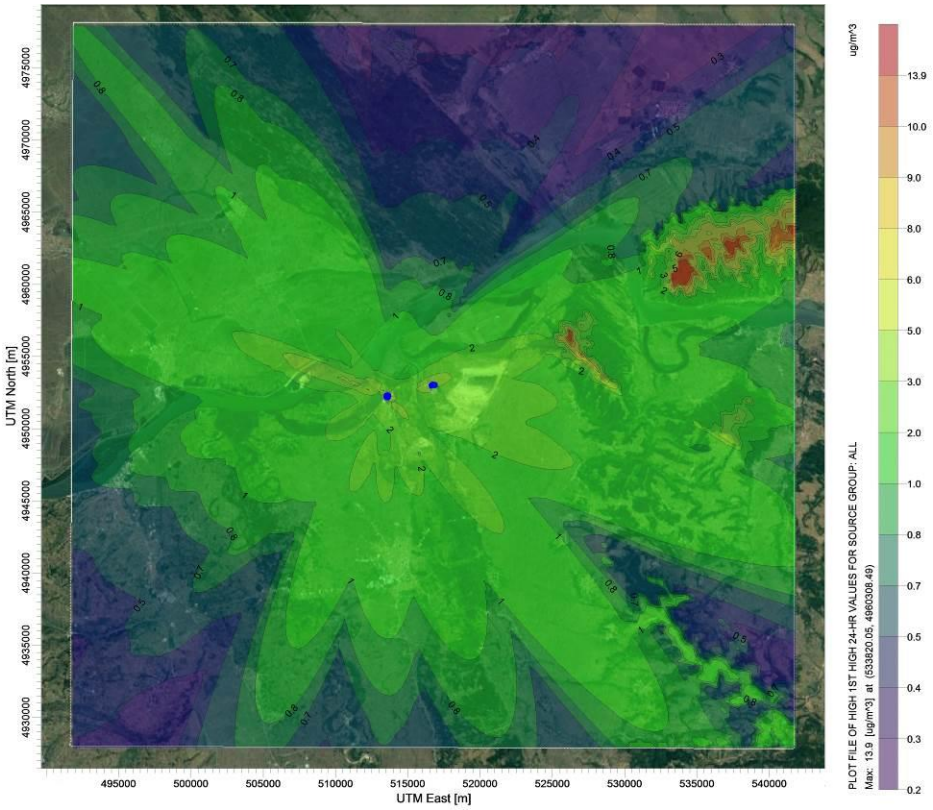

Figure 14. *TPP Kostolac A - Daily maximum concentration [g m^{-3}]*

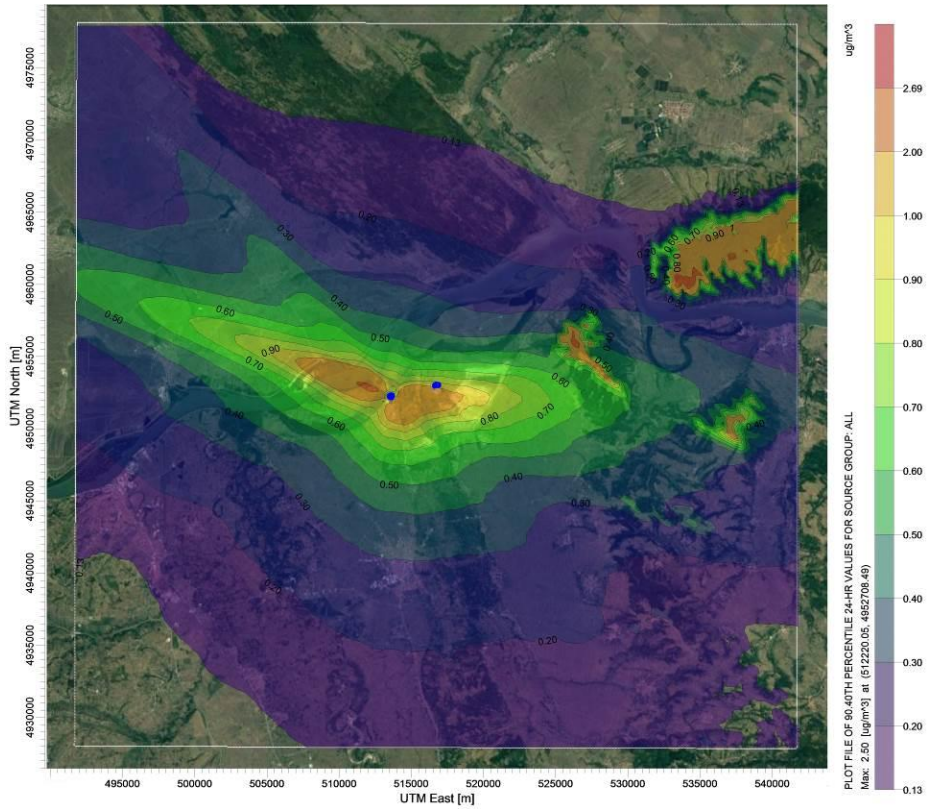

Figure 15. *TPP Kostolac A - 90.40th percentile of daily mean concentration [g m^{-3}]*

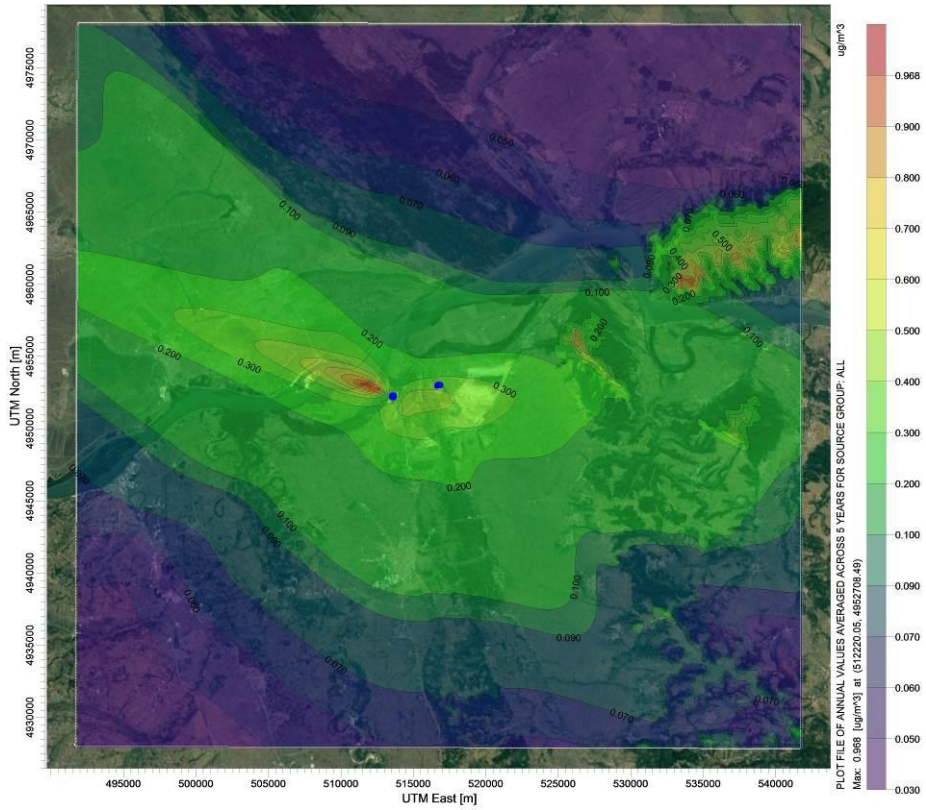

Figure 16. *TPP Kostolac A - Annual mean concentration [g m^{-3}]*

The results for TPP Kostolac A confirm the assumption that TPP Kostolac A has had a dominant influence on PM_{10} ground level concentration at model domain. Bearing in mind that meteorological and relief data are same for all scenarios, this result is directly connected to the height of TPP Kostolac A's stacks (105 m for Unit A1 and 110 m for Unit A2), respectively effective heights of TPP Kostolac A's stacks. While in the same manner it could be concluded that the effective heights of TPP Kostolac B's stacks provide an almost negligible influence of TPP Kostolac B on PM_{10} ground level concentration at model domain.

The effective heights of TPP Kostolac B's stacks are responsible for slightly higher concentration comparing Scenario 1 and Scenario 2 for daily maximum concentration (Table 3). Namely, the flue gas flow and mass flow of PM_{10} are significantly reduced for Scenario 2 as compared to Scenario 1, *stack height is reduced from 250 m to 180 m and flue gas temperature is decreased from 178,4* °C to 66,2 °C, which leads to a decreased effective height of TPP Kostolac B's stacks.

CONCLUSION

In order to investigate the influence of the newly built FGD system at TPP Kostolac B on ground level concentration of PM_{10}, this paper discussed 3 different modelling scenarios: modelingThe AERMOD dispersion model was used. Hourly meteorological data (5 years in row), from a representative measuring station, SRTM1 terrain data and deatiled source parameters were the primary inputs. Considering that these models' runs did not take into consideration background pollution, the results obtained by this modeling do not represent overall ambient air quality in the models' area, but only considered the contribution of TPP Kostolac A and B, as major PM_{10} source, to overall air quality, which gives the opportunity to make conclusions of FGD influence. Firstly, according to the presented results and based on the National Air Quality Objectives, ambient concentrations obtained as a result of all scenarios are below the prescribed regulatory limits. Maximum results in both scenarios are 14.61 g m^{-3} and 2.69 g m^{-3} for daily maximum concentration and 90.40th percentile of daily mean concentration, and 1.11 g m^{-3} for annual mean concentration, while National Air Quality Objectives gives 50 g m^{-3} for 90.40th percentile of daily mean concentration and 40 g m^{-3} for annual mean concentration. Further, based on additional modeling scenario, it is concluded that TPP Kostolac A has a dominant influence on PM_{10} ground-level concentration in the model

domain, due to effective heights of the stacks (105 m and 110 m are *physical stacks' height*), while TPP Kostolac B has negligible influence for both scenarios. In Scenario 1 common stack of 250 m height and other sources characteristics give favorable conditions from an air dispersion point of view, while within Scenario 2 apart from a reduced physical stack height to 180 m and other changed source parameters, it kept same insignificant influence on model domain.

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6.3. PM_{10} 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 $\mu g \cdot m^{-3}$ while the concentration levels of $PM_{2.5}$ fraction were in range from 5 to 370 $\mu g \cdot m^{-3}$.

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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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are gaseous or particle-associated compounds formed in almost every process of incomplete combustion from anthropogenic and natural sources. The United States Environmental Protection Agency (US EPA) has classified 16 PAHs as priority pollutants due to their mutagenic and carcinogenic properties. For the assessment of particle-bound PAHs, biomonitoring using a "moss bag technique" represents a complementary method to the convenient instrumental measurements. The common analysis of PAHs in moss and air samples involves extractionand evaporation of the solvent, and cleaning steps before determination by high-performance liquid chromatography (HPLC) or gas chromatography (GC) . Thanks to novel upgrades, ultra-performance convergence chromatography (UPC^2) outperforms HPLC and GC in the domain of PAH determination. In this study, the method for determination of PAHs in moss samples by UPC^2 was developed.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are toxic compounds commonly found in nature as constituents of coal and petroleum. The United States Environmental Protection Agency (US EPA) has classified seven PAHs as probable human carcinogens (Abdel-Shafy and Mansour, 2016). Simultaneous analysis of 16 PAHs is challenging due to their different properties and concentrations. A typical chromatographic method involves extraction and evaporation of the solvent, sample clean-up and its reconstitution in an organic solvent followed by high performance liquid chromatography (HPLC) with Ultraviolet-visible (UV/Vis) detection, or long gas chromatography (GC) analysis. Currently, liquid chromatography (LC) is used as a separation process for both the analytical and preparative scales. However, today's scientific demands require quicker and more sensitive methods for PAH analysis (Popp et al, 1997).

Classic HPLC analysis of PAHs takes 30 min without a sample preparation. Great progress was made when the ultra-performance liquid chromatography (UPLC) system was introduced in 2004, which can operate at a higher pressure (> 1000bar), and enable the operation of UPLC columns with smaller particles, thereby reducing the runtime to 10 min, and increasing the separation power and sensitivity (Yeudakimauet et al, 2013):The preparation of the sample still remains a problem in terms of duration. A conventional method includes a Soxhlet or ultrasonic extraction in a non-polar solvent such as dimethyl carbonate (DMC) or heptane, evaporation, purification by solid phase extraction (SPE) cartridges, re-evaporation and, finally, reconstitution in a solvent suitable for reverse phase liquid chromatography (RPLC). The greatest advantage of convergence chromatography is the use of carbon dioxide (CO_2) liquid as the primary mobile phase that is non-polar. This allows for starting the analysis after the extraction and concentration of the sample while the sample remains in the non-polar solvent. This principle enables one to take advantage of normal and reverse phase chromatography, as well as, gas chromatography.

Convergence chromatography shares the same selectivity possibilities as normal-phase LC while providing an alternative approach to reversed-phase LC. The primary mobile phase is liquid CO_2, which minimizes the use of toxic solvents typical for normal-phase LC. Convergence chromatography shares the same technology as supercritical fluid chromatography (SFC). A supercritical fluid is any substance that is at a temperature and pressure above its critical point, where distinct liquid and gas phases do not exist. Essentially, the substance takes on properties that are intermediate to both a gas and a liquid resulting in fast and efficient chromatography. The critical values of CO_2 (TC = 304.12 K, pC = 73.74 bar) are effortlessly achievable. Besides, CO_2 has other positive properties as it is non-toxic, non-flammable, can be easily purified and is relatively cheap (Kalíková et al, 2014).

This paper describes a determination of PAH in moss material by UPC^2 chromatograph using a photo diode array detector (PDA) and a UHPLC chromatograph with a fluorescence detector (FLR) with the aim to compare the performance possibilities of each technique. The study is an attempt to evaluate literature listed comparative advantages of UPC^2as a "green" technique over traditionally used UHPLC.

METHODOLOGY

Sample preparation

The 16 US EPA PAHs were extracted from moss *Sphagnum girgensohnii* Russow (Aničić et al. 2017) using dichloromethane, DMC (Prochem, Picograde, for Residue Analysis, LGC Standards) as an extraction solvent. For the development of the method 0.5g of the moss samples were spiked with different concentration levels consisting of 25, 50, 100 and 500 ppb standard PAH solution (PAH mix AccuStandard, Z-014G-R, USA). After ultrasonic-assisted extraction in DCM extract, the sample was transferred to a 2 mL vial, evaporated and reconstituted in 1 mL DMC, and injected into Acquity UPC^2 system. For UHPLC analysis, an additional clean up step using solid phase extraction (SPE) was required.

UPC^2 instrument method

The analyses were performed with a Waters Acquity UPC^2 with PDA detector (Waters, Milford, MA, USA). Separation was achieved on an AcQuityUPC^2 Torus 2-PIC column (1.7 µm, 100 mm × 3.0 mm i.d.). During the analysis, the column was kept at 40°C and the flow rate was 1.5 mL min^{-1}. The injection volume was 5.0 µL. The mobile phase consisted of compressed CO_2 as solvent A and methanol as solvent B (*Chromaslov*, for UPLC/MS and SFC/CC analyses). The following gradient elution condition was used: 1% B for 0.5 min, ramp to 35% B in 3.5 min, and hold at 35% B for 0.5 min B. The wavelengths for every compound are in Table 1.

UHPLC instrument method

For UHPLC analysis, the sample extracts were additionally cleaned up using fluorosil SPE cartridges (Macherey-Nagel, Chromabond, Na_2SO_4/Florisili 2/2g), evaporated and reconstituted in 1 mL of acetonitrile, (ACN). The analysis was performed on Waters Acquity ARC UHPLC system coupled with Waters Acquity 2998 PDA and 2475 FLR detector (Waters, Milford, MA, USA). Separation was performed on Waters PAH column (5 µm, 250 mm × 4.6 mm i.d.). Analysis time was 30 min, flow rate 1.2 mL min^{-1}, gradient was formed using purified water Type I (Sartorius, Arium UV PRO water system, Germany) as mobile phase A and acetonitrile (*Sigma Aldrich*, 99.99%) as mobile phase B. The gradient condition was 60%B to 100% B in 12 min, hold for 11min, back to initial condition in 2 min and hold it for 5 min. The column temperature was 40°C, and the injection volume 20 µL (Titato and Lanças, 2007). Values for fluorescence excitation (EX) and emission (EM) are given in Table 1. All data were acquired using Empower 3 CDS software (Waters, Milford, MA, USA).

Tabele 1. *PDA and FLR detector parameters*

PAH	UV max (nm)	EX (nm)	EM (nm)	PAH	UV max (nm)	EX (nm)	EM (nm)
Nap	220	277	330	**Chr**	287	284	390
Acy	229	NA	NA	**B[b]F**	267	270	367
Fl	227	270	323	**B[k]F**	256	298	436
Ant	261	265	310	**B[a]P**	307	303	432
Phen	251	252	365	**DB[a,h,**	296	280	410
Fla	252	250	402	**I[cd]P**	297	294	398
Pry	236	284	467	**B[g,h,i]**	299	290	420
B[a]A	240	332	378	**Chr**	287	284	390
Chr	287	284	390	**B[b]F**	267	270	367

RESULTS AND DISCUSSION

Comparison of the efficiency of analysis of PAH concentrations in moss tissue by UPC^2 and UHPLC

Calibration curves for the measured PAHs with concentrations ranging from 25 to 500 ppb are given in Figure 1. The linearity range spanned three orders of magnitude with $R^2 > 0.97$ for both UPC^2 PDA and UHPLC FLR analysis. With UHPLC and UV detection, a desirable sensitivity was not reached.

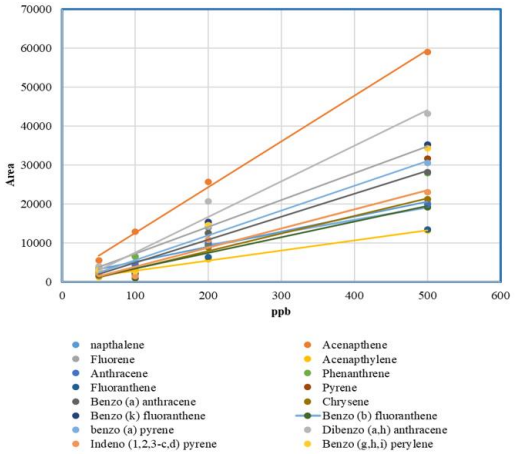
Because of a limited quantity of the moss, only 0.5g per moss sample, a current limitation of UPC^2 coupled with optical PDA detection during analysis of PAH compounds is sensitivity - 25ppb, which is low for this type of sample, where the expected concentration are below this value (Vukovic et al. 2015). Regarding sensitivity, FLR is a better choice, unfortunately, FLR detection for UPC^2 is still unavailable (Zhang et al. 2010). This can be solved by adding mass spectrometer to UPC^2 with APCI or APPI ion sources, which are suitable for PAH analysis (Smith et al, 2009).

Table 2 shows the retention times of the investigated PAHs as well as the correlation coefficients that describe the dependence of the PAH concentrations in the standard solutions (50, 100, 200 and 500 ppb) of the surface area below the chromatographic peak obtained by developing the method for determining PAHs in the moss material by UHPLC and UPC^2 instruments. The high values of the parameter R^2 indicate the satisfactory quality of the calibration curves obtained for both chromatograph analyses (Figure 1), but the coefficients were higher in the case UPC^{2}usage. The application of UPC^2 reduced the retention times of the PAHs, which significantly accelerated the time of analysis.

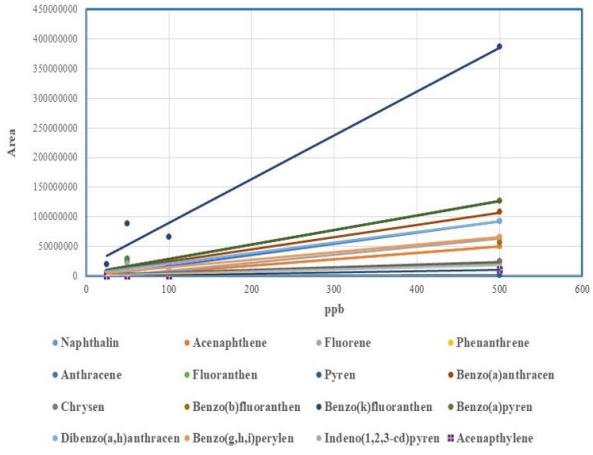
The process of 30 min on the UHPLC device was reduced to 4 min using UPC^2, and a more selective separation of the chromatographic peaks was achieved (Figure 2). The improved speed of analysis is attributed to the inherent compatibility between UPC^2 and low polarity analytes, which minimizes the risk of on-column degradation of the analytes. Moreover, the UPC^2 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.

Both HPLC and SFC are able to achieve similar efficiencies; the biggest difference being that increased linear velocity allows for shorter retention time (Figure 2). With significant developments in both instrumentation and column chemistry, the UPC^2 method provides separation performance of lower dispersion instrumentation and smaller particles, in combination with the improved diffusivity, and therefore speeds up the analysis of supercritical fluids (Sciascera et al. 2013, *Giddings et al. 1965*).

UHPLC analysis with FLR detector is already a proven method, the biggest impact on separation have lower system dispersion when compared with HPLC systems. This advantage allows sharp and narrow peaks, giving better resolution and therefore more time form switching wavelengths. Fluorescence detection is much more selective and sensitive than UV and the influence of the matrix effect is minimized. The downside is a high flow rate, a much larger solvent consummation and longer run time.



(a)

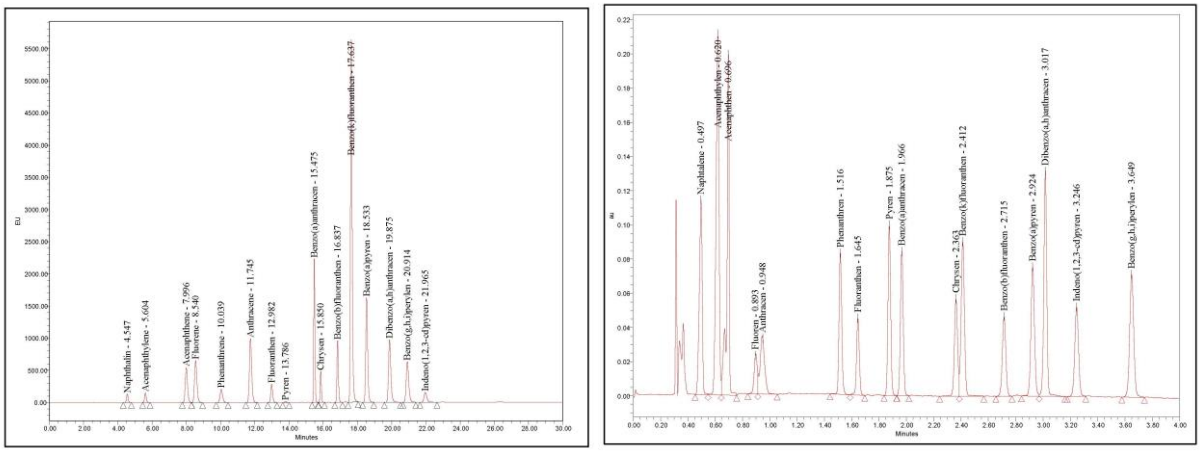


(b)

***Figure 1**. Calibration curves for all PAH compounds acquired with a) UPC^2 PDA and b) UHPLC FLR*

***Table 2.** Retention time and correlation coefficients (R^2) obtained by optimizing the method for determining PAH in moss samples using ultra high performance (UHPLC) and convergence chromatography (UPC^2).*

	UHPLC FLR		UPC^2 PDA			UHPLC FLR		UPC^2 PDA	
PAH	**R^2**	**Rt (min)**	**R^2**	**Rt (min)**	**PAH**	**R^2**	**Rt (min)**	**R^2**	**Rt (min)**
Nap	0.9857	04.54	0.9915	0.50	**B[a]A**	0.9765	15.56	0.9951	1.97
Acy	0.9896	05.60	0.9902	0.62	**Chr**	0.9760	15.85	0.9819	2.37
Acp	0.9976	07.70	0.9978	0.69	**B[b]F**	0.9754	16.84	0.9919	2.72
Fl	0.9988	08.54	0.9976	0.90	**B[k]F**	0.9753	17.64	0.9982	2.41
Ant	0.9926	11.47	0.9845	0.95	**B[a]P**	0.9743	18.53	0.9742	2.93
Phen	0.9988	10.39	0.9978	1.52	**DB[a,h,]A**	0.9747	19.87	0.9644	3.02
Fla	0.9872	12.98	0.9948	1.64	**I[cd]P**	0.9756	21.96	0.9652	3.25
Pry	0.9852	13.78	0.9983	1.88	**B[g,h,i]**	0.9476	20.91	0.9979	3.65



(a) *(b)*

***Figure 2**. Chromatograms of the standard mixture of PAHs extracted from S. girgensohnii moss and analysed with (a) UHPLC FLR system, 30 min and (b) UPC^2 PDA system 4 min*

INFLUENCE OF SAMPLE PREPARATION

Sample preparation is the most often cited area for improvement and it is identified as the bottleneck in the entire workflow. Most sample preparation techniques are not compatible with their current separation technique; this is because many matrices will respond best and will be more soluble in an organic phase. Standard sample preparation includes drying, grinding, Soxhlet or ultrasonic extraction, evaporation and sample clean up using, for example, solid phase extraction. Because of this, additional steps are necessary to convert the organic solution, or extract, into something that is compatible with their analysis. This approach is very common if the final chromatographic method is reversed-phase chromatography. All this can lead to poor recovery values and lose the component of interest.

In this study, these additional steps were potentially eliminated by injecting directly the DCM-extracted samples onto a UPC^2 system because it is directly compatible with a large number of sample preparation techniques and organic phases. In addition, due to reduced sample preparation time, the speed of analysis was significantly faster

(Fountain et al, 2014), and the most important parameter was better correlation from the calibration curves (Table 1).

CONCLUSION

The UPC^2 method was successfully developed to separate the 16 PAH compounds from the moss tissue in less than 4 min. The method was 8 times faster than traditional methods of analysis, thereby reducing organic solvent consumption by up to 85%. The short analysis time also minimized the risk of on-column degradation of the analytes. The improved speed of analysis is attributed to the inherent compatibility between UPC^2 and low polarity analytes. Using DMC as the extraction solvent, the resulting PAH extract could be injected directly into an ACQUITY UPC^2 System for analysis without the need for time-consuming evaporation and reconstitution steps often associated with RPLC-based methodology and gas chromatography. Excellent reproducibility and accuracy were also demonstrated in the moss sample analyses. The high throughput UPC^2 method is ideally suited for scientific laboratories performing extensive (bio) 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 consists of compounds that are a mixture of gases, vapors and particulate matter (PM). Particulate matter PM_{10} 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, PM_{10} and $PM_{2.5}$ 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 $\mu g/m^3$. Exceedances of the daily limit values of 50 $\mu g/m^3$ 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 PM_{10} in the 2016 were measured in Valjevo 566 $\mu g/m^3$ and Užice 438$\mu g/m^3$.

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, PM_{10}, $PM_{2.5}$, 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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INTRODUCTION

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 $PM_{2.5}$ and PM_{10} 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 particle number concentration. 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 particle number concentration 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 Condensation Particle Counter (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 a relative humidity of the aerosol below 40% at the inlet of the CPC and particle losses to be less than 30% at 7 nm.

Tab. 1: *CPC performance criteria (Excerpt from CEN/TS 16976 [1])*

Performance characteristic	Criteria
Actual flow rate	≤ 5% difference to nominal flow rate
	≤ 2% difference to the factory-certified flow rate
Concentration response	
Slope	1 ± 0.05
Linearity	All residuals < 4% of the measured value
Detection efficiency at low particle size	D_{50} = 7 nm ± 0.7 nm
	D_{90} < 14 nm
Number concentration measurement range	
Lower limit	≤ 100 cm^{-3} (based on at least 1500 particle counts)
Upper limit	≥ 10 000 cm^{-3} (including coincidence correction)

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. The 3772-CEN CPC also 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.

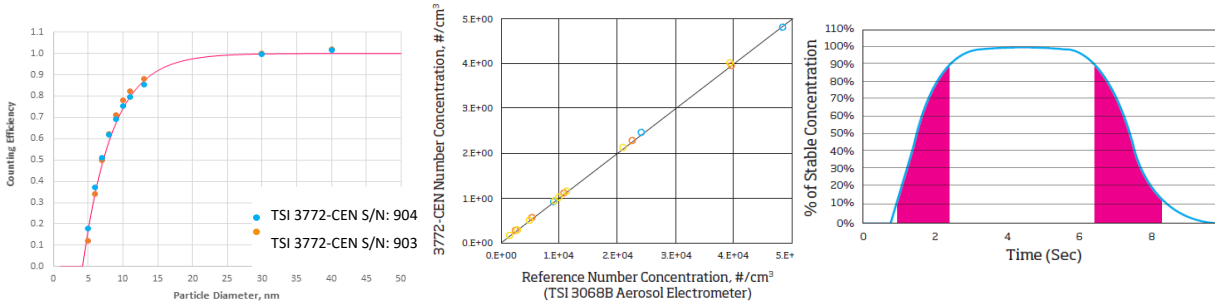

Figure 1. *a) Counting efficiency (D50 of 7 nm) for silver particles generated with the evaporation / condensation method b) Linearity. Data points show data for 4 different CEN-CPC units, black line shows 1:1 line c) Response time. Shown are rise and fall time with trise < 2 s and tfall < 2 s*

The custom-designed sampling system was designed to minimize diffusion losses of the airborne particles. It draws 16.67 L/min through a PM_{10} 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 relative humidity, temperature and ambient pressure for automatic logging in the 3772-CEN CPC.

CONCLUSIONS

The European Committee for Standardization (CEN) developed the Technical Specification CEN/TS 16976 as a first step of harmonizing the continuous measurement of particle number concentration 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 designed for the standardized, routine monitoring of particle number concentration in ambient air.

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

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ABSTRACT

The aim of this study was to determine carbonaceous aerosols in the Belgrade city centre close to Terazije tunnel and to compare the results obtained with those from other urban tunnels. The sampling of particulate matter ($PM_{2.5}$ and PM_{10}) was done in May of 2016. Mass concentrations of PM were determined gravimetrically according to the SRPS EN 12341 standard. Organic carbon (OC) and elemental carbon (EC), in both fractions were analysed using a Thermal/Optical transmittance aerosol carbon analyser following the NIOSH protocol. The average $PM_{2.5}$ mass concentrations were similar in the morning and the afternoon, while the PM_{10} values were about 25% higher in the afternoon. The average 24-hour values were approximately 80% higher in PM_{10} fraction. In both fractions, the average OC and EC values were the highest in the afternoon. The OC/EC ratio during the rush hour was around 1.

Key words: Urban air quality, Particulate matter, Organic Carbon, Elemental carbon,

INTRODUCTION

One of the greatest environmental problems urban areas face is associated with air pollution. Vehicle emissions significantly contribute to an increment of atmospheric particle concentrations. Atmospheric particulate matter (PM) is a heterogeneous mixture of extremely small particles and liquid droplets that get into the air (World Health Organization (WHO), 2006). The physical properties and chemical composition of PM depend on meteorological conditions and emission sources (Hinwood et al, 2006). The most detrimental effect to health can be attributed to the presence of respirable particles (RP). It is due to their small size (<100 nm) and large surface area, which enables them to have longer residence times in the air and penetrate deeper into the lungs. Recent epidemiological studies have shown that exposure to PM is associated with respiratory and cardiovascular diseases, premature delivery, birth defects, low birth weight and premature death (Du et al, 2017; Erickson and Arbour, 2014). Airborne PM consists of a huge number of different compounds. In urban areas, particles contain 30-40% of carbonaceous particulate matter (Cao et al, 2004, Saarikoski et al, 2008). Carbonaceous compounds are commonly divided into two categories: organic carbon (OC) and elemental carbon (EC). OC consists of a large variety of organic compounds, emitted from combustion sources or formed due to photochemical activity. EC chemical structure is similar to impure graphite, mainly derived from incomplete combustion of fossil fuel, biomass burning and other carbon-containing materials.

It is important to emphasise that there are currently no available literature data from Serbia dealing with carbonaceous compounds. For this reason, the aim of this study is to determine the concentrations of fine and coarse PM, derived predominantly from vehicle emissions, close to the Terazije tunnel over a 3 h and 24 h period. Furthermore, the preliminary mass concentrations of carbonaceous compounds from both fractions along with their ratio are discussed.

METHODOLOGY

Fine and coarse PM samples were collected on Quartz fibre filters (Whitman® QA-M, 47 mm) from 18th to 29th May 2016 close to the Terazije tunnel. The samplers were installed on a terrace, above a pedestrian passage, about 10 m away from the portal near the tunnel, at a height of 1.5 m above ground (Fig. 1). The tunnel is 230 metres long, with an average hourly traffic density of 4000 vehicles in the period 07:00 – 22:00 h, reducing to below a half that during the night. Reference gravimetric pumps, LVS Sven Leckel with flow rates of 2.3 Lpm were used for collecting $PM_{2.5}$ and PM_{10}. The samples were collected during rush hour, in the morning (from 08:00 to 11:00) and in the afternoon (from 14:00 to 17:00) and during a 24-hour period. PM mass concentrations of both fractions were determined by gravimetric measurements using the Radwag microbalance (reading precision of 1μg) following SRPS EN 12341 standard (2005). The filters were conditioned at a constant temperature (20 ± 1) ˚C and relative humidity (50 ± 5) % for a period of 48 h, before and after sampling. All filters were weighed twice and the

gravimetric mass was calculated by subtracting the weight of the filter after sampling from that of the prior sampling. The mass concentrations of OC and EC in both fractions were determined by a Carbon Aerosol Analyzer (Sunset Laboratory Inc), using the NIOSH protocol and following the thermal optical transmittance method (TOT) (Birch and Cary, 1996).

Figure 1. *The sampling location near Terazije tunnel.*

RESULTS AND DISCUSSION

The values of mass concentrations of PM, OC, EC, as well as OC/EC ratios in $PM_{2.5}$ and PM_{10} fractions are shown in Table 1. As it can be seen, the average $PM_{2.5}$ mass concentrations were similar in the morning and afternoon while the PM_{10} values were 25% higher in the afternoon. The average 24 h values were 80% higher in PM_{10} fraction. It is important to emphasize that during the examined period, the average concentrations in both fractions were exceeded WHO guideline values for acceptable daily levels, and were up to 50% higher both during the morning and afternoon. For the $PM_{2.5}$ fraction, the values for OC and EC in the morning were around 30% lower than in the afternoon, although both sampling periods can be attributed to peaks in traffic.

Table 1. *Mass concentrations of PM, OC, EC and OC/EC ratios in $PM_{2.5}$ and PM_{10} fractions.*

	PM2.5				PM10			
	μg/m^3			OC/EC	μg/m^3			OC/EC
	PM	OC	EC		PM	OC	EC	
				MORNING				
Max	74.18	11.33	12.01	0.94	107.08	23.21	16.38	1.42
Min	26.45	4.37	2.59	1.69	53.61	7.10	3.96	1.79
Average	48.47	7.94	8.12	0.97	77.89	14.83	10.70	1.39
				AFTERNOON				
Max	72.91	22.52	22.80	0.99	120.73	38.77	23.89	1.62
Min	36.19	5.60	4.91	1.14	79.15	8.87	6.01	1.48
Average	51.20	14.31	13.10	1.09	97.56	23.57	15.65	1.51
				24h				
Max	43.32	19.38	3.82	5.07	81.78	30.44	4.23	7.20
Min	28.72	8.33	2.18	3.82	48.16	12.97	1.91	6.79

Average	34.76	12.92	2.95	4.39	62.65	20.10	3.12	6.44

A possible explanation for these results is likely the deeper mixing of boundary layers in the afternoon. In addition, during the second week, (Fig. 2.) the morning OC and EC values were 15% lower in comparison to the first week, while the afternoon values were around 50% higher. The OC values in comparison to EC were the same in the morning or 10% higher (afternoon). In the PM_{10} fraction, the EC and OC concentrations in the morning were slightly lower than in the afternoon. During the second week, OC and EC values in the morning were 6% lower and around 40% higher in the afternoon as compared to values in the corresponding periods from the first week. It was also observed (and more prominent in the second week of sampling) that the OC concentration in PM_{10} fraction was, in most of the cases, 25-50% higher than the EC. The ratio between OC values corresponding to $PM_{2.5}$ and PM_{10} was around 60%, while the same ratio for EC values was around 80%.

According to available literature data, OC and EC concentrations varied depending on the length of the tunnel, traffic flow, types of motor vehicles and ventilation in a certain tunnel (Ancelet et al, 2011, Brito el al, 2013). In most studies, the average OC and EC concentrations were higher than the values obtained in this study. However, taking into account that the Terazije tunnel is shorter compared to other tunnels studied (Zhou et al, 2014, Alves et al, 2016), the average OC and EC concentrations are considered high and comparable with the values recorded for longer tunnels with more intense traffic flow. Interestingly, the Jânio Quadros (JQ) road tunnel in São Paulo (Brito el al, 2013) which is almost nine times longer than Terazije tunnel, measured EC is lower. A possible reason is likely that the Terazije tunnel is an urban tunnel, where traffic flow is heavy, especially during rush hour. Additionally, a large number of diesel vehicles without any after-treatment devices (pre EURO IV) are still present in Serbia, as compared to the predominantly petrol-fuelled vehicles driven in Brazil.

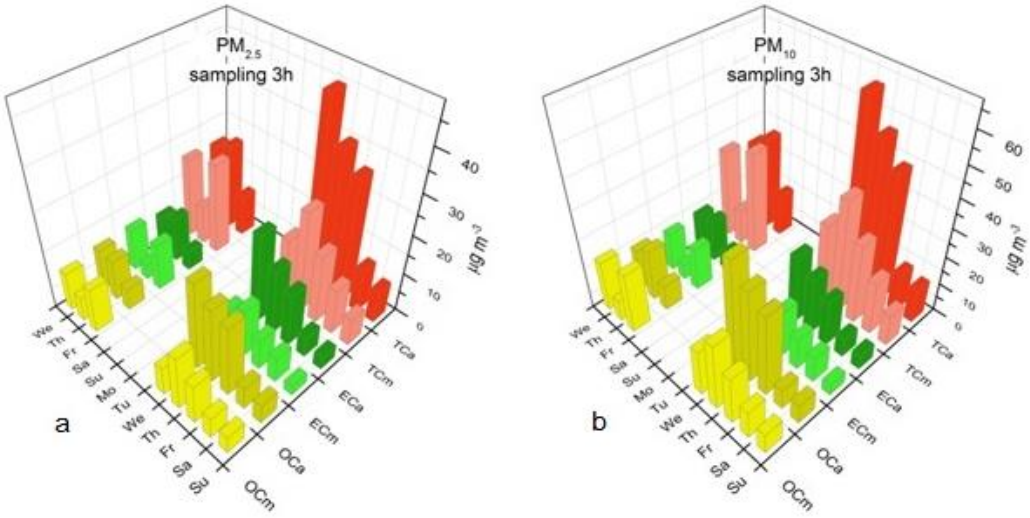

Figure 2. *3D dependence of mass concentration of OC, EC and TC in 3 hour samples (m- morning and a-afternoon) in the case of $PM_{2.5}$ (a) and PM_{10} (b).*

The OC/EC ratios are commonly used for estimation of emission and transformation characteristics of carbonaceous aerosol (Cachier et al, 1996). The range of EC concentrations in rural and remote areas is from 0.2 to 2.0 μg/m^3 and in urban areas from 1.5 to 20 μg/m^3 (Seinfeld and Pandis, 1998). In general, the OC/EC ratios are more than 2 in the urban ambient air (Zhou et al, 2014): OC/EC ratio in most of the tunnel studies was about 1. In this study, maximum levels of OC/EC ratio for $PM_{2.5}$ and PM_{10} were measured during the afternoon (~ 1 and 1.5). For 24 h samples, OC/EC ratios were much higher for both PM fractions (~ 4 and 6). OC/EC ratio between 1 and 3 indicate a high probability that the emissions come exclusively from vehicular sources (Mancilla and Mendoza, 2012) that is in line with the results from this study.

CONCLUSIONS

The sampling of fine and coarse PM was conducted in the Belgrade city centre close to a busy tunnel in May of 2016. The collected particles were predominantly derived from vehicle emissions. Mass concentrations of PM, OC and EC as well as OC/EC ratios were determined for 3h (rush hour) and 24h samples. The average $PM_{2.5}$ mass concentrations were similar in the mornings and the afternoons, while the PM_{10} values were about 25% higher in the afternoon. The average 24 h values were around 80% higher in the PM_{10} fraction. In both fractions the average OC and EC values were the highest in the afternoon. An OC/EC ratio between 1 and 3 indicates a high probability that the emissions come exclusively from vehicular sources that is in line with results from this study. Although the Terazije tunnel is shorter compared to other tunnels, the average OC and EC concentrations are considered high compared with the values recorded for longer tunnels with more intense traffic flow.

ACKNOWLEDGEMENTS

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6.8. SCOPE OF AMBIENT AIR PM_{10} MONITORING WITHIN THE NETWORK OF LOCAL PUBLIC HEALTH INSTITUTIONS IN SERBIA

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ABSTRACT

Coal burning power plants, household fuel burning, industrial contamination, traffic and topographic positions of urban settings are key reasons for high PM levels in Serbia. Our aim was to present the scope of urban ambient air PM_{10} monitoring within the network of local public health institutes (PHIs) in Serbia, for the period 2012-2016. The research tool used is a database formed by the Institute of Public Health of Serbia during the continuous air quality (AQ) monitoring process for the Ministry of Health, and through regular reporting of local PHIs. In a 5-year monitoring period for 19 towns, only 5 towns had continuous PM_{10} monitoring (Beograd, Bor, Niš, Užice, and Šabac). 79.31% of mean annual PM_{10} concentrations exceeded the annual limit values (ALV), thus PM_{10} presence in urban ambient air in Serbia could be considered a serious public health risk for the exposed population. Local programmes of AQ monitoring, conducted by the Network of PHIs give an incomplete coverage of potential public health threats for the burden of disease originating from air pollution.

Keywords: air quality, PM_{10}, monitoring, local Institutes of Public Health

INTRODUCTION

Elevated atmospheric particulate matter (PM) concentrations have significant adverse health effects [1-3],, affecting ecosystems and visibility. Particulate matter (PM) consists of a 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 [4].

Obrenovac, Lazarevac, Veliki Crljeni), household fossil fuel combustion (Kraljevo, Ivanjica, Čačak), industrial contamination (Bor), traffic (Beograd), and topographic position of the urban setting (Užice).

Overall, 25 institutions comprise the Network of Public Health Institutes (PHIs) in Serbia (Figure 1), lead by the National PHI (1 + 24), of which AQ laboratories are operational in 20 of them.

Figure 1. *Network of PHIs (www.batut.org.rs)*

PM is a mixture with physical and chemical characteristics varying by location. Common chemical constituents of PM include sulfates, nitrates, ammonium, other inorganic ions such as ions of sodium, potassium, calcium, magnesium and chloride, organic and elemental carbon, crustal material, particle-bound water, metals (including cadmium, copper, nickel, vanadium and zinc) and polycyclic aromatic hydrocarbons (PAH). In addition, biological components such as allergens and microbial compounds are found in PM [5].

The reasons for the appearence of high ambient air PM_{10}, together with high levels of heavy metal presence in Serbia are of different natures: coal burning energy plants (Obrenovac, Lazarevac, Veliki Crljeni), household fossil fuel combustion (Kraljevo, Ivanjica, Čačak), industrial contamination (Bor), traffic emissions (Beograd), and topographic position of the urban setting (Užice). Overall, 25 institutions comprise the Network of Public Health Institutes (PHIs) in Serbia (Figure 1), lead by the National PHI (1 + 24), of which AQ laboratories are operational in 20 of them.

Our aim was to present the scope of urban ambient air PM_{10} monitoring undertaken by the above-mentioned laboratories, as part of a mix of stations belonging to both the State Network of automatic stations and the network of local measuring stations, for the period 2012-2016. Besides PM_{10} concentrations, we aimed to present a decreasing trend in monitoring traces of heavy metals and metalloids in PM_{10}.

METHODOLOGY

For this retrospective study, the research tool is a database formed by the Institute of Public Health of Serbia (IPHS) during continuous air quality (AQ) monitoring process for the Ministry of Health, through regular reporting of local PHIs, monthly and daily, according to the annually revised Programme of National Interest towards the Ministry of Health. A local network of measuring points was established for the purpose of AQ monitoring in the territory of a defined local self-government unit, which is implemented according to the programme adopted by the competent body of the given local self-government. Such a programme determines the following elements: Timeframe (usually an annual or bi-annual period), number and precise location of the measuring points, which parameters to follow depending on the environmental threats on the ground, measuring frequency, and standardized methods of measurement and analysis. Adoption of such AQ monitoring programmes is defined by the Law on Air Protection [6].

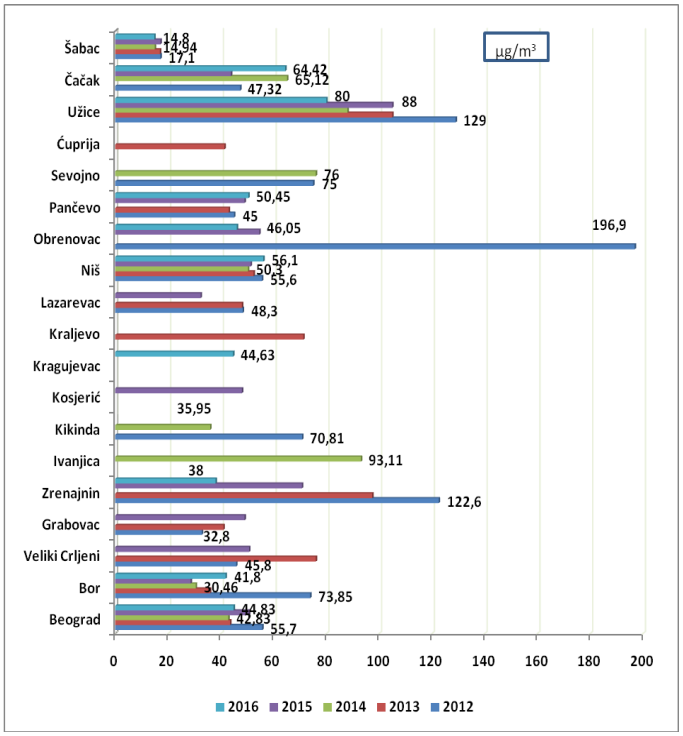

Figure 2. *Mean annual PM_{10} values measured in the Republic of Serbia for 2012-2016*

Specifically, PM_{10} monitoring at the local level is, mostly, subject to the negotiation process among the local PHI and local self-government, according to the local pProgramme of AQ monitoring, being approved by the Ministry responsible for environment protection for each local community. PM_{10} monitoring and measuring procedures were aligned with the standards given by the dDecree on the air quality monitoring conditions and requested air quality, such as the standard gravimetric method for PM_{10} fraction determination and measurements obtained by automatic measuring instruments [7]. Distribution of measuring stations was presented by using the Geographic Information System (GIS).

RESULTS AND DISCUSSION

Results are given for 19 urban settlements (Figure 2). The Aanalysis of a 5 -year monitoring period shows that only in 5/19 out of 19 towns PM_{10} concentration was monitored continuously (Beograd, Bor, Niš, Užice, and Šabac), in which average annual PM_{10} values show a steep decline in Bor (28.55 - 73.85 $\mu g/m^3$), Užice (80 - 129 $\mu g/m^3$), and Šabac (14.8 - 17.1 $\mu g/m^3$), while in Belgrade the decline iswas of a moderate kindnature, although all values were beyond the limit value (42.83 - 55.7$\mu g/m^3$), according to the national legislation (40 $\mu g/m^3$).

This pollutant was monitored for 4 out of 5 years in Čačak, Zrenjanin and Pančevo, 3 out of 5 years in Veliki Crljeni, Grabovac, Lazarevac and Obrenovac (coal mining and coal burning power plants, IPH Belgrade), 2 out of 5 years in Kikinda (oil extracting wells) and Sevojno (copper roller). From the limited data available, it is clear that 79.31% of all noted annual average PM_{10} concentrations, exceed the ALV given by the national legislation (40 $\mu g/m^3$), meaning that PM_{10} presence in urban ambient air in Serbia could be considered a serious public health risk for the exposed population (Figure 3).

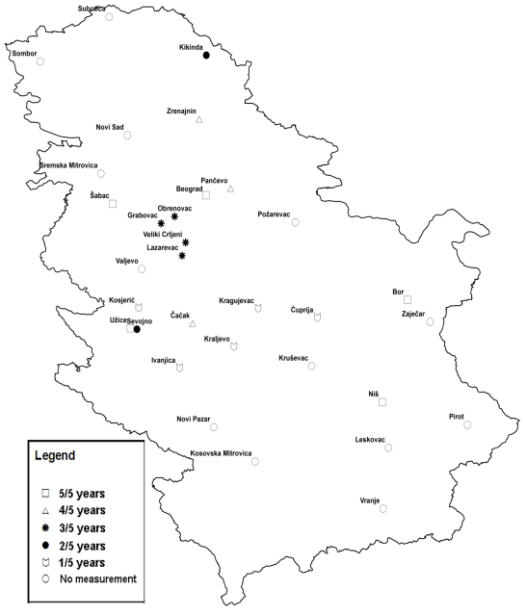

Figure 3. *GIS distribution of PM_{10} measurement inconsistency for 2012-2016*

Analysis of the frequency of monitoring of the concentration of heavy metals and metalloids content of PM_{10}, is presented in Table 1. The concentration of Cd, As and Ni is monitored to an even lesser degree in Serbia, and, similarly to the case of PM_{10} with the rate of follow-up being irregular and inconsistent, despite the fact of their almost continual presence in the environment (in Bor, for example) [8].

In all 5 years, during which As in PM_{10} was monitored in Bor, the mean annual concentrations of this metalloid exceeded the given limit values. Also, only in the year 2015, did the annual mean value for Cd in PM_{10} in Bor not breach the limits given by the national standards. A revisionew of the results calls attention to the fact that the town of Bor is the only urban environment in which constant follow-up for the presence of heavy metals and metalloids in PM_{10} was implemented, contrary to the other 11 towns and municipalities in Serbia which lack monitoring continuity of these parameters. The fact that arsenic in ambient air PM_{10} is continuously monitored in Bor, and that its concentration is not yet decreasing, without any thorough investigation into the health impacts, is a

worrying sign. Until now, the only case study providing data on human biomonitoring in a population exposed to arsenic, was a study aiming to provide evidence of the cardiological effects of naturally occurring arsenic in groundwater in Zrenjanin, Serbia [9], with no such a study provided for the exposed population of Bor [10].

Table 1. *Concentrations of Cd, As and Ni in PM_{10}*

	2012			2013			2014			2015			2016		
	Cd	**As**	**Ni**	**Cd**	**As**	**Ni**	**Cd**	**As**	**Ni**	**Cd**	**As**	**Ni**	**Cd**	**As**	**Ni**
	ng/m^3			ng/m^3			ng/m^3			ng/m^3			ng/m^3		
Beograd	0.4	**6.1**	13.2	0.5	6.0	14.0	/	/	/	/	/	/	/	/	/
Bor	**5.1**	**97.1**	<1.0	**7.4**	**64.4**	9.8	**7.9**	**43.8**	3.8	2.8	**34.5**	3.8	**6.9**	**105.8**	4.2
Grabovac	0.4	**8.7**	4.8	0.2	**12.9**	5.3	/	/	/	/	/	/	/	/	/
Kosjerić	1.4	5.7	/	/	/	/	0.2	0.9	6.0	0.3	0.8	5.6	/	/	/
Kragujevac	3.0	/	/	3.0	/	/	/	/	/	/	/	/	0.4	3.2	6.7
Lazarevac	0.5	**17.9**	5.7	0.5	**29.7**	6.8	/	/	/	/	/	/	/	/	/
Niš	1.0	3.0	4.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	1.0	2.0	3.0	2.0	/
Novi Sad	2.0	4.2	**39.2**	/	/	/	/	/	/	/	/	/	/	/	/
Pančevo	1.0	5.1	1.1	1.3	4.1	2.6	/	/	/	1.0	2.4	4.6	0.6	0.8	4.9
Sevojno	4.7	**6.3**	/	/	/	/	2.4	2.5	8.4	1.9	0.8	5.1	/	/	/
Užice	2.0	**8.3**	16.2	2.0	3.6	12.6	3.0	2.0	13.0	1.3	1.3	14.9	1.0	1.2	11.3
V.Crljeni	0.1	6.4	2.0	0.3	**18.5**	8.4	/	/	/	/	/	/	/	/	/
Rakovica	0.7	3.5	58.2	1.3	5.2	8.2	/	/	/	/	/	/	/	/	/
ALV	**5.0**	**6.0**	**20.0**	**5.0**	**6.0**	**20.0**	**5.0**	**6.0**	**20.0**	**5.0**	**6.0**	**20.0**	**5.0**	**6.0**	**20.0**

CONCLUSIONS

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

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6.9. EVALUATION OF THE TRAFFIC DENSITY AND METEOROLOGICAL CONDITIONS INFLUENCE ON $PM_{2.5}$ 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 (CO_2, CO, NO_X, PM AND VOC) ON OUTDOOR TEMPERATURE AND THERMAL COMFORT IN A COMPLEX URBAN ENVIRONMENT

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ABSTRACT

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

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

For estimating outdoor temperature in a complex urban environment with CFD simulations, a large number of parameters are required, and most of them have to be additionally measured or calculated. Traffic emissions in real time is very complex and the parameters used for the CFD simulation are obtained by traffic contamination modeling. The COOPERT method used is one of the most comprehensive methods of modeling the emissions of traffic for CO_2, CO, NOx, PM and VOC.

Numerical simulations of the outdoor temperature were performed for part of Belgrade city centre using measurements that have been completed for the complex urban geometry of this city.

Based on the results obtained, it was noted that the ambient temperature was 1.5-3 °C higher near the streets where traffic flow was higher or in places with larger buildings, than in other parts of the city.

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

INTRODUCTION

The extent and rate of global environmental changes are driven largely by the rapid growth of the Earth's human population [1]. Cities, and their inhabitants, are key drivers of the global environmental change. Given the large percentage of the world's population living in cities, and the disproportionate share of resources used by these urban residents, cities have a direct impact on the climate. This influence is not on the global-scale climate, rather the effects are on the regional and local city climate. Distinct urban climates at these scales have long been recognized [2]. They present a greater magnitude than projected global-scale climate change and enhance the vulnerability of urban residents to future global environmental change. Urban planning, as well as reducing emissions from local sources, has the potential to mitigate, both directly and indirectly, broader environmental change.

Phenomena of the urban heat island (UHI) are one of the most important issues concerning thermal pollution in urban areas [3,4]. There have been a number of papers of published with measurement data and numerical simulations of UHI, but only a few studies have been performed to investigate the correlation of urban pollution levels, primarily from vehicles, with the effects on the outdoor temperature. It is a well-known fact that local temperatures are influenced by complex impacts of different effects such as wind, evaporation and rain, and even atmospheric pollution from tri-atomic pollutant gases such as CO_2, NO_X, SO_X, H_2O, as well as particulate matter. Since the polluted urban air is non-transparent matter, high levels of pollutants in the urban atmosphere will be heat trapping and cause the urban upper atmosphere to be hotter. It is a generally known fact that the presence of pollution would then cause a higher level of downward long-wavelength radiant energy, thus increasing urban heating.

Motor vehicles are a major source of air pollution with a significant impact on the urban environment.

Air pollutants such as CO_2, CO, hydrocarbons, NO_x, particulate matter (PM), benzene, formaldehyde, acetaldehyde, 1, 3-butadiene, O_3, nitrates, and inorganic and organic acids are emitted by motor vehicles. Case study simulations of one part of Belgrade were performed based on the numerical model. This model has been validated by measurement data. The measurement was performed at different times of day, morning, the most crowded traffic period, afternoon, and after sunset.

The fact that the atmosphere above the urban area is a non-transparent media, and the effective atmospheric emissivity is related to the concentration of the tri-atomic gases (H_2O, CO_2 and O_3) [14], it is assumed that the variation of CO_2 is significant, resulting in an increased outside temperature in the urban environment.

Also, it is assumed that in the observed urban environment, the prevailing contribution to the source of CO_2, is the urban traffic. In order to determine the values of the pollutant, a calculation was made using computer software.

This study has focused on the investigation of the influence of urban pollution (mainly of traffic) on the level of outdoor temperature using measurement and numerical simulation.

METHODOLOGY

The following pollutants were measured and calculated for the urban area, figure 1, based on air temperature, relative humidity, wind velocity and direction, temperature of the facade, grass and roads and global solar radiation, as well as the number of vehicles per category, length of the road and average speed of the vehicle.

Figure 1. *Urban structure of Belgrade Center.*

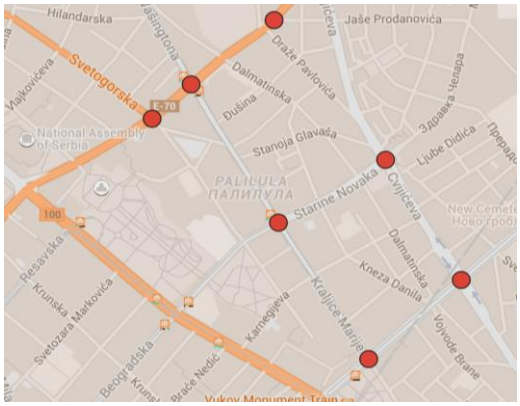

Figure 2. *Location of traffic intensity measurement*

In urban locations, traffic classification was used in measurements at the 7-studied crossroads, Figure 2. The selected vehicles are categorized in one of 7 groups: Bicycles, motorcycles, passenger vehicles, vans, buses, light trucks and heavy-duty trucks.

COPERT software was used to conduct the analysis of the traffic flow data measured. The software is designed to estimate the emissions of the most important, harmful, substances and individual heavy metals emitted by the different categories of vehicles. Based on the data entered, CO_2, VOC, NOx, CO and PM levels at street level and intersections were obtained. COPERT Street level [5] was designed to calculate hourly emissions, so the activity data are available for each hour of the day and for every traffic type. The required input is provided by the traffic model.

The 3D model of the selected urban area is presented in Fig. 3. The green infrastructure (parks) is denoted by green polygons. Numerical simulations have been performed by PHOENICS computer code [6]. The model domain has been selected to be slightly wider than the urban area 1536 x 1425 x 200 metres, discretized by 100 x 100 x 43 cells in the x, y, z directions, respectively. The conservation equations of mass, heat and momentum can be written in the form of partial differential equation with the general dependent variable, denoted by Φ:

$$\frac{\partial}{\partial x_i}\left(\rho U_j \Phi\right) - \frac{\partial}{\partial x_i}\left(\Gamma_\Phi \frac{\partial \Phi}{\partial x_i}\right) = S_\Phi \qquad (1)$$

where:

ρ - Air density,

U_j - Wind velocity components (j=*1, 2, 3*),

Φ - General dependent variable (summarized in table 1).

Γ_Φ - Diffusion coefficient of variable Φ (summarized in table 1).

S_Φ - Source terms of variable Φ (summarized in table 1).

Table 1. *Summarized terms in equation (1)*

Equation:	Φ	Γ_Φ	S_Φ
Continuity	*1*	*0*	*0*
Momentum	U_i	μ_{eff}	$-\partial p/\partial\, x_j + \rho g_i(T_a - T_{ref})$
Energy	T	γ_{eff}	$\varepsilon_a \sigma(T_{rad}^4 - T_a^4)$
Species	Y_{CO2}	γ_{CO2}	*0*
Turbulence kinetic energy	k	ν_t/σ_k	$P_k + G_k - \varepsilon$
Dissipation rate of turbulence	ε	ν_t/σ_ε	$(\varepsilon/k)(C_{\varepsilon 1}P_k + C_{\varepsilon 3}G_k + C_{\varepsilon 2}\varepsilon)$
Radiant temperature	T_{rad}	γ_{rad}	$-\varepsilon_a \sigma(T_{rad}^4 - T_a^4)$

$$\mu_{eff} = \mu_{mol} + \mu_t, \gamma_{eff} = \gamma_{mol} + \gamma_t$$

$$\mu_t = \frac{C_\mu \rho k^2}{\varepsilon}, P_k = \nu_t(\partial_k U_i + \partial_i U_k)\partial_k U_i, G_b = \nu_t \beta g_i \partial_i T$$

$$(\sigma_k, \sigma_\varepsilon, C_{\varepsilon 1}, C_{\varepsilon 2}, C_\mu, C_{\varepsilon 3}) = (1.0, 1.314, 1.44, 1.92, 0.09, varies)$$

$$\gamma_{rad} = (16/3)\sigma T_{rad}^3\{1/(\varepsilon_a + s_a + 1/X_{gap})\}, \varepsilon_a = \varepsilon_a(H_2O) + \varepsilon_a(O_3) + \varepsilon_a(overlap) + \varepsilon_a(CO_2)$$

The significance of the symbols in table 1 are: p - pressure, g_i - gravitational acceleration, T_{ref} - reference air temperature and σ - Stefan-Boltzmann constant, and ε_a- effective atmospheric emissivity.

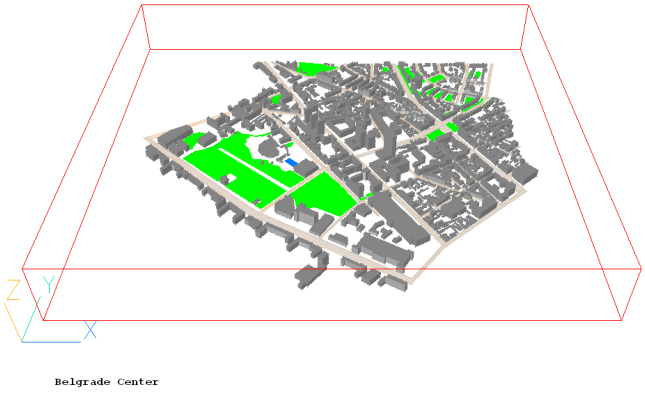

Figure 3: *3D solid model of Belgrade Centre.*

RESULTS AND DISCUSSION

The case study of scenarios is the warmest day in the measurement campaign. It was selected as the most convenient to represent the typical summer day in Belgrade. Input data of atmospheric parameters are taken from the measurement database depend on time of day, as shown in Table 2.

Table 2. *Atmospheric parameters*

Time	8:00-9:00	14:00-15:00	18:00-19:00
Air temperature [^{o}C]	35.9	40.8	37.6
Relative humidity [%]	33.1	21.4	25.4
Atmosphere pressure [hPa]	1000.1	1000.3	999.8
Wind velocity (at 10 metres a.g.l.) [m/s]	1.1	2.8	3.1
Wind direction [degree]	300	330	322
Global solar radiation [W/m^2]	410	794	217

The mean surface temperatures of trees, grass, building façades and roofs, pavements, streets and water, used as input parameters, are given below:

- Temperature of trees: 26 ˚C
- Temperature of grass: 27˚C
- Temperature of building façades and roofs: 37˚C
- Temperature of pavements and streets: 37˚C
- Temperature of water surface: 18˚C

Table 3 presents the average values of numerical simulation of the number of vehicles using COPERT computer software. The highest concentrations of CO_2, CO, NO_x and PM were observed at Crossroad 5 during the morning and afternoon. This was to be expected since this is the crossroad of two streets with dense traffic flow during popular commute times. The highest concentration of VOC was observed in the same location, but during the afternoon hours, due to an increase in temperature during the day, leading to the evaporation of organic matter. By contrast, the lowest concentrations of pollutants were observed on Street 11, which experiences a comparatively smaller amount of traffic. Generally, the concentrations of CO_2, CO, PM and NO_x were highest during the morning and afternoon at all locations due to traffic emissions. As daily temperatures rose, there was an increase in VOC concentrations reaching a maximum during the afternoon hours.

Figure 4. *Ambient air temperature at a height of 1.8 metres in the morning, 08-09h*

Figure 5. *Ambient air temperature at a height of 1.8 metres in the afternoon, 14-15h*

***Table 3**. Results of numerical simulation of the determination of the concentration of CO_2, CO, NO_x, PM and VOC depending on the intensity of traffic*

Measurement location	Pollutant [g]	08:00 - 09:00	14:00 - 15:00	18:00 - 19:00	Measurement location	Pollutant [g]	08:00 - 09:00	14:00 - 15:00	18:00 - 19:00	Measurement location	Pollutant [g]	08:00 - 09:00	14:00 - 15:00	18:00 - 19:00
Crossroads 1-Cvijićeva-Zdravka Čelara-Starine Novaka	CO_2	245339	228025	184396	**Street 5-Kraljice Marije**	CO_2	83443	98119	86187	**Street 10-Džordža Vašingtona**	CO_2	95635	115250	93260
	CO	411.1	424.9	325.3		CO	138.6	188.9	170.9		CO	140.6	183.6	166
	NO_X	452.7	390.6	327.7		NO_X	165.7	185.8	161.5		NO_X	182.7	209.6	166.8
	PM	8.3	7.4	5.9		PM	3	3.5	3		PM	3.3	3.7	3
	VOC	87.1	102.7	71		VOC	26.5	51.2	46		VOC	20.6	32.9	33.6
Street 1-Zdravka Čelara	CO_2	119007	116064	91670	**Street 6-Beogradska**	CO_2	117344	141862	107948	**Crossroads 4-Takovska-Svetogorska**	CO_2	197061	198724	180215
	CO	199.4	216.3	161.7		CO	191.2	261.4	198.6		CO	280.7	319.1	297.3
	NO_X	219.6	198.8	162.9		NO_X	224	265.6	199.2		NO_X	394.4	405.9	328
	PM	4	3.8	3		PM	4	5	3.6		PM	6.9	7.4	5.8
	VOC	42.3	52.3	35.3		VOC	32.8	67.8	47.1		VOC	39.6	72.6	61.1
Street 2-Cvijićeva (od Bul. Despota Stefana to Crossroads 1)	CO_2	140705	145184	106457	**Street 7-27 Marta**	CO_2	48171	60530	47939	**Street 11-Majora Ilića**	CO_2	25632	30173	27050
	CO	222.7	254.5	183.1		CO	75.5	106	87.1		CO	36.5	48.4	44.6
	NO_X	267.8	269.2	190.9		NO_X	92	112.1	87.4		NO_X	51.3	61.6	49.2
	PM	4.8	5	3.4		PM	1.6	2.1	1.6		PM	0.9	1.1	0.9
	VOC	41.9	60.1	39.1		VOC	12.3	24.6	19.6		VOC	5.1	11	9.2
Street 3-Cvijićeva (from Crossroads 2 to Ruzveltove)	CO_2	117740	122731	101448	**Crossroads 3-27 Marta-Takovska**	CO_2	47817	57625	46630	**Street 12-Takovska (from Crossroads 4 to Bilevara Kralja Aleksandra)**	CO_2	211752	212250	187840
	CO	193.7	219.3	174.9		CO	70.3	91.8	83		CO	301.7	340.8	309.9
	NO_X	229.6	230.8	189.3		NO_X	91.4	104.8	83.4		NO_X	423.8	433.5	341.8
	PM	4.2	4.3	3.4		PM	1.6	1.9	1.5		PM	7.4	7.9	6
	VOC	41.4	51.4	39.4		VOC	10.3	16.5	16.8		VOC	42.5	77.5	63.7
Street 4-Starine Novaka	CO_2	101432	100455	80049	**Street 8-Takovska (from Crossroads 3 to Jaše Prodanovića)**	CO_2	100075	107483	97840	**Crossroads 5-Ruzveltova-Cvijićeva**	CO_2	296152	272975	229387
	CO	167.7	186	144.5		CO	152.6	163.8	157.9		CO	481.5	476.5	390.2
	NO_X	190.3	181	145.2		NO_X	192.3	201.6	180.7		NO_X	596.9	537.5	439.3
	PM	3.4	3.4	2.6		PM	3.5	3.6	3.1		PM	11	10	7.9
	VOC	32.3	46.8	33		VOC	23.7	27	26.1		VOC	103.6	109.8	89.4
Crossroads 2-27 Marta-Starine Novaka	CO_2	176695	219759	171030	**Street 9-Takovska (from Crossroads 3 to Svetogorske)**	CO_2	61684	64949	55867	**Street 13-Ruzveltova**	CO_2	82280	71229	61653
	CO	287.9	405	314.7		NO_X	120.7	125.4	100.8		NO_X	167.7	138	117.6
	NO_X	337.3	411.5	315.5		PM	2.1	2.3	1.8		PM	3.1	2.6	2.2
	PM	6	7.7	5.7		VOC	12.8	21.1	19.5		VOC	28.9	36.8	33.9
	VOC	49.4	105.1	74.7		NO_X	120.7	125.4	100.8		NO_X	167.7	138	117.6

Figure 6. *Ambient air temperature at a height of 1.8 metres in the evening, 18-19h*

The horizontal distribution of air temperature at 1.85 metres, obtained by numerical simulation, are presented in figures 4, 5 and 6. The ambient temperature is higher near the street where traffic intensity is higher, or in places where there exists a larger concentration of buildings than in other parts of the city.

CONCLUSIONS

Ambient temperature was 1.5-3 °C higher near the streets where traffic intensity is higher or in places where the is a larger concentration of buildings than in other parts of the city,

CO2 and NOx pollutants affect more than other pollutants high temperatures in the city,

This study showed that simulations can be successfully utilized to predict the outdoor temperature in complex urban area,

Simulations can be successfully used to develop different scenarios for energy consumption and outdoor thermal comfort,

From the presented study, it can be recommended that green spaces and wider green infrastructure should be a minimum of 0.5 - 1.0 ha in order to achieve a cooling effect at significant distances beyond the site boundaries,

Such research can be beneficial 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 (NO_2 and NO_x), carbon monoxide, ozone (O_3), 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 $PM_{2.5}$, PM_{10}, NO_2, NO_x, CO, and O_3 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 traffic-related 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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ABSTRACT

A large body of evidence has documented that particulate matter (PM) in the ambient air has an adverse effect on human health as well as on the environment. Air pollution monitoring for the presence of sulphur dioxide and soot in the ambient air in Nis (Serbia) was started in 1966 by Public Health Institute. An 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. An investigation of the levels, and potential sources, affecting ambient particulate matter (PM) and the associated risk to public health was started in Nis in 2011 by the regional Public Health Institute. Also, particulate matter monitoring ($PM_{2.5}$, PM_{10}) 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 $PM_{2.5}$ concentrations in the ambient air as part of a scientific project, funded by the relevant Serbian Ministry. Since 2011, the degradation of the ambient air quality in the city of Niš has been primarily caused by high PM_{10} concentrations. According to the "Annual Report on the Environment in the Republic of Serbia" by the Ministry of the Environment, Mining, and Spatial Planning, the mean annual ambient air PM_{10} concentration in 2010 was 51 μg/m3 (maximum allowed level: 50 μg/m3), whereby limit values were exceeded for 123 days. According to the Public Health Institute monitoring during the period 2011-2016, the annual mean concentrations of PM_{10} were over the limit together with a large number of days with PM concentrations over tolerable limits. The most likely sources of PM in Niš, especially during the winter, are from vehicular traffic, combustion activities and domestic fuel burning, as well as industrial activities. Several epidemiological studies regarding the health impact of ambient PM on the population were performed on risk groups (pre-school children, school children, pregnant women and persons older than 65). Our studies demonstrate that PM significantly affected the health of the vulnerable population and increased morbidity. These findings are useful for developing risk management actions for PM on a local and national level. Although most sources of outdoor air pollution are well beyond the control of individuals, there is still an opportunity for personal action, like healthy behaviour. Further development of a network and system for monitoring the ambient PM in Serbia's urban areas can significantly contribute to disease prevention, primarily for the vulnerable population. Emission reduction policies administered in conjunction with epidemiological studies are needed to understand the benefits of sustainable control measures for PM mitigation.

INTRODUCTION

Particulate matter (PM) affects more people than any other pollutants and they are one of the six EPA "criteria pollutants" that have been determined to be harmful to public health and the environment. A large body of evidence has documented that PM in the ambient air has an adverse effect on human health, as well as on the environment (1-5).

Air pollution monitoring in Nis started in 1965 at two monitoring sites by measuring daily concentrations of sulphur dioxide, black smoke and sediments (6). The Serbian National Monitoring Network Program for air quality control has been conducted since 1992 on 82 sites where 20 pollutants are being monitored(7).

The city of Nis is the third largest Serbian city and is the administrative centre of the Nišava District and South-Eastern Serbia region. According to the 2011 census, the urban area of Niš had a population of 187,544, while the administrative area had a population of 260,237 inhabitants. Niš is situated at the 43°19' latitude north and 21°54' longitude east, in the Nišava river valley, enclosed from three sides. The city is at 194 m (636 ft) above sea level and covers a surface area of about 597 km^2. The dominant wind is the North-West and its direction diverges so that natural ventilation is obstructed. Nis has a moderate continental climate with an average annual temperature of about 11.2°C.

The analysis of air quality (8) indicated that the city of Niš belongs to a group of cities characterized by the third category of air quality (excessive air pollution).

METHODOLOGY

We searched the relevant literature and papers regarding the objective of the paper.

RESULTS AND DISCUSSION

An investigation of levels and potential sources affecting ambient particulate matter (PM) and the associated risk to public health by regional Public Health Institute was started in Nis in 2011. Also, particulate matter monitoring ($PM_{2.5}$, PM_{10}) in the city was conducted by means of two automatic monitoring stations, operated by the Environmental Protection Agency of the Government of the Republic of Serbia (9).

In 2012 and 2013, the Faculty of Occupational Safety in Niš conducted measurements of $PM_{2.5}$ concentrations in ambient air, as part of the scientific project, funded by the relevant Serbian Ministry (8).

From 2011, the degradation of the ambient air quality in the city of Niš has been caused primarily by high PM_{10} concentrations. According to the "Annual Report on the Environment in the Republic of Serbia" by the Ministry of the Environment, Mining, and Spatial Planning, the mean annual ambient air PM_{10} concentration in 2010 was 51 $\mu g/m^3$ (maximum allowed level: 50 $\mu g/m^3$), whereby limit values were exceeded for 123 days. According to Public Health Institute monitoring, in the period 2011-2016, the annual mean concentrations of PM_{10} were over limit.

Table 1. *Concentration of PM_{10} ($\mu g/m^3$) in the period 2011-2016 (measuring point Public Health Institute Niš)*

Year	2011	2012	2013	2014	2015	2016
Measurement number	52	52	52	52	55	53
X -annual	43,25	53,3	50,9	51,4	51,3	56,1
C50	30,98	35,3	40,6	38,68	35,7	38,6
C98	128,65	193,7	149,7	179,6	156	265,2
Min	13,76	15,76	3,66	18,19	8,8	6,7
Max	228,70	257,76	161,1	197,2	176,8	295,2
Number (%) of days above GV-daily	16 (31)	15 (29)	16 (31)	19 (37)	17 (31)	17 (31)
Number (%) of days above TV-daily	11 (21)	11 (21)	8 (15)	10 (19)	10 (18)	9 (16)

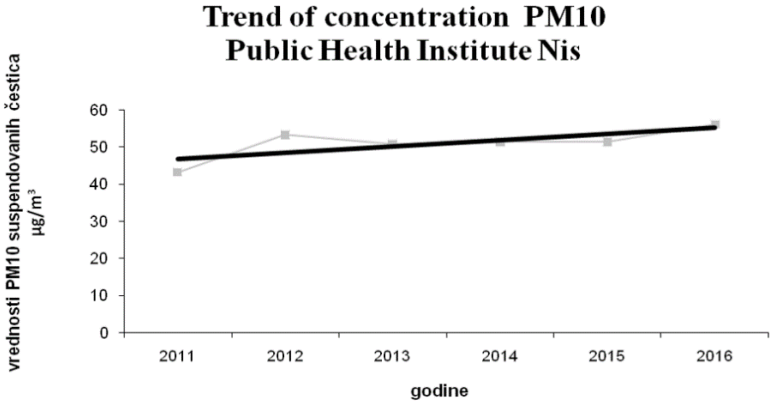

Figure 1. *Trend of PM_{10} level in Niš*

Up to the early 1990's, Niš was an industrially developed city. The predominant sources of air pollution were industry and local heating. During the 1990's, Niš, among other cities in Serbia, underwent a very difficult period of economic sanctions and poverty. The main sources of air pollution in Niš today are heating and transportation.

The most likely sources of PM in the Niš city area, especially during the winter, are vehicular traffic, combustion activities and domestic fuel burning, as well as industrial activities. Biomass burning is a relevant source with a larger contribution during autumn and winter because of the influence of domestic heating, however, is not negligible in the spring and summer.

Determinants of PM Levels are weather patterns, wind, stability (vertical movement of air), turbulence, precipitation and topography.

Even in areas with relatively low levels of air pollution, public health effects can be significant and costly. This is because the effects can occur at very low levels and a large number of people inhale such pollutants.

Exposure to particulate matter is a risk factor for a variety of diseases. Health effects are dependent on the type of polution, its concentration in the air, length of exposure, other pollutants in the air and environment, other environmental factors, individual susceptibility and human behaviour.

Several theories have been advanced as to the mechanism of action. It is likely that more than one mechanism is involved in causing PM-related health effects. Theories include the following:

1. PM leads to lung irritation which leads to an increase in the permeability of lung tissue,
2. PM increases susceptibility to viral and bacterial pathogens leading to pneumonia in vulnerable persons who are unable to clear these infections,
3. PM aggravates the severity of chronic lung diseases causing rapid loss of airway function,
4. PM causes inflammation of lung tissue, resulting in the release of chemicals that impact heart function,
5. PM causes changes in blood chemistry that results in clots that can cause heart attacks.

Poor people, people with malnutriton, the very young and the very old, individuals who work/exercise outdoors and people with pre-existing chronic diseases are more at risk. Children are more susceptible to air pollution than adults for many reasons. Firstly, more than eighty percent of alveoli are formed postpartum, and changes in the lung tissue continues throughout adolescence. Secondly, children have a larger lung surface area per kilogram of body weight than adults and, under normal breathing, they inhale 50% more air per kilogram of body weight than adults. Finally, children are more exposed to many air pollutants because of higher minute ventilation and, usually, higher levels of physical activity.

Until the mid-1990s, most research focused on the association of PM exposure with respiratory disease. Since then, there has been growing evidence of cardiovascular health effects from PM.

Niš is one of rare Serbian cities where epidemiological studies are regularly performed monitoring the health effect of air pollution. Several epidemiological studies (8,10) regarding the health impact of ambient PM on the population were performed on risk groups (pre-school children, school children, pregnant women and persons older than 65) and they were reported health effects at low concentrations of ambient PM.

Exposure to PM exists in the city of Nis and requires action by public authorities at the national, regional and international level.

As a result of EU legislation, much progress has been made in tackling air pollutants such as sulphur dioxide, lead, nitrogen oxides, carbon monoxide and benzene. However, despite a reduction in some harmful emissions, air quality continues to cause problems. Clearly, more needs to be done at the local, national, European and international levels.

Compromised air quality, as an exogenous component, together with other biological, economic and/or social factors, are all significant aggravators of respiratory diseases. Socio-economic factors may correlate with spatial variation in air pollution. Indeed, lower socio-economic groups are likely more exposed and more susceptible to air pollution.

The mechanisms underlying the observed associations may involve multiple genetic influences, gene-environmental interactions, and the interactions between air pollution and other exposures such as *in utero* maternal smoking and parental stress. Oxidative stress and inflammation have been hypothesized as the main mechanisms through which ambient air pollution can affect human health. With regard to lung function, toxicological evidence on mechanisms is sparse.

CONCLUSIONS

To conclude, the data presented demonstrate that PM significantly affects the health of the vulnerable population and an increase of morbidity in Nis. Taking into account the fact that there are cities in Serbia where measured

pollutant concentrations were higher in comparison to Nis, it is necessary to perform epidemiological studies in these cities too.

The findings are useful for developing risk management actions for PM on the local and national levels.

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 the ambient PM in Serbia's 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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ABSTRACT

The aim of this study is to present the first analysis of PM_{10} altitude distribution in Belgrade using the innovative concentration weighted boundary layer hybrid receptor model. The model employs a two-dimensional grid and a planetary boundary layer height as a frame of reference. The results indicate that the PM_{10} concentrations were highest in the ground layer throughout the year and exhibited a rapid decrease with height. Although similar patterns were observed for all seasons, the significant differences in winter and summer planetary boundary layer height are reflected in the PM_{10} altitude profiles. It can be concluded that the CWBL-derived pollutant altitude profiles exhibit the complexity of several factors that affect the pollutant behavior and distribution in the atmosphere, and provide the possibility for more accurate estimations of the urban or regional background levels.

INTRODUCTION

The studies dealing with coarse particulate matter (PM_{10}), its atmospheric reactions and transport pathways in urban environments have practical and scientific significance because it has been proven that these particles affect human life and the environment. Due to deteriorating air quality, urban residents in Serbia experience pollution-related health burdens on a daily basis (Stanišić Stojić et al, 2016a). Our previous studies published over the past few years were aimed at better understanding of the origin and the spatio-temporal distribution of coarse and fine aerosol fractions, as well as their relationship with mortality caused by circulatory, respiratory and malignant diseases in the Belgrade area (Stojić et al, 2016, Stanišić Stojić et al, 2016b, Perišić et al, 2017).

This study represents the first analysis of the PM_{10} altitude distribution in Belgrade and was performed using the new hybrid receptor model: concentration weighted boundary layer (CWBL). The three-dimensional (3D) versions of conventionally applied hybrid receptor models, potential source contribution function (Stojić and Stanišić Stojić, 2017, Kim et al, 2016) and concentration weighted trajectory (Stojić and Stanišić Stojić, 2017) are used for the identification of potential source regions as defined by longitude, latitude and altitude, without providing information on altitude distribution of pollutant concentrations. CWBL is designed to fill this gap and enable the analysis of pollutant vertical profile along the transport pathway and within the planetary boundary layer (PBL), or any height in general.

METHODOLOGY

The concentration weighted boundary layer is designed to provide information on pollutant altitude distribution along the transport pathway, and above the receptor site by coupling the planetary boundary layer (PBL) height with pollutant concentrations obtained at the receptor site. For the purpose of this study, we used PM_{10} concentrations measured from January 2011 to December 2015 at the New Belgrade urban site by the Institute of Public Health Belgrade and PBL heights at the receptor site calculated using GDAS1 (Global Data Assimilation System, 2017) and MeteoInfo software (Wang, 2014).

As explained in Stojić and Stanišić Stojić (2017), the estimated contribution of transport to pollutant concentrations measured at the receptor site is attributed to all volume cells within the PBL at each endpoint location along the corresponding trajectory that arrives at the receptor site (Figure 1, left). The calculation of the CWBL is illustrated in Figure 1, right. As can be seen, the CWBL value at each 2D grid cell is obtained by averaging the transport contribution to pollutant levels that correspond to all endpoints falling into the selected cell (i,j) within the corresponding PBL heights, as follows:

$$CWBL_{ijh} = mean(C^{e}_{l|_{PBLH^{e}_{ijl} \geq h}})$$

where C_l^e is the concentration attributed to each endpoint e of trajectory l, and $PBLH_{ijl}^e$ refers to the PBL height at each endpoint at the moment when the air parcel passed grid cell (i, j).

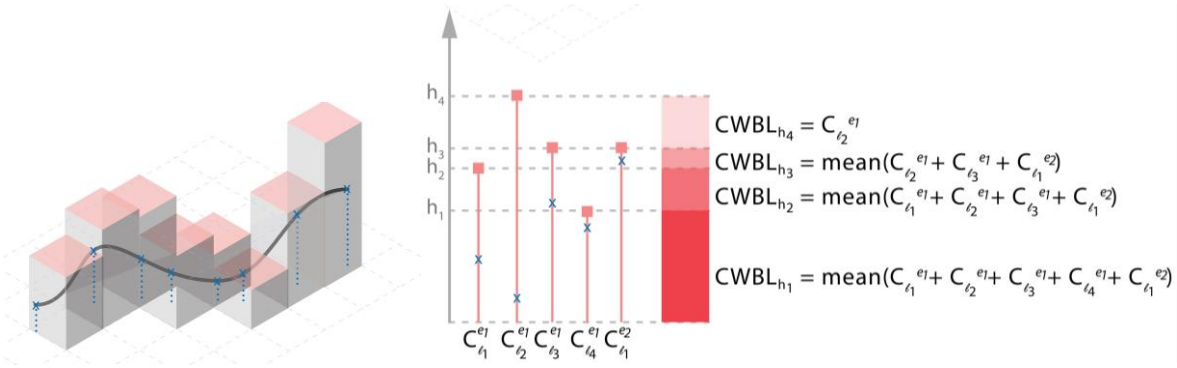

***Figure 1**. The concept of CWBL hybrid receptor model (left) and CWBL graphical illustration (right) (Stojić and Stanišić Stojić, 2017).*

RESULTS AND DISCUSSION

As defined by Stull (1988), the PBL represents a part of the troposphere that typically responds to surface emissions with a timescale of about 1 hour or less. Its height fluctuations, which can range from several tens to several thousands of meters, determine the volume of air where mixing controls the vertical dispersion of pollutants. According to our results, the variations of the seasonal PBL height were in the range from 800 m agl in winter to over 2000 m agl in summer, with an average value of 1600 m. The PBL height distribution for the measurement period is presented in Figure 2.

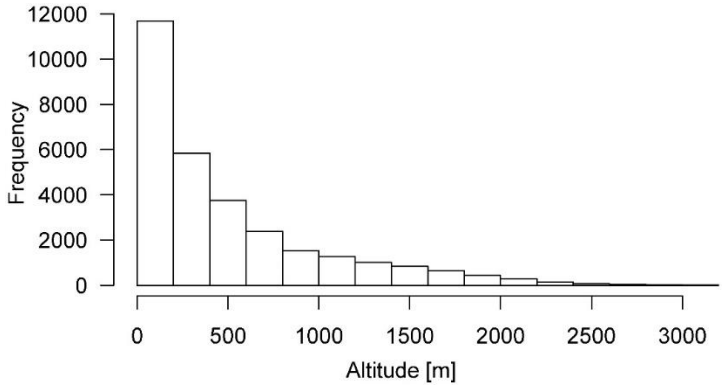

***Figure 2.** PBL height distribution obtained for the period from January 2011 to December 2015 in New Belgrade.*

As can be noted, PM_{10} concentrations remained high in the ground layer of the troposphere throughout the year and exhibited a rapid decline with height, reaching the minimum values for the highest PBL (Figures 2 and 3). These findings comply with the aerosol altitude distribution described by Stull (1988), as well as with the findings of some recent empirical studies. In the study of Tao et al. (2016), the altitude profile of $PM_{2.5}$ concentrations within the PBL was retrieved by a new measurement technology combining a charge-coupled device (CCD) side-scatter LIDAR with simultaneous ground level measurements. It has been shown that the empirically evidenced altitude distribution of $PM_{2.5}$ depicts a similar declining tendency in pollutant levels with height, with maximum values being registered in the near-surface layer.

In addition, the pollutant altitude profiles obtained using CWBL display the complexity of several factors that govern spatio-temporal PM_{10} distribution. As described by Bravo-Ananda et al. (2017), the PM_{10} concentrations in the ground layer are directly influenced by spatial distribution of emission sources and their activities, whereas the concentrations and residence time of particles in the upper levels are additionally affected by topography, meteorological conditions, as well as by complex atmospheric reactions, further leading to the formation of secondary aerosol species. Similarly, Wu et al. (2015), who examined the contributions of different emission sources to pollutant concentrations at a specific height within the PBL, have concluded that the near-ground height (5-10 m) pollutant concentrations are extensively influenced by anthropogenic emissions, whereas the concentrations at greater heights could be representative of urban or regional horizontal scales. The latter

observation might be important given the regional background cannot be measured directly and choosing the appropriate values is sometimes challenging because background concentrations are dependent on several factors, including regional anthropogenic and natural emissions, as well as long-range transport. In the study of Han et al. (2015), the nocturnal $PM_{2.5}$ concentrations at a height of 220 m were used for estimating the aerosol background concentrations associated with the regional-scale pollution within 100 km of the receptor site. This suggests that the pollutant altitude profiles obtained using CWBL can be useful for estimating the urban or regional background levels and their contributions to total pollutant concentrations.

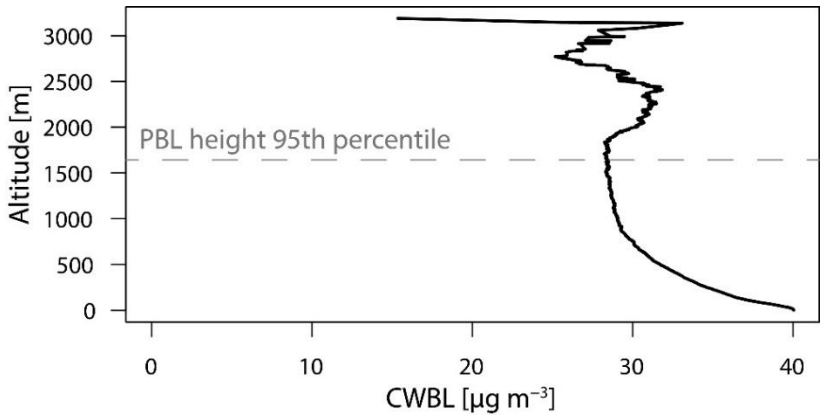

***Figure 3**. CWBL derived PM_{10} altitude distribution.*

According to Pecorari et al. (2013), the local source contributions account for 70% of total pollutant concentrations in summer, while the impact of regional sources becomes equally important during the cold season. However, the authors pointed out that the reported results were due to specific meteorological conditions in the research area. If the PM_{10} concentrations at the top of the PBL were representative of the background, it could be concluded that the major contribution to the total PM_{10} concentrations in Belgrade area was associated with an urban or regional background.

The impact of PBL height on pollution distribution, in the context of seasonal variations is illustrated in the Figure 4. As shown, the significant differences in winter and summer PBL heights is reflected in the PM_{10} altitude profiles. Although similar patterns within PBL were observed for all seasons, the gradient of pollutant concentrations was most pronounced in the cold season, whereas the lower spring and summer concentrations registered near the surface seem to remain more stable throughout the altitude profile due to increase in PBL height.

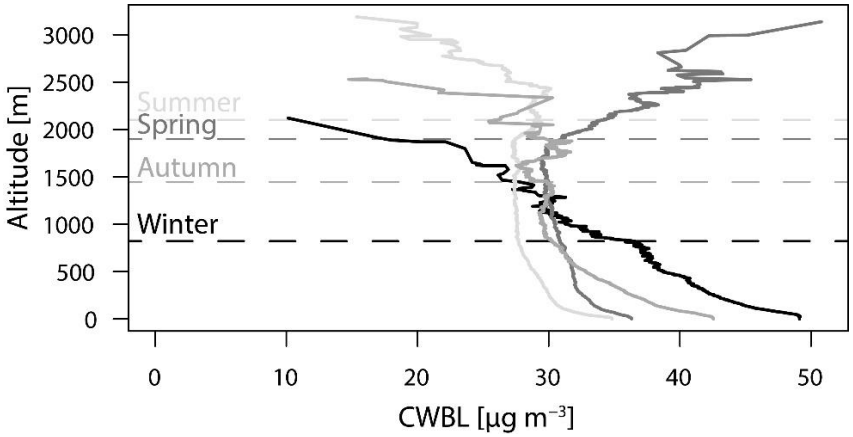

***Figure 4**. Seasonal variations of PM_{10} altitude distribution derived by CWBL. Dashed lines represent PBL height in the 95th percentiles.*

CONCLUSIONS

It can be concluded that the presented CWBL model can be successfully applied for analysing the altitude profile of PM_{10} concentrations. Moreover, this approach enables estimating the impact of the PBL height on pollutant distribution, especially in the context of diurnal or seasonal changes. High PM_{10} concentrations in the ground layer of the troposphere exhibit a rapid decrease with height, and the CWBL-obtained altitude distribution follows the findings of recent empirical studies. We strongly believe that future methodological enhancements of hybrid receptor models are of vital importance for better understanding the complex factors that govern spatio-temporal PM_{10} distribution and for more accurate estimates of regional background concentrations.

ACKNOWLEDGEMENTS

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8.2. ESTIMATION OF PM EMISSIONS FROM CRUISE SHIPS IN KOTOR BAY

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ABSTRACT

Cruise ship tourism has experienced massive growth in the last few years. However, some of the most popular cruise ship destinations are those which are the most sensitive to environmental disturbance. Cruise ships generate hundreds of tons of waste of every kind, including exhaust emission of pollutants and greenhouse gases as fossil fuels are burned. The city of Kotor, positioned at the end of Kotor Bay, is the leading cruising destination on the Montenegrin coast, and has experienced multiple advantages of the cruising tourism development. The emission of pollutants from cruise ships, along with emissions from road traffic, represent the majority of anthropogenic emissions of pollutants in the Bay area, since there are no large industrial plants. In this paper, the exhaust emission of PM from cruise ships in Kotor Bay was estimated by implementing a 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 sulphur 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 sulphur content of 2,67% m/m and the second when ships use only distilate marine fuel oils with maximum sulphur content of 0,1 % m/m. In high sulphur scenario, the 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 sulphur 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. A somewhat larger increase of estimated PM emission in this period (high sulphur scenario 20,3 % and low sulphur scenario 22,4 %) was measured than accounted for by cruise ship calls (for 16,4 %), which is considered mainly due to a change in the classes of cruise ships and retention times in port of Kotor area.

INTRODUCTION

The fast growth of the world merchant fleet directly affects natural resources and quality of life in coastal city areas and surroundings. Additionally, emission of different types of pollutants from merchant ships creates serious risks internationally, especially from airborne emissions. The consequences could be fatal in some cases, both for human health and ecosystems. In response to such a global problem, the International Maritime Organization (IMO) developed and adopted a set of regulations to limit and control air pollution from ships through Annex VI of the MARPOL Convention entitled “Regulations for the Prevention of Air Pollution from Ships”. Annex VI was adopted with an aim to limited emission of sulphur and nitrogen oxides, particulate matter, volatile organic compounds, ozone depleting substances and greenhouse gases which are the most serious compounds of exhaust emission from ship engines (IMO, 2009). Since there is no specific regulation adopted by IMOs Marine Environment Protection Committee (MEPC) which shall reduce and limit particle emissions the only efforts made in that sense are through adoption of Regulation 14 of MARPOL Convention titled ‘Sulphur oxides (SOX) and particulate matter’ in 2008 (Svensson, 2011).

Increased interest in cruising during the last thirty years illustrated statistically with an average annual passenger growth rate of approximately 7.2 % per year since 1980s (Pallis et al, 2016). In 2015, it was reported that approximately 23 million international passengers visited the most popular cruising attractions, which represents about 4 % more passengers in comparison to data from 2014 (Pallis et al, 2016). Growing interest in cruising led to development of around 1000 new cruise ship ports around the world (Pallis et al, 2016). In general, the most attractive regions are the most vulnerable too. Hundreds of tons of generated on-board waste on mega-cruise ships represents significant risks for ports of call and its surroundings. Exhaust emission creates one of the most hazardous waste types in consideration of about health and environmental impacts. In undeveloped industrial regions, this problem is even more significant.

Lately the Adriatic Sea region has become one of the top cruising destinations. Increasing numbers of cruise ships entering Adriatic ports each day create a lot of potential for economic development of the whole region, but as well as of positive effects, there are numerous negative implications such as poor quality of life, damage to human health and degradation of environment (Pallis et al, 2016).

The Port of Kotor, which is positioned at the end of the Boka Kotorska Bay is one of the 13 cruising ports located in the Adriatic Sea. The Old Town of Kotor and surrounding area are UNESCO-protected natural and cultural

monuments. Also, the specific and unique topography of Boka Kotorska Bay, which is quite similar to Norwegian fjords, is an interesting natural phenomenon for international tourists who come to visit this area (Fig.1).

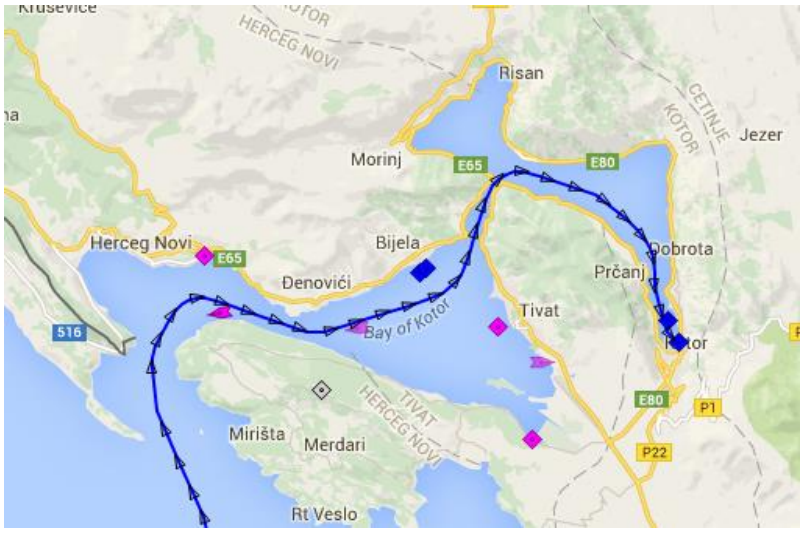

Figure 1: *Navigation route through Boka Kotorska Bay (Traffic, 2007)*

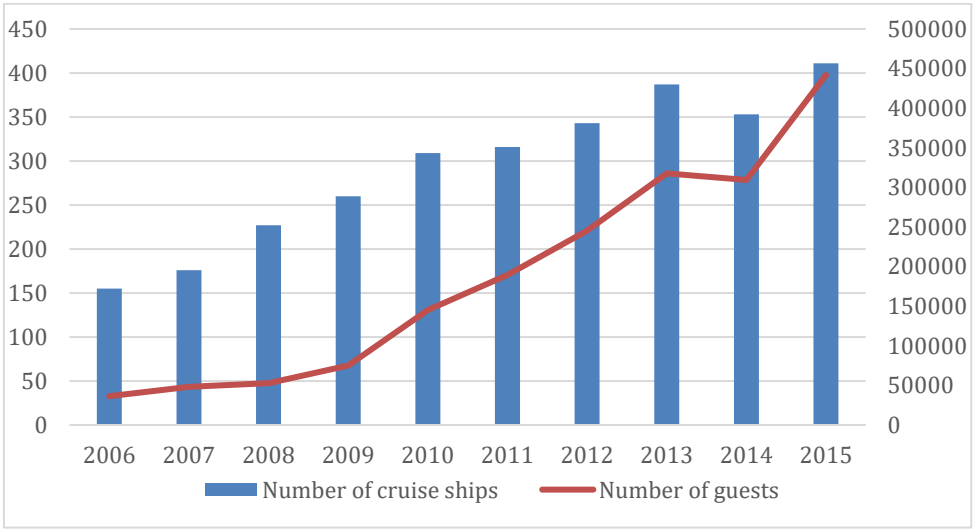

Figure 2: *Numerical indicators of increasing trends in cruise ships call and number of visitors in the Port of Kotor (Kotor, 2016)*

The Port of Kotor reported an increase in the number of cruise calls in 2015 by 16 % compared to 2014, and by 33 % compared to 2010, Fig. 2. At the same time, the port of Kotor recorded an increase in number of passengers by 43 % between 2014 and 2015, and by 204 % between 2010 and 2015, Fig. 2 (Pallis et al, 2016). These figures positioned the Port of Kotor as the third most popular cruise destination in Adriatic Sea region.

These points characterize the Port of Kotor as a highly active cruising destination. However, there are some issues related to rapid development of cruising on the local environment, including exhaust emission of pollutants while maneuvering and berthed. Exhaust emissions from cruise ships represent the majority of anthropogenic emissions of pollutants in this area, since there are no merchant ports and large industrial plants. This paper gives an estimation of annual particle emissions from cruise ships while entering the Boka Kotorska Bay.

METHODOLOGY

Nowadays, there is a global trend of significant effort focused on development and implementation of stringent legislation on airborne pollution. Even if regulatory measures are developed, it is crucial that they are well-established and effectively implemented. In this regard, supportive monitoring and quantification actions should be continually deployed to observe advantages and constraints of enforced requirements, either globally or nationally.

The EMEP/EEA guidebook is an inventory for estimation of emission of pollutants in the transportation sector. It represents a direct response to obligatory measures to estimate and report emissions according to UNECE Convention on Long-range Transboundary Air Pollution and the EU National Emission Ceilings Directive (Trozzi, 2010). This tool is based on bottom-up methodology for estimation different pollutant types on three levels of complexity (tiers) (EMEP/EEA, 2009).

'Tier 1' represents a simplified methodology which uses proposed emission factors chosen upon the scenario. 'Tier 2' includes technology-specific emission factors and may also include differentiation of activity data according to the operation complicity (EMEP/EEA, 2009). The most complex approach in calculation of emission of pollutants is 'Tier 3' which requires particular input information such as ship movement data, technical specifications of ships (engine type, size and technology, power installed or fuel use information, operation mode, load factor, time spent in different modes etc.) and specific emission factors grounded on scientific experience and knowledge (Trozzi, 2010).

Decision making about the exact methodology to be used is based on evidence of the complexity of the scenario and scope of information available. It is always more valuable to use 'Tier 2' or 'Tier 3', if possible. 'Tier 1' is recommended to be used when only statistical information on fuel consumption is known (Trozzi, 2010). Also, 'Tier 1' or 'Tier 2' are appropriate for analysis at a national levelwhile 'Tier 3' is more suitable for local analysis purposes (Carletti et al, 2012). Besides, this detailed approach includes individual ship analysis which provides more accurate final data.

However, there are numerous methods of gathering information which mostly involve comprehensive databases e.g. Lloyd's Register, IHS Markit etc., together with specific data received from national or local authorities, agencies, agents and other experts.

For example, the methodology used for this research comprises of a preparation phase (studying the situation in Port of Kotor and Boka Kotorska Bay, the total number of cruise ship calls, frequency of calls per month, duration of hoteling mode, hoteling/maneuvering ratio, technical specifications of ships - technology and fuel used, power output, etc.) and an estimation phase (experimental analysis of sulphur content and calculation of total emission per year). Further details will be presented in the elaboration of the case study.

The main differences between detailed and simplified methodologies for estimation of emission are mostly based upon the usage data on ship movement and technical characteristics. Accordingly, the calculations can be made with real-time data provided by Automatic Identification System (AIS), which mostly includes the ship's position, route, speed and navigation mode (Tichavska & Tovar, 2015) (Jalkanen et al, 2012) (Jalkanen et al, 2012). However, a detailed approach can also include the time category - as a duration of specific operation mode - where the exact information each moment is not necessary (Trozzi, 2010). Operational modes are generally divided as: cruising, maneuvering and hoteling.

For this paper, the technical database covers information such as gross tonnage, main engine type and technology, fuel oil type, load factor and specific movement data. Also, the implemented methodology included emission factors according to the specific technical and navigation details (Trozzi, 2010) (Carletti et al, 2012).

Total emissions for a round trip will be expressed as it follows (EMEP/EEA, Technical report No 9/2009, 2009):

$$Et = Ec + Em + Eh \quad \textbf{(1)}$$

In respect to previously explained 'Tier 3' implemented inventory can be described by following linear regression equation:

$$E_{i,j,m} = \sum_p \left[T_p \sum_e \left(P_e * LF_e * EF_{e,i,j,m,p} \right) \right] \quad \textbf{(2)}$$

where are:

E - total emission for round trip [tons],

T - time [hours],

P - engine nominal power [kW],

LF - engine load factor [%],

EF - emission factor [kg/kWh],

e - engine category,

i - type of pollutant,

j - engine type,

m - fuel type,

p - operational mode.

For the engine category, only main engine details are taken into account because data for auxiliary power are missing. For the analysis of cruise ships berthed and moored in Port of Kotor during 2014, data show that 59 % of main propulsion was diesel engine, diesel/electric 39 % and gas turbine 2 %. In 2015, 57 % was pure diesel while 41 % diesel/electric propulsion.

According to world's fleet data analysis, approximately 76.98 % of passenger ships were driven by medium-speed diesel engines using heavy fuel oils, 5.68 % were driven by medium-speed diesel engines using marine diesel or gas oils, 4.79 % were driven by gas turbines using marine diesel or gas oils, etc (Trozzi, 2010). Accordingly, it is assumed that main engine type is medium-speed diesel engine.

Regarding to the gross tonnage data, it is found that most of cruise ships entering Boka Kotorska Bay in 2014 were classified in categories of small and mid-size ships, while in 2015 in categories of a large resort and mid-size ships appeared as in Table 1. Cruise ships with less than 1000 GRT are not taken into account.

Table 1: *Categorization of cruise ships in the port of Kotor in 2014 and 2015 (Ward, 2015)*

Cruise ship category	**Gross Tonnage**	**Number of cruise ships Year 2014**	**Number of cruise ships Year 2015**
Boutique ship	1,000 - 5,000	15	14
Small ship	5,000 - 25,000	23	12
Mid-size ship	25,000 - 50,000	20	19
Large resort ship	> 50,000	11	21

Nominal power data were collected from different sources of information available online and other relevant publications (Ward, 2015).

Selection of proposed ship emission factors is based on the engine type, fuel used and specific engine operational mode. For the purposes of this paper, adequate emission factors are generated from different relevant publications (EMEP/EEA, Technical report No 9/2009, updated, 2011) (Entec, 2002). Emission factors implemented in calculation are given in Table 2.

Ship fuels are categorized in two main groups: residual marine fuel oils and distillate marine fuel oils. Nowadays, marine fuel oils account approximately 20% of total global fuel demand where about 72% are residual and 28% are distillate fuels (Pappos & Skjølsvik, 2002) (Entec, 2002).

In this respect, it is accepted that the considered engine systems on cruise ships use heavy fuel oil (HFO) or marine distillate oils (MDO). Sulphur content data differs between these two fuel categories, HFO contains much more sulphur than MDO.

Table 2: *Emission factors for medium-speed diesel engines in different operational modes for PM [g/kWh] (EMEP/EEA, Technical report No 9/2009, updated, 2011)*

Engine type / Fuel type	Mode	PM
Medium speed diesel / HFO	Cruising	0,8
	Maneuvering	2,4
	hoteling	2,4
Medium speed diesel / MDO	Cruising	0,3
	Maneuvering	0,9
	hoteling	0,9

Corresponding to the previously mentioned points, the majority of cruise ships generally use MDO with lower sulphur content during maneuvering and hoteling modes. In this research, the national situation is quite different since there are no stringent regulatory measures and laws that influence the implementation and monitoring activities regarding usage of low sulphur marine fuel oils in Montenegrin seashore areas and in ports. In that sense, both scenarios are taken into consideration as potentially occurring.

The specific study of Boka Kotorska Bay considerefd just two operational modes: maneuvering and hoteling. These two operational modes are divided into three phases as follows:

Maneuvering I, from the moment when cruise ship enters the Boka Kotorska Bay until the mooring or docking in the port of Kotor,

Hoteling, represents time spent at the dock or at anchor,

Maneuvering II, from the moment of departure from dock or anchor until the cruise ship leaves Boka Kotorska Bay and reaches cruising speed in open sea.

Cruising mode was not considered because of the specific character of the navigation operations in the Boka Kotorska Bay.

Load factor data and time category are accepted and defined in respect of the research results and experience of pilots engaged in the Port of Kotor.

It is accepted that the load factor for main engines in manoeuvering and hoteling is 20% (EMEP/EEA, Technical report No 9/2009, updated, 2011).

Time spent for hoteling mode is defined on the basis of ship's pre-notification of arrival or voyage schedule - with itineraries provided by the Port Authorities (Kotor, 2016). The manoeuvring mode comprisesapproximately 4 hours necessary for both phases according to the pilot’s statement.

RESULTS AND DISCUSSION

Calculations were conducted for each ship in the period from January to December 2014 and 2015. Estimations of total particle emissions from cruise ships in the Boka Kotorska Bay are given in Tables 3 and 4.

There was an increase in cruise ship calls by 16,43 % in 2015 compared to 2014. At the same time, increasing trends shows that in the first scenario of HFO usage particle emissions were of about 20,3 %, while in case that MDO is used increase of about 22,4 % is calculated.

From table data, it could be assumed that total exhaust emission increase from 2014 to 2015 and it will additionally contribute the amount if main marine fuel used is HFO with higher sulphur content.

In addition, general conclusion can be made if compare contribution to total exhaust emission of considered navigation modes hoteling and maneuvering, in following ratio: on 2014 – 4,66 while on 2015 – 4,27. This further means that majority of exhaust emission from cruise ships which entered Boka Kotorska Bay in last period is emitted in Port of Kotor area, in vicinity of Old Town Kotor which is under UNESCO protection.

***Table 3**: Estimation of total particle emissions from cruise ships in Boka Kotorska Bay for 2014 and 2015, in tons*

Year / Scenario	PM 10, PM 2.5
2014 / HFO	54,65
2014 / MDO	20,5
2015 / HFO	65,73
2015 / MDO	25,09

***Table 4**: Estimation of total particle emissions per month in 2014 and 2015, in tons*

Month (2014)	HFO	MDO
Jan	1,77	0,66
Feb	2,23	0,84
Mar	1,74	0,65
Apr	3,55	1,33
May	5,31	1,99
June	7,44	2,79
July	7,73	2,90
Aug	6,98	2,62
Sep	8,66	3,25
Oct	4,68	1,75
Nov	2,46	0,92
Dec	2,10	0,79

Month (2015)	HFO	MDO
Jan	1,49	0,56
Feb	2,23	0,84
Mar	1,68	0,63
Apr	2,81	1,05
May	8,26	3,10
June	9,26	3,47
July	7,87	2,95
Aug	8,38	3,14
Sep	9,02	3,38
Oct	7,42	2,78
Nov	4,61	1,73
Dec	2,70	1,01

CONCLUSION

Exhaust emission from cruise ships accounts for majority of anthropogenic emissions of pollutants in Boka Kotorska Bay. In this paper, concentrations of specific parameters of exhaust emission from cruise ships in the Bay area were calculated by implementing detailed emission estimation methodology, a Tier 3 EMEP/EEA air pollutant emission inventory. This inventory considers specific cruise ships data relating to the defined two operating modes, maneuvering and hoteling. According to the increased number of cruise ship calls for 16,43% in 2015 total emission of PM shows growing trends. Total particle emissions from cruise ships entering the Kotor Bay area in 2015 were estimated as 65,73 t y-1 in case of HFO and 25,09 t y-1 in case of MDO.

Also, retaining time at the anchor and at the berth in Port of Kotor is directly related on the increased results of PM. In high season period (May – October) identified amounts are even 6 times higher than in low season period. Major part of total emission of PM is concentrated in the Port of Kotor during the Hoteling operational mode.

All previously mentioned directly affects health issues and environmental issues in Kotor city area which led to serious long-term consequences and it requires much more attention to be paid on this crucial problematic in future.

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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 (~ 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 THE CREATION AND VALIDATION OF LUR BASED MAPS

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ABSTRACT

One of the most important aspects of high-resolution mapping using the land use regression (LUR) approach, is creation of explanatory variables with sufficient resolution. Buffer type variables typically require 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. This paper presents several helper tools developed for the purpose of the creation of high resolution LUR based maps for Belgrade targeting NO_2 and $PM_{2.5}$ pollutants. Provided the necessary input data is available, these tools allow for the relatively straightforward and speedy creation of air pollution maps for urban regions.

INTRODUCTION

In order to be able to accurately estimate exposure to certain air pollutants, or to plan routes which minimize exposure, it is necessary to have air pollution maps with a high spatial resolution. One of the first problems encountered is availability of air pollution data. If we limit ourselves to data obtained via monitoring instrumentation, the most typically encountered situation is that we have some combination of two types of data sets at our disposal: One set being a small number of high-quality measurements (for example data from state run networks) and the other set being larger number of measurements, however of lower quality in terms of reliability and total uncertainty (data from low cost sensor networks, or citizen science efforts). It is clear that neither of the two data sets is sufficient to create high resolution maps and that it is necessary to employ some kind of modelling. Modelling approaches that are typically used can be divided into physical modelling and statistical modelling: It is of course possible to use some combination of the two [1,2].

Unfortunately, the physical processes that govern air pollution phenomena are complex. Even if we possessed, and wanted to use, previously developed physics-based models, there still exists the often insurmountable issue of large amounts of data that need to be provided as an input for the model in order to achieve useful output. The problem of the underlying physical complexity can be partially addressed using statistical modelling which is only partially guided by the underlying physics, but does not try to model the full complexity of the physical processes. Among statistical modelling approaches, land use regression is one of the most prominent methods, and has been successfully used to model air pollution in selected urban environments, and more generally in the wide modelling of the air pollution phenomena in Europe. Land use regression (LUR) modelling as a geostatistical modelling technique for air pollution was pioneered by professor Briggs' team [1]. Once the model is established it can be used to deduce (spatially extrapolate) the concentration of air pollutants over the observed area, based on values of only predictor variables and not relying on any additional data sets. The process of developing a LUR model can be distilled to two major steps. The first step is to take measurements of air pollution in a certain, previously determined number of points (typically more than 30: a rough guide is about 10 measurement points per predictor, though the desirable number depends on the particular situation). Note that this data collection does not need to be conducted simultaneously, but it is necessary to simultaneously derive many possible predictor variables associated with each measurement point. The second step is to correlate the air pollutant to the predictor variables, and select the most important predictor variable(s) from an initial large set of all possible predictors. The predictive power of the model can be tested through the validation process. A popular method is to use the leave-one-out cross-validation method, since there are often insufficient data to use the training/test split approach typically used in machine learning. After these two steps have been performed, we have at our disposal a validated LUR model that can be further used. One of the common use cases of LUR created maps of air pollution is for exposure assessment at the population level. Similarly, route planning which minimizes exposure would be derived if final set of predictors in the model may be calculated in a larger area of interest. In this case it is also possible to create high resolution air pollution maps based on the LUR model.

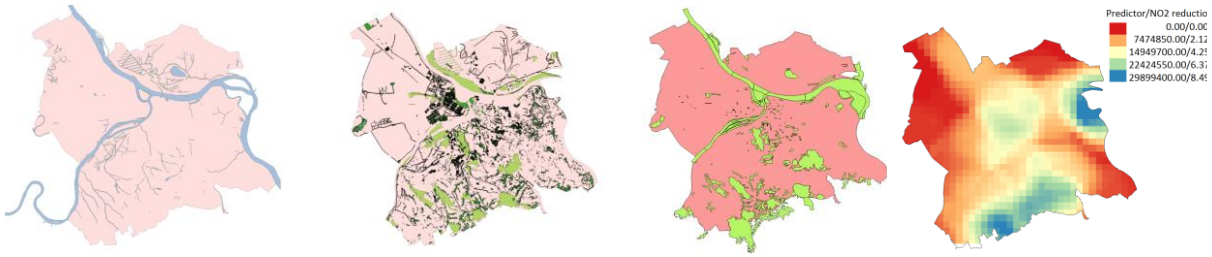
In the next section we will describe some of the typically used predictors in LUR approach. We will focus not on the physical interpretation of the predictors, but rather on the way in which the predictors are calculated, and describe the commonly followed steps in GIS software used to calculate predictors. Next, we will describe our modification of this commonly-used approach which allows for a much faster calculation of the predictor variables,

which are of the circular buffer type. We will also describe one possible approach to simple traffic modelling, since researchers often do not have access to, or enough resources to use, advanced traffic modelling software commonly used in city traffic planning. Finally, we will briefly analyse the obtained results and give guidance for future work.

CALCULATION OF PREDICTOR VARIABLES IN LUR MODELING

The link between the underlying physics and statistical modelling, that was mentioned earlier, can be achieved via classification of predictor variables according to the physical process the predictor variable may be associated with. The physical processes associated with air pollution can be classified as emission, dispersion, transport and deposition processes of particular air pollutants. Having this in mind, predictors such as total traffic in a buffer (e.g. daily average of number of vehicles), total length of different classes of roads in a buffer (e.g. total length of primary roads in a buffer) and similar can be associated with pollution emissions. It is also almost self-evident that the process of dispersion, that is related to the amount of air volume in certain area, can play an important role in the observed concentrations of air pollutants. This may be especially important for locations where buildings may create narrow street canyons, consequently pollution is diluted in a significantly smaller volume of air compared to more open spaces. Predictors that could model this phenomenon would, for example, include an average volume occupied by the buildings within a (3D) buffer. Predictor variables associated with the process of deposition typically take into account areas where emissions are not a dominant physical process, such as green spaces, recreational areas (e.g. the total area of parks in a buffer, total area of water surface in buffer etc.). Note however, that while the physical processes for all air pollution may be divided into emission, dispersion, transport and deposition, the exact details of these processes are very different for gaseous and particulate matter pollutants. A further way of avoiding purely statistically based reasoning is enforcement of the sign of the predictor variable in the regression equation. The sign of the predictor variable can either be specified in advance, or, as an alternative, either sign can be allowed in the algorithm, and then only models with clear physical meaning of predictor variable signs can be accepted. More generally predictors can model some known vector of air pollution creation, for example it is known that the type of domestic heating, in urban areas where there are numerous local heating boilers, can influence air quality and therefore it makes necessary to include variables such as number of houses connected to a district heating plant in a buffer.

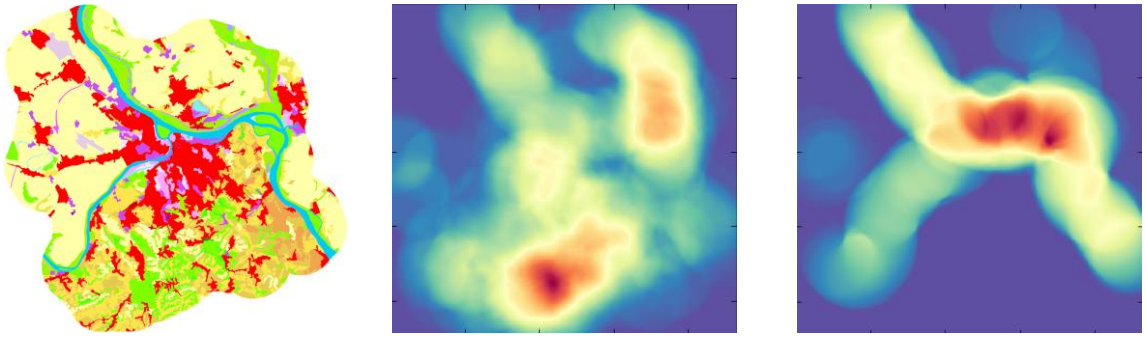
It is pertinent to note that the main, and basically the only difference between general multilinear modelling and LUR modelling is that the calculation of predictors for LUR requires the use of GIS software. The ways in which predictors are calculated, are the focus of this section. The most common GIS operations are buffer intersection and nearest distance to layer feature. Buffer-type variables typically induce most of the CPU and memory cost, and if the algorithm used is inherently slow, it will be very challenging (sometimes even impossible) to create high resolution explanatory variables. Starting from the input dataset, such as CORINE [3], buffer type variables, (e.g. total area of green spaces), are usually calculated in the following manner. The first step is to create a buffer layer with the appropriate buffer radius and appropriate buffer placement. In this step, in QGIS [4], it is also necessary to specify the polygon which will approximate the circular buffer. The problem encountered in this step is that we need very large number of buffers when making high resolution map.



(a) (b) (c) (d)

Figure 1. *Example of input layers for GIS analysis for area covered by Master plan of Belgrade a) detailed water surfaces b) detailed green surfaces c) simplified green and water surfaces with much less detailed d) low resolution layer illustrating NO2 reduction due to natural surfaces according to Wang LUR model*

The second step is to intersect each feature in the input layer with each buffer. This step creates a large temporary layer with size being proportional to the product of the number of buffers and number of input layer features. A feature count can hinder the computation (which can even prevent us from calculating the predictor variable since the software can crash, freeze, use all available disk space etc.). Common mitigation strategies include the reduction of grid resolution, simplification of input layers, subdivision of input layers or subdivision of buffer layers. The third step is to calculate the length or area of each intermediate layer feature and assign it (add it) to the appropriate grid points. This step finalizes the layer creation. While the procedures described above use common GIS tools, it has disadvantages, for certain combination of inputs, it can perform very poorly. During the development of the LUR model, values of predictor variables are only needed in the points where the measurements are taken, however, during map creation, the values of the predictor variables are needed at *each point of the map*. For example, if an urban area is 10 km by 10 km in size, and we want to produce an air pollution map based on LUR model with a 100 m spatial resolution, each predictor variables needs to be calculated at 10^4 points. The number of points in which predictors need to be calculated and feature count of layers directly increases the computational cost, which can very quickly overrun available resources. In such cases it is necessary to either decrease the map resolution or use simplified layers with smaller feature counts (see Figure 1 for illustrative example). Later in this paper we will propose and detail, simpler, more efficient algorithms specifically tailored for the creation of a *circular* buffer type explanatory variable.



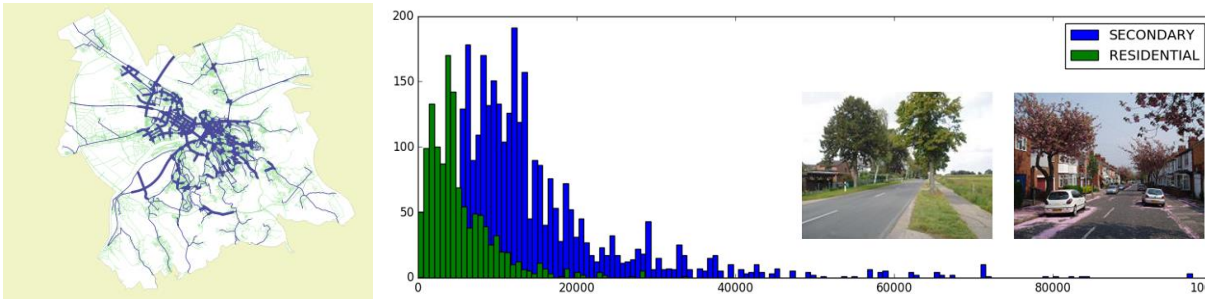
(a) (b) (c)

Figure 2. *a) CORINE input later for Belgrade master plan b) green areas in 5km buffer c) water areas in 5km buffer*

We have used the LUR model developed by Wang (2014) which was formulated using data from several hundred sites in Europe. In the Wang LUR model, predictors for NO2 were: the regional background concentration, traffic load in 50 m, road length in 1,000 m, natural and green in 5,000 m, traffic intensity on the nearest road and intercept (of the linear model). From this list of final predictor variables, it is immediately clear that the calculation of a 5,000 m buffer with fine resolution would be very computationally expensive, even more so using the previously described algorithm. While in principle and methodologically correct, it is not particularly well-suited for high resolution mapping. Similarly, buffer type predictors (traffic load in 50 m and road length in 1,000 m) are also very computationally expensive. Workflow for the proposed algorithm is the following. The first step is to mesh (triangular or linear mesh corresponding to either area or length within buffer calculation) the input layers. The second step is to iterate over each mesh element and add its area (or length) to all the grid points which are within the buffer radius distance from the centre of the 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. The algorithm for determining whether a grid point belongs to a circular buffer was inspired by a general ray object intersection algorithm [5] adapted to planar circle and grid line intersection. Figure 2 shows the CORINE input layer for Belgrade's master plan with a 5 km margin, 5 km buffer variable corresponding to green areas and water surfaces.

Another issue is the availability of the suitable traffic models. OpenStreetMap data proved very useful, providing a detailed categorization of roads (15 categories in Belgrade) sufficiently accurate for reasonable routing and captures the importance of the roads very well. Two traffic models were created and used. The first model was simpler and used an average daily median of the traffic on roads of a certain category, for example the median for a secondary road category for Belgrade, based on most recent traffic counting campaign, was approximately 11600 vehicles/day, while the median for residential roads was approximately 4000 vehicles/day (see Figure 3b). The second model was slightly more complex and used traffic counts where available. If there were no available data,

the procedure was to fall back on the first model. Figure 3 shows the distribution of the traffic counts for secondary and residential roads in Belgrade.



(a) (b)

Figure 3. *a) Road network in Belgrade (green - all roads, thin blue - public transport lines, thick blue - places of counting campaign 2015) b) Example of distribution of traffic counts for secondary and residential roads in Belgrade. X axis is in vehicles/day), while Y axis is number of road segments of certain category for which the counting campaign was conducted in 2015*

The above described input layers (in addition to several others) were used to calculate and validate NO2 mass concentration map for Belgrade based on Wang European model [6]. Since the Wang model wasn't developed using data for Belgrade, all available Belgrade data were suitable for validation. Since traffic data were from 2015, we used the available yearly averages for 2015, from a total of 19 locations from the Serbian Environmental Protection Agency and Public Health Institute Belgrade. Various metrics are possible for validation, and we opted for mean normalized gross error [%] and RMSE [ug/m3], which are shown for two traffic models in Table 1.

Table 1. *Validation of NO2 mass concentration map for Belgrade based on Wang European model, for two different traffic models*

	Traffic model	
	Median	Counts + fallback on Median
RMSE [ug/m3]	18.22	14.43
MNGE [%]	27.08	21.15

CONCLUSION

Several adaptations of the familiar GIS algorithms enabled a simple and efficient layer creation of LUR based maps. The 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. Future work will include use of a similar approach to test the possibility of the development of LUR maps for other pollutants, for example CO LUR map. Additionally, the possibility of the adaptation of $PM_{2.5}$ Wang model to include data from the temporary network of low-cost sensors (that was deployed in Belgrade during FP7 CITI-SENSE project campaigns) will be explored.

ACKNOWLEDGEMENTS

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9. EXPOSURE TO TOXIC AND INFECTIVE PM AGENTS

9.1. MICROBIOLOGICAL QUALITY OF AIR IN PHARMACEUTICAL LABORATORIES

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ABSTRACT

In special theatres such as pharmaceutical facilities, quality of indoor air is strictly regulated by contemporary standards. The aim of this study is to investigate, qualitatively and quantitatively, the microbiological quality of air, to compare the sensitivity of different sampling methods, and to investigate the efficacy of filter cleaning. Before filter cleaning, 44 samples were collected using an automatic impinging method, and 34 samples using a passive air sampling method. Before there were 93,18% positive impinged samples and 76,47% positive passive air samples. After filter cleaning, positive samples significantly decreased, to 23,81% and 8,70%, respectively. The number of colony forming units (cfu/m^3) was significantly higher in samples collected by the impinging method both before and after filter cleaning (13,84 cfu/m^3 in positive impinged samples before vs. 0,38 cfu/m^3 after filter cleaning, i.e. 2,97 cfu/m^3 in positive passive air technique samples before vs. 0,13 cfu/m^3 after filter cleaning). Before filter cleaning, the most dominant were *Micrococcus spp*, *Staphylococcus epidermidis*, and *Bacillus spp*. After filter cleaning, only *Sarcina spp* and *Staphylococcus saprophyticus* remained, and formed very poor colonies. The microbiological quality of air in the investigated facility was of an acceptable level. Not one pathogenic bacterium was isolated, and in all samples number of cfu/m^3 was under 100. The automatic impinging method was more sensitive compared to the passive method. Filter cleaning provides efficient improving of microbiological quality of air in controlled spaces.

INTRODUCTION

The microbial indoor air pollutants of relevance to health are widely heterogeneous, ranging from pollen and spores of plants coming mainly from outdoors, to bacteria, fungi, algae and some protozoa emitted outdoors or indoors. They also include a wide variety of microbes and allergens that spread from person to person. There is strong evidence regarding the hazards posed by several biological agents that pollute indoor air, however, the WHO working group convened in October 2006, concluded that the individual species of microbes and other biological agents that are responsible for health effects cannot be identified. This is due to the fact that people are often exposed to multiple agents simultaneously, to complexities in the accurate estimation of exposure and to the large numbers of symptoms and health outcomes due to exposure. The exceptions include some common allergies, which can be attributed to specific agents, such as house-dust mites and pets (WHO, 2009).

In April 2016, the German Society of Hygiene, Environmental Medicine and Preventative Medicine (Gesellschaft für Hygiene, Umweltmedizin und Präventivmedizin (GHUP)) together with other scientific medical societies, German and Austrian medical societies, the physician unions and experts provided an AWMF (Association of the Scientific Medical Societies) guideline: ”Medical diagnostics for indoor mold exposure” (Hurras et al, 2017).

The proliferation of air-diffused microorganisms inside public buildings, such as schools and particularly hospitals, is often indicated as a possible health risk (Grisoli et al, 2009). The air inhaled by people is abundantly populated with microorganisms, also are called bioaerosols. Bioaerosols are a colloidal suspension, formed by liquid droplets and particles of solid matter in the air, whose components contain or have attached to them viruses, fungal spores and conidia, bacterial endospores, plant pollen and fragments of plant tissues. They account for 5-34 % of indoor air pollution (Gizaw Z et al, 2016).

Clean rooms, and associated controlled environments, provide for the control of contamination of air and, if appropriate, surfaces, to levels considered appropriate for accomplishing contamination-sensitive activities. Contamination control can be beneficial for the protection of products, or process integrity, in applications in such industries as aerospace, microelectronics, pharmaceuticals, medical devices, healthcare and food (The British Standards Institution 2016). Safety requirements for laboratory ventilation require a relatively high air flow rate and the use of 100% fresh air (Foster and Robertson 2001).

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 a total number of bacteria below 100 cfu/m^3. The microbiological quality of air is provided by special devices in these controlled spaces. The isolation and identification of bacteria is difficult, and the results are often dependent on the method of sampling and detection (Karkkainen et al, 2010, Pietarinen et al, 2008, Radakovic et al, 2014).

METHODOLOGY

The aim of this study is to investigate qualitatively and quantitatively the microbiological quality of air in a controlled space, to compare the sensitivity of different sampling methods, and to investigate the efficacy of filter cleaning. The conditions in the pharmaceutical theatre were as follows: air in an ISO8 class controlled space passes through an EU9 class prefilter, then H13 class HEPA filters. This space is over-pressurized, and the pressure is balanced according to the specific activities occurring, with a determined number of air changes. The ratio of fresh air is 100%. Temperatures and relative air humidity are monitored and regulated within prerequisite ranges (22±3 °C, and 45±15% respectively). In a pharmaceutical facility before filter cleaning, 44 samples were collected using the automatic impinging method, and 34 samples using a passive air sampling technique, which was the settle plate method (Petri dish exposed for 30 minutes). The samples were analysed after 48 h incubation at 37° C, following a 48 h at 20° C, and isolation and identification was performed using BBL crystals.

RESULTS AND DISCUSSION

Before filter cleaning, there were 41 (93,18%) positive impinged samples and 26 (76,47%) positive passive air samples. After filter cleaning, the number of positive samples significantly decreased, either collected by impingement or by passive air sampling method, to 5 (23,81%) and 2 (8,70%), respectively (Figure 1).

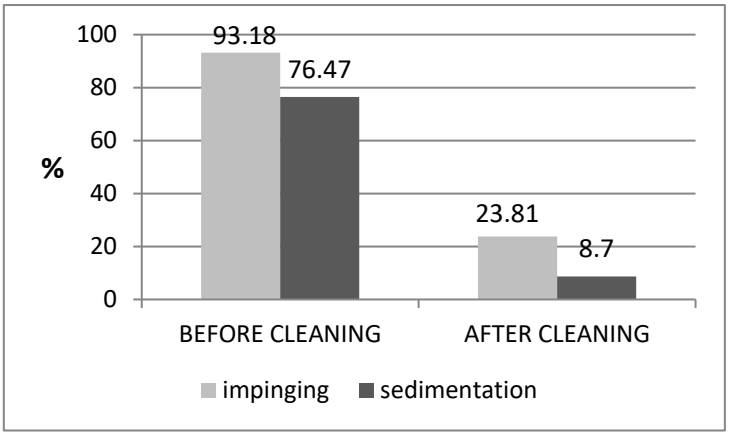

Figure 1. *Ratio of positive samples before and after filter cleaning*

The number of colony forming units (cfu/m^3) was also significantly higher in the samples collected by the impingment method as compared to the passive air sampling method, both before and after filter cleaning (13,84 cfu/m^3 in positive impinged samples before vs. 0,38 cfu/m^3 after filter cleaning, i.e. 2,97 cfu/m^3 in positive passive air technique samples before vs. 0,13 cfu/m^3 after filter cleaning) (Figure 2). The highest cfu/m^3 number was 80 and was recorded by the impingment method before filter cleaning.

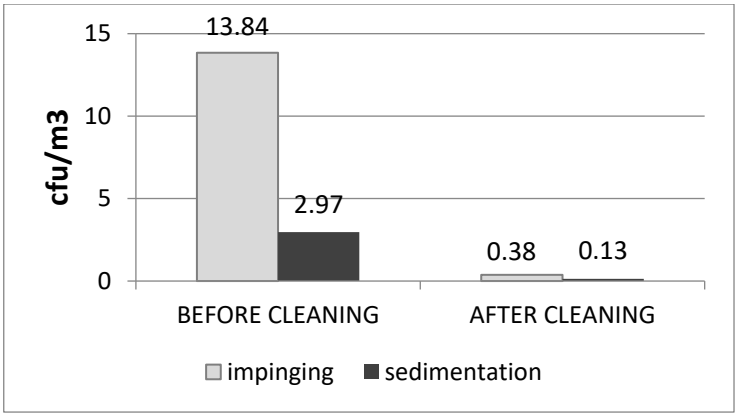

Figure 2. *Average number of colonies before and after filter cleaning*

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 impinging and 21 positive samples by open air technique), then *Staphylococcus epidermidis* (in 27 and 1 sample respectively), and *Bacillus spp* (in 10 and 1 sample respectively) (Figure 3).

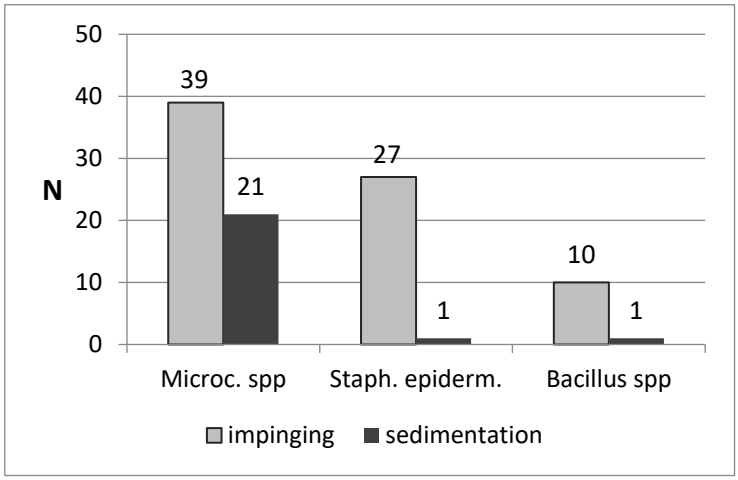

Figure 3. *Isolated bacteria types*

In some samples more than one bacterium were identified. After filter cleaning, only *Sarcina spp* and *Staphylococcus saprophyticus* remained, and formed very poor colonies.

The problem of microbial indoor air quality, as well as the efficiency of the air-condition systems, were assessed by several studies conducted in various environments such as high school and college gymnasia, university classrooms, offices, industries, shopping centres. The overall microbial contamination was seasonally dependent, for the highest values of fungal counts in gymnasia were observed between April and October, nevertheless, students were exposed to relatively low concentrations of airborne micro-organisms (Dacarro et al, 2003). Other research conducted in some university classrooms also showed very little contamination as measured by The Global Index of Microbial Contamination (GIMC per cubic metre), and the results were related different phases of air treatment, which underlines the efficiency of the system and of the maintenance protocols (Grisoli et al, 2012).

In a large study conducted in Brazil for the period of 1998 to 2002, the microbial contamination levels in 3060 samples of offices, hospitals, industries, and shopping centres were evaluated. Considering each environment, 94,3 to 99,4% of the samples were within the allowed limit for Brazil (750 CFU/m^3). The temperature and air humidity had no significant influence on the sample's dispersion patterns (Nunes et al, 2005).

Buildings equipped with heating, ventilation and air conditioning (HVAC) systems, showed a medium-low level of bacterial contamination (50- 500 CFU/m^3*)* in the indoor air. *Staphylococcus* and *Micrococcus* were the most commonly found genera, likely due to human presence (Bonetta et al, 2010).

Although these results indicate a good overall microbial quality of indoor air, and the benefits of using ventilation systems, some clean spaces, such as hospitals, laboratories, and pharmaceutical facilities require specific conditions. The hospitals' results showed an average of 200 CFU/m^3 in Brazil (Nunes et al, 2005), while in Warszawa, the levels of air contamination in 28 investigated medical facilities were between 0 and 23 CFU/m^3, with a prevalence of *Acinetobacter* spp. and coagulase - negative *Staphylococci* (Bielawska-Drozd et al, 2017).

Other studies performed in African and Asian hospitals showed higher levels of microbial contamination in the indoor air: 318-608 CFU/m^3, with a predominance of *Staphylococcus spp* (Luksamijarulkul et al, 2014, Luksamijarulkul et al, 2015), *Staphylococcus aureus*, *Staphylococcus epidermidis*, *Bacillus cereus*, *Bacillus* sp., *Serratia marcescens* and *Micrococcus* sp. *Staphylococcus aureus* (91,3%) and *Staphylococcus epidermidis*, especially during the wet season (Ekhaise et Ogboghodo, 2011, Agbagwa et Onyemaechi, 2014). However, the major factor that contributes poor indoor air quality in medical facilities is inadequate ventilation systems, and presence of common bacterial species *Gemella morbillorum* in such environments (Hazrin et al, 2015).

Conditions in the pharmaceutical clean room environment are established according to the ISO Class 8 standard, which is present in our study. The average indoor air temperature in the laboratory in our research was within the recommended acceptable range (22,5-26 ºC in the ASHRAE Standard 55) (ANSI/ASHRAE Standard 55, 2004), as well as the humidity level (below the maximum allowable value of 70%). Favorable conditions for growth and multiplication of bacteria like temperature (26,5-29,5 ºC) and humidity (65,5-85%) (Gizaw et al 2016). Microbial contamination was also within the recommended limits for the monitoring of clean areas (Commission Europeenne, 2008).

Even before filter cleaning, the average number of colony-forming units in our investigation was below the allowed maximum. The impingment method enabled the detection of higher levels of bacterial contamination compared to the open plate technique. The latter method is common in such investigations, and considered sufficiently precise (Yassin et Almouqatean, 2010). The same types of saprophytic bacteria were identified regardless of the sampling method: *Micrococcus spp* and *Staphylococcus epidermidis* were predominant before filter cleaning, while after cleaning only *Sarcina spp* and *Staphylococcus saprophyticus* remained in small number of samples, indicating that the cleaning methods were efficient in decreasing the bacterial contamination of indoor air.

In their study of bacterial diversity in the indoor air of pharmaceutical environments, Park and coworkers showed the predominance of *Micrococcus* and *Staphycococcus* when analysed using conventional culture-based methods, which is similar to our results. However, they reported a large discrepancy between the culture-based and pyrosequencing analysis of the same samples, which indicated that *Proteobacteria* was the most abundant group at phylum level, followed by *Actinobacteria* and *Firmicutes* (Park et al, 2013). In addition, the same authors in their later study identified a proteobacterial strain R1-3T affiliated to the genus *Sphingomonas*. (Park et al, 2015). The authors conclude that pyrosequencing analysis provides insight into novel bacterial diversity, which is somewhat different from the results provided by the common culture-based method.

CONCLUSIONS

According to the results, the microbiological quality of air in the investigated facility is of an acceptable level, even before filter cleaning. Not one pathogenic bacterium was isolated, and in all samples number of cfu/m^3 was under 100. The automatic impingment method was more sensitive when compared to passive sedimentation. Filter cleaning efficiently improves the microbiological quality of air in controlled spaces.

ACKNOWLEDGEMENTS

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9.2. DEVELOPMENT OF AN EVIDENCE BASE FOR RESPIRATOR SELECTION FOR BIOAEROSOLS

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ABSTRACT

Biological aerosol hazards are frequently encountered but usually lack exposure limits. Exposure measurement is often not straightforward, which complicates selection of appropriate respiratory protective equipment. To address this, in its 2011 edition, Canadian Standard CSA Z94.4 included guidance for selection of respirators for biological aerosols based on a control banding method. Extensive work was undertaken for the 2018 update of this standard. Inputs from a user survey were analysed to determine workplace practices, sources of guidance and compliance with them, and a comprehensive literature survey based on nine key questions was undertaken to develop an evidence base to direction refinement of the methodology. Relevant studies were assessed through an established critical appraisal process as used for medical interventions. The difficulty of controlling adequate wear compliance and consistent bioaerosol exposure contributed to the conclusion that there were no studies conducted to generate statistically significant evidence to warrant changing the 2011 methodology.

BACKGROUND

Biological aerosols are prevalent both in healthcare-related and many general workplaces. Very few such aerosols have documented exposure limits, and selection of protective equipment is usually based on expert opinion. A method for selection of respiratory protection for airborne biological particulate matter based on control banding was 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.

This selection method uses a semi-quantitative assessment of critical exposure and then 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 exposure situations. Since issue of this standard, a similar protocol with slight differences has been developed and adopted by the Province of Québec.

Recent work examined the need to update the Canadian Standard by surveying current users to and by seeking an evidence base to identify needed changes, improve selection guidance for the 2018 update.

USER SURVEY

A wide-ranging survey was undertaken, both 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. This included not only healthcare facilities, but laboratories, veterinary operations, training, consulting, regulatory and some general industry organisations. There were 28 questions covering responder demographics in location and employer type, the nature 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. The survey was deployed in both English and French languages and included multiple-choice selection and free text responses. The responses were analysed so that cross-correlation plots could be created, and the free text responses were also classified to yield further information.

A total of 414 responses was received, 191 in English, 233 in French. The survey was useful in many areas to provide information on:

- General knowledge of bioaerosols and the level of understanding of the current standard,
- Adherence to its requirements such as training, fit testing, cleaning and maintenance,

- Deployment of applicable training and fit testing in key sectors such as healthcare'
- Correlation of respiratory protection usage with the hazard level of bioaerosols present in workplaces,
- Sources and types of information used for guidance.

The outcomes were used to upgrade information in the standard and provide relevant worked examples of respiratory selection as well as to build ancillary information documents on critical respirator programme requirements and training materials.

One example of useful information was to identify the reported levels of respiratory protection in use in comparison with the bioaerosol types present in workplaces. Bioaerosols were classified by the US National Institutes of Health risk grouping level on a 1 to 4 scale where data were available, or as non-specified aerosols or fluids. Results are summarized in Table 1.

Table 1: *Summary of Numbers of Responses for the Highest Equipment Assigned Protection Factor Used for Various Biological Agents*

Type of Biological Agent Reported Present*	Highest Reported Assigned Protection Factor of Respiratory Protection Used					
	1**	10	25	100	1,000	10,000
RG1		1	1			
RG2		29	7	8	2	2
RG3		28	5	8	1	2
RG4		2		1		
Bioaerosols not otherwise specified	2	55	4	9	4	10
Biological fluids	6	58	6	15	2	5
Don't Know	6	45	1	5	1	2

*RG1 etc. is the US National Institutes of Health Risk Grouping (RG1 lowest risk to RG4 highest risk)

** An assigned protection factor of 1 means that no effective respiratory protection was in use.

The reported data show a prevalence of usage of equipment with a protection factor of 10, which corresponds with filtering facepiece or half-mask elastomeric types of respiratory protection. In some cases, much higher levels of protection were used than required by the type of agent.

A further observation from the outcomes highlighted the origin and type of guidance information used in workplaces. There were 225 responses to this question, and the cited information sources could be classified into those which were based on infection control guidance, and those based on occupational hygiene guidance. The division of information sources for healthcare and non-healthcare responses is shown in Table 2. Infection control guidance generally considers that there are discrete forms of biological aerosol – which either remain airborne or settle quickly according to size. Occupational health guidance generally considers that aerosols responsible for infection transmission can be a wide spectrum of sizes, subject to evaporation and possibly remaining for long durations in air and dispersing over distances. These differing rationales significantly affect respiratory protection selection decisions and potential adverse health effects. Internal guidance alone, where reported, did not specify its basis.

Table 2: *Summary of Types of Sources of Guidance Information Used*

Type of Guidance	Healthcare	Non-Healthcare
Occupational Health / Internal Guidance	20.3%	46.3%
Infection Control / Internal Guidance	58.0%	25.6%
Both Occupational Health and Infection Control Guidance	8.4%	11.0%
Internal Guidance Only	13.3%	17.1%

CRITICAL APPRAISAL OF THE LITERATURE

An evidence base to support respirator selection guidance was sought through a comprehensive literature search to establish supporting data for nine key questions. These addressed workplace practices, selection rationales and studies of aerosol mobility, and are summarized in Table 3 with the conclusions from the appraisal and associated certainty concluded from the data. A total of 435 papers were obtained through searches at libraries of CSA committee members. These were reviewed for relevance to the specific questions by an expert committee, and about half passed to an external organisation (Medlior Inc., Calgary, Alberta Canada) for critical appraisal. The Infection Prevention and Control Guidelines Critical Appraisal Tool Kit used by the Public Health Agency of Canada was adopted for this appraisal. Application of criteria to rule out unacceptable studies for appraisal filtered the number of papers down to 27 studies to address the key questions.

Table 3 – *Key Questions and Summarized Critical Appraisal Outcomes*

Question		Conclusion	Certainty
To Reduce Chance of Infection:			
1	Does wearing exposure-appropriate respiratory protection reduce the prevalence of adverse health effects* in workers exposed to bioaerosols/infectious agents?	Randomized control trials comparing prevalence of infection between workers wearing surgical masks or N95 respirators had mixed findings. Issues were selection and information bias, group comparability and control of confounding issues. Systematic reviews noted that a lack of high-quality data in this area to limits conclusions	Poor quality of data, selection and control of compliance
2	Does the level of wear compliance (as regards %wear time, improper practices) of respirator users in contaminated environments change the prevalence of adverse health effects in exposed workers?	Lack of compliance was a major issue, good compliance reduces infection rate	Good supporting data
3	Does the ventilation efficiency of a location in which exposure is possible affect exposure duration and concentration and the selection of respiratory protection for workers exposed to bioaerosols/infectious agents?	No Acceptable Studies	

4	Does the position of the emission source with respect to the exposed individual affect prevalence of infection/contamination in exposed workers?	No Acceptable Studies	
6	Does the bioaerosol/infectious agent generation process (rate, particle size, form, aspect ratio, dry or wet) affect the prevalence of adverse health effects (as before) in in exposed workers?	No studies were identified meeting the pre-defined inclusion criteria.	
8	Does repeated donning/doffing of exposure-appropriate respiratory protection influence the prevalence of adverse health effects in exposed workers?	Workplace studies observed low compliance with proper donning/doffing procedures, and continuous use more efficacious than intermittent N95 respirator usage	Poor donning/doffing frequently observed
9	Does the type of exposure-appropriate respiratory protection influence the prevalence of adverse health effects in exposed workers?	No data were available in studies to distinguish types	

Affecting Dispersion and Persistence?			
5	Does the initial particle size range/ generation rate affect the dispersion/persistence of bioaerosols/infectious agents in workplaces or simulated environments in space and time?	Lab and field studies provide data to confirm distribution based on particle size and generation rate	Various consistency issues in lab and field studies
Affecting Respirator Selection?			
7	Does the size distribution of an aerosol affect respirator selection?	Several laboratory studies support of impact of particle size on respirator efficiency, but selection depends more on other factors	Lab Studies provide better supporting information

*Adverse health effects include: infection, contamination, colonization, sensitization, toxic response or other adverse response)

Although this was a very comprehensive study, the conclusion of the critical appraisal was that there were no sufficiently technically significant studies of adequately compliant respirator usage to warrant changing the selection protocol used in the 2011 version of the Canadian standard. It was noted that some common confounding factors for comparing the effects of respirator usage versus non-usage for preventing infection in workplace settings were:

- Accurate reporting of usage duration and environment,
- Proper fit and wear compliance,
- Multiple exposure environments,
- Variable exposure over time and across population,
- No control of infection acquired outside the workplace.

OTHER INFORMATION ADDED TO THE STANDARD UPDATE:

Bioaerosol Concentration Measurements: studies measuring 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 into the database in the guidance.

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

STANDARD UPDATE:

The updated standard was issued in 2018. Survey data and observations from some of the published studies were used to improve the description of the methodology and associated guidance. Twenty scenarios were included to provide worked selection examples to aid users, and correspondence with existing guidance demonstrated where available. The literature studies 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 guidance information around the selection protocol combine to improve the guidance of workers and the selection of respiratory protection for biological aerosols, and so contribute to the reduction of avoidable adverse health effects.

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9.3. AEROSOL TRANSMISSION OF INFECTIVE AGENTS: POSSIBLE IMPACTS

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ABSTRACT

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. The particle diameter, delineates between airborne (≤5μm) and droplet (>5μm) transmission (Fernstrom&Goldblatt, 2013). Infective aerosol particles up to 100 μm 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 biological (B) agents could be transmitted by aerosols (smallpox, variola, Ebola, Marburg, influenza, SARS, anthrax etc.) (Ristanovic, 2015).

Key words: infective agents, aerosols, particles, transmission

INTRODUCTION:

Infectious particles may be generated from infectious persons and animals, heating, ventilation, air conditioning systems, cooling water towers, ceiling tiles, carpets and transmitted to susceptible individuals by airborne, contact and droplet pathways. The droplet and airborne particles are usually heterogeneous consisting of mixtures of cells, spores and viruses carried by both respiratory secretions and inert particles (e.g., dust) (Cole & Cook, 1998). Airborne pathogens - viruses, bacteria, and fungal spores - may disperse over great geographic distances by air and come into contact with sensitive individuals (Mohr, 2005). The infective particle diameter delineates between airborne (≤5μm) and droplet (>5μm) transmission (Fernstrom & Goldblatt, 2013). The range of particle sizes in an infectious aerosol depends on a number of factors including the mechanism of aerosol generation and the liquid content and viscosity of the aerosolized fluid (Duguid,1946). If the infective aerosol particles are 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, healthcare facilities, office buildings, travel and leisure settings - airplanes, ships, hotels and resorts (Roy, 2010) as well as for biodefence because many possible biological (B) agents could be transmitted by aerosols (smallpox, variola, Ebola, Marburg, influenza, SARS, anthrax etc.). The knowledge in this field was misused during the Cold War era for weaponization of potential B agents. (Ristanovic, 2015). Therefore, it is particularly important to understand the basic principles of aerobiology and physics by which infectious particles can be transmitted via airborne and droplet means, as this has an impact on infection transmission control and resulting consequences of infection spread, affecting public health, the economy, tourism, industry, politics, security and biodefence.

AEROBIOLOGICAL AND MICROBIOLOGICAL BASIS OF INFECTIVE AGENTS TRANSMISSION

Droplet infection is transferred by particles that are likely to settle to a surface quickly, making contact with nearby susceptible targets' respiratory tract, eyes, mouth, nasal passages (Wells, 1934). In contrast, airborne transmission is a characteristic of smaller particles that remain in air for a long period, exposing a higher number of susceptible individuals at a much greater distance from the infection source, depending on the environmental factors (e.g. meteorological conditions, pressure, etc.) (Gralton et al, 2011). As already mentioned, a particle's size is of central importance in determining whether it becomes and remains airborne (Nazaroff, 2004), although even large-sized droplets (up to 100 μm) can remain suspended in air for long periods when the velocity of air moving throughout a room exceeds the terminal settling particle velocity (Cole & Cook, 1998). The rate at which particles desiccate is also important: particles up to 50 μm can desiccate completely within 0.5 seconds upon expulsion into the air, since the smaller and lighter infectious particles will remain airborne longer (Fernstrom & Goldblatt, 2013).

Particles carrying infectious microorganisms can disperse by airborne or droplet transmission, or by both manners simultaneously (Gralton et al, 2011). As no single way is used by small-particle aerosols causing virus transmission, the concept of aerosol transmission was proposed and experimentally confirmed using various pathogens such as

Ebola virus, dangerous pathogens and possible bioweapons, SARS CoV (severe acute respiratory syndrome coronavirus) and Noroviruses (Jones & Brosseau, 2015).

An aerosol is a collection of solid or liquid particles suspended in a gas (Hinds, 1999). The ability of the aerosol to cause an infection depends on the concentration of the microorganism, the human infectious dose, and the virulence of the organism (Cole & Cook, 1998). Devastating diseases can be acquired through exposure to very low levels of infectious particles: even a single organism is infective dose for *Francisella tularensis* - a dangerous pathogen and potential class A bio-weapon. The infectious dose for influenza virus is also very low (Blachere et al, 2009), as well as for the tuberculosis agent - *Mycobacterium tuberculosis*, whose viable bacilli survive in air over tens of minutes. Infection transmission has been demonstrated by experimental animals with bacilli carried in air from tuberculosis hospital wards (Clark et al, 2011, Jensen et al, 2005).

Aerosols can be generated in many bodily processes and medical procedures, and the aerosol particles may contain pathogens in conjunction with body fluids. The several well-known primary sources of infectious particles are: vomiting, sneezing, coughing, and talking as well as toilet water aerosolization from flushing (Thompson et al, 2009). A single sneeze generates as many as 40,000 large droplet particles, most of them desiccate immediately into small, infectious droplet nuclei, with 80% of the particles being smaller than 100 μm (Jennison, 1942). When talking, one person could generate 36 particles per 100 words, and 710 per cough, depending on the frequency. While a single sneeze may produce more total infectious particles than a cough (Morrow,1980), coughing is, for example, more frequent than sneezing in the case of Coxsackievirus A infection (Couch et al,1966).

Infectious individuals are not always the immediate source of airborne infectious particles. People spend considerable time in office buildings, for example, exposed to various non-human naturally-occuring airborne pathogens (e.g., moulds, toxins, pollen, pet dander, pest droppings) associated with disease, toxicoses, and allergic diseases. An exposure to indoor biological air pollutants has been associated with "sick building syndrome," a set of non-specific mainly upper-respiratory symptoms, headaches, fatigue, and rash linked to time spent in a building, without identifiction of specific causative agent (Radakovic et al, 2014).

Some studies suggest that particles over 6 μm tend to deposit mainly in the upper airway, while particles under 2 μm deposit mainly in the alveolar region (Darquenne, 2012). Others conclude that particles under 10 μm can penetrate deeper into the respiratory tract, and particles over 10 μm are less likely to penetrate into the lower pulmonary region (Radakovic et al, 2014). Deposition regions of the respiratory tract for various particle sizes are shown in figure 1. Aerosol transmission may also occur among pathogens that cause infections in parts of the body other than the respiratory tract, and respiratory pathogens may also reach the respiratory tract through other portals (Bitko et al, 2007). The respiratory tract may serve as a portal of entry to the gastrointestinal tract, or pathogens in the respiratory tract may overtake and subvert immune cells and processes resulting in dissemination throughout the body (Jones & Brosseau, 2015).

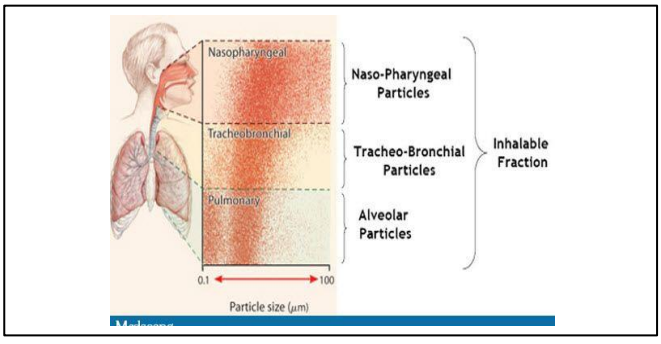

Figure 1. *Deposition regions of the respiratory tract for the various particle sizes (source: Roy CJ, Milton DK. N Engl J Med. 2004,350:1710-1712)*

Pathogens may also deposit onto skin and penetrate the skin through abrasions and cuts. So, aerosol transmission is biologically plausible when: aerosols containing the pathogen are generated by or from an infectious person, the pathogen remains viable in the environment in sufficient time and the target tissues are accessible to the aerosol (Jones & Brosseau, 2015). The location of target tissues can be identified through *in vitro* studies of tissues and cellular receptors or studies *in vivo* in human and animal models.

Laboratory-based evidence of the infective components present in the aerosol can be obtained by classic culture-based methods (culturable pathogens) and/or culture-independent procedures that identify genome segments of the pathogens (PCR, DNA hybridization etc.). Many pathogens lose their viability over a period of time, so the laboratory studies of the pathogens aersolized in body fluids as well as their detection in emitted aerosols over time can demonstrate the timescale of pathogen inactivation (Jones & Brosseau, 2015).

Computational fluid dynamics simulations and other models, or pathogen measurement can determine a plausible path and determine the exposure and likelihood of infection, as a dose-response function. Future work will identify specific workplaces and work practices in which aerosol transmission is more likely to occur so that risk assessments and exposure controls can be more efficiently targeted (ABSA, 2015, Jones & Brosseau, 2015).

There is greater complexity with respect to potential biological warfare or bioterrorism when the agents (bacteria, viruses, fungi or toxins) are designed as a weapon suitable for aerosol transmission respecting many biological, physical, chemical and meteorological conditions. Biological agents can be used alone (one agent or their combination) or combined with chemical, nuclear/radiological and/or conventional weapons. The best meteorological conditions for aerosol transmission of bio-weapons are: at wind speed 5-15km / h, in isothermal conditions of vertical airflow, in the summer with clear sky, in the morning and in the afternoon until midnight, during cloudy winter days, at a temperature not lower than -20^0C, and using virulent micro-organisms in liquid suspension. Special procedures are used for conservation or lyophilization of pathogenic microorganisms. Microorganisms prepared thus must retain biological and toxic properties for a longer period and can be put in accessories for the launch: biological bombs, aerosolizers and atomizers for the production and dispersion of aerosols (Ristanovic, 2015).

An understanding of aerobiology, typical origins of aerosol infections, and how different environmental factors affect aerosol particles is critical to any discussion of the mitigation of infectious particle transmission.

AEROSOL TRANSMISSION OF INFECTIVE AGENTS IN THE OFFICES, BUILDINGS, HOSPITALS, TRAVEL SETTINGS: ENVIRONMENTAL AND PUBLIC HEALTH CONSIDERATIONS

Temperature and relative humidity are the environmental factors that most influence the airborne transmission of viral, bacterial, and fungal particles, but in different manner (Cole & Cook, 1998), and thus influence directly the aerosol transmission of infective agents.

It is known that virus survival decreases as temperature rises (Tang, 2009). Lower temperatures are ideal for airborne influenza survival, with survival decreasing progressively at moderate and high temperatures, across a range of relative humidities (i.e., 23%-81%) (Lowen et al, 2007). There are also reports that minimal survival for both lipid-enveloped and non-lipid-enveloped viruses occurs at relative humidities between 40% and 70% (Arundel et al, 1986).

The survival of airborne bacteria is more complicated (Cox, 1998). Temperatures above 75.2^{o}F (24^{o}C) reduce airborne bacterial survival as has been found in *Pseudomonas* sp., *Pasteurella* sp., *Salmonella* sp., *Serratia* sp., *Escherichia* sp., *Bacillus* sp., *Bordetella* sp., *Chlamydia* sp., and *Mycoplasma* sp. (Fernstrom & Goldblatt, 2013, Handley & Webster, 1995). The survival of aerosolized gram-negative bacteria (including *Pseudomonas* sp., *Enterobacter* sp., and *Klebsiella* sp.) has been the greatest at high relative humidity and low temperature (Marthi et al, 1990). Some airborne gram-negative bacteria (e.g. *E. coli*, *Salmonella* sp., etc.) do not survive well at increased relative humidity, while some airborne gram-positive bacteria (*Staphylococcus albus, Streptococcus haemolyticus, Bacillus subtilis,* and *Streptococcus pneumoniae* (type 1)) poorly survive at intermediate relative humidities (Dunklin & Puck, 1948).

More than viruses or bacteria, airborne fungi and their spores have the potential to enter a building that uses natural ventilation. Certain fungal species (e.g. *Aspergillus* sp.) are potentially life-threatening airborne contaminants when introduced to immunocompromised patients e.g. in a healthcare facility (Vonberg & Gastmeier, 2006). Other fungi (*Blastomyces* sp., *Coccidioides* sp., *Cryptococcus* sp., *Histoplasma* sp.) are also hazardous to the immunocompromised (Hardin et al, 2003). Even in healthy people, individuals working consistently in indoor environments (such as an office or school) have shown hypersensitivity reactions such as rhinitis, sinusitis, or asthma in response to fungi exposure (Tang, 2009). Relatively few laboratory studies have examined the airborne transmission of fungi and their spores in relation to temperature and relative humidity. Generally, fungi and their spores appear to be more resilient than viruses and bacteria, being able to withstand greater stresses due to dehydration and re-hydration, as well as UV radiation (Hardin et al, 2003).

There are two principal challenges with respect to indoor aerosol infections: preventing infiltration and preventing transmission. These are discussed in the context of office buildings, healthcare facilities, travel and leisure settings subsequently.

Occupants of office and commercial buildings are exposed to all kinds of airborne particles. Routes of infiltration would include: unintentional introduction by the building's occupants, the intentional introduction of dangerous biological agents and the accidental entrance of viruses, bacteria, allergens, and moulds (e.g., through an open door or window), especially in the context that many commercial buildings are not configured or maintained to limit their occupants' exposure to airborne particles, so the majority of people are continually exposed to infectious microorganisms (UPMC Center for Biosecurity, 2008). HVAC (*heating, ventilation, air-conditioning*) systems are energy-efficient and cost-effective methods intended to provide for the health, comfort, and safety of occupants by maintaining thermal and air quality conditions that are acceptable to the occupants, but affect the transmission and/or reduction of transmission of airborne particles in a building under normal conditions (Bearg, 2001). They are also expected to be responsive to hazardous exposures under extraordinary conditions (Hitchcock et al, 2006).

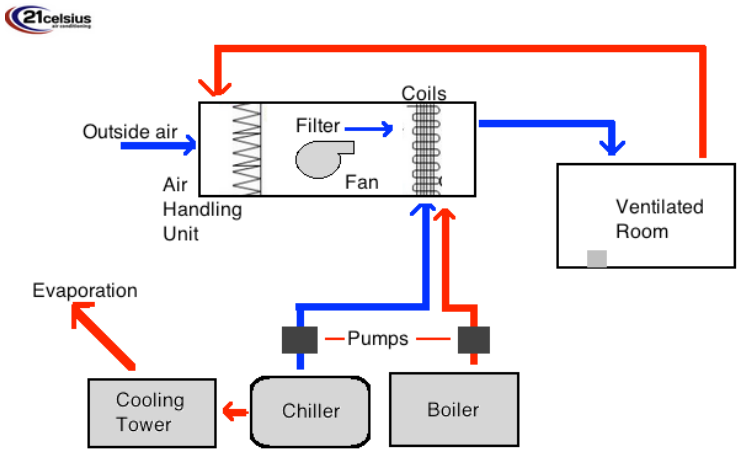

Figure 2. *HVAC (heating, ventilation, air-conditioning) system components*

A typical HVAC system as shown in figure 2 has three basic components: (1) outdoor air intake and air exhaust ducts and controls, (2) air handling units (i.e. systems of fans, heating and cooling coils, air filters, and controls), and (3) air distribution systems (i.e. air ducts, diffusers and controls, return and exhaust air collectors, grilles, and registers, return and exhaust air ducts and plenums) (Bearg, 2001).

HVAC systems simultaneously perform multiple functions, including controlling three central variables affecting aerosol infectious particle transmission: temperature, relative humidity, and air currents. Bacteria, molds, and allergens can easily enter a building through an HVAC air intake, spreading throughout via the air-handling system. Building materials, carpets, clothing, food, pets, and pests are also known sources of introduction of airborne particles into an office or commercial building. Moulds and fungi can grow in damp or wet places and then serve as a continued source of contamination. Some bacteria and moulds can also grow in places of water collection (e.g. ceiling tiles, carpeting, and insulation). Viruses can be brought into a building by infected individuals and potentially enter the return air system and be spread by the HVAC system (UPMC Center for Biosecurity, 2008). Taking all mentioned into serious consideration, a working group from the UPMC Biosecurity Center recommended actionable items that building owners and operators can undertake to immediately reduce the risk of building occupants to airborne particles (Hitchcock et al, 2006, Fernstrom & Goldblatt, 2013).

Healthcare facilities are subject to the same infectious challenges as all office and commercial buildings, but they also face a unique challenge regarding infection control: a high density of potentially contagious and immunocompromised people. As many pathogens, including the aerosol transmissive, that can cause hospital-acquired infections have become ubiquitous (Schwegman, 2009), so healthcare facilities are now a common source for highly drug-resistant pathogens. While recommendations for hospital hygiene include hand, instrument, and surface hygiene, even outstanding hygiene protocols for these vectors do nothing to prevent the transmission of

infectious airborne particles that can be expelled during many routine patient bodily functions in large quantities and in a wide size ranges (bacterial cells and spores: 0.3 to 10 μm, fungal spores:2.0 to 5.0 μm, viruses:0.02 to 0.30 μm in diameter (Owen et al, 1992)) and in various compositions (single cells, spores, their aggregates or biologic material carried by other non-biologic particles (e.g., dust) (Nevalainen, 1993). Most infectious particles are generated from human respiratory sources as droplet nuclei, allowing them to remain airborne — and highly infectious — for extended periods of time (Cole & Cook, 1998). It is estimated that approximately one-third of all hospital-acquired infections involve airborne transmission at some point between the origin and the susceptible host (Kowalski, 2007). Anyway, healthcare facilities will continue to have a difficult task quantifying their facility-specific risk of airborne transmission and so remain tentative in investing to reduce it (Fernstrom & Goldblatt, 2013). Healthcare facilities are subject to regulations and requirements relating to their HVAC systems (Ninomura, 2006) with attempts to reduce the airborne infectious disease load by: (1) increasing the air changes per hour and (2) utilizing different ventilation configurations and systems in specific areas (e.g., operating rooms, patient rooms, etc.) (Memarzadeh & Manning, 2002). Although removing 90% or more of infectious particles from the air may be helpful, it is not sufficient to eliminate airborne transmission, particularly for viruses and bacteria that are extremely virulent (e.g., influenza A, *Francisella tularensis*, and *Mycobacterium tuberculosis*) (Cole & Cook, 1998). So, it is clear that airborne particles spread throughout a space evenly and quickly regardless of HVAC configuration. International guidelines and recommendations for airborne infection control have been also issued by the Centers for Disease Control and Prevention and the World Health Organization and based on a three-pronged approach to controlling airborne infections: administrative (depending on resources), environmental (natural ventilation, mechanical ventilation, and upper-room UV light) and personal protection (respiratory masks and other devices) (Memarzadeh & Xu, 2012, Escombe et al, 2009).

Travel and leisure settings can also be good routes for spreading airborne pathogens. An enclosed passenger cabin of a commercial airplane is a conducive environment for spread of pathogens carried by passengers or crew members (Mangili & Gendreau, 2005). The frequency of commercial airline travel with over 1 billion passengers annually enable the spread of airborne pathogens over great distances (Ryan et al, 2002). Although the environmental control systems used in commercial aircraft restrict aerosol transmission, a finite risk exists of droplet and airborne disease transmission (Chin, 2000). One of the most critical factors is cabin ventilation or its absence) (National Research Council, 2002). One air change per hour of well-mixed air in any space is thought to remove 63% of the airborne organisms in that space (Riley & Nardell, 1989). Typically, modern commercial aircraft cabins experience 15-20 changes of air each hour and proper ventilation helps to reduce the transmission of airborne infectious particles (Mangili & Gendreau, 2005). At the very least, the recirculation of cabin air is known not to be a risk factor for contracting upper respiratory track infections (Zitter et al, 2002). Tuberculosis, SARS, influenza, meningococcal disease, and measles have been recognized as pathogens most often associated with droplet and airborne transmission in aircraft cabins (Wang, 2000, Wilder-Smith et al, 2003, Laurel et al, 2001, CDC, 1983). Hotels and cruise ships share the same concerns as an office building or aircraft cabin, as they have enclosed spaces with large, dense populations susceptible to airborne and droplet transmission via any of the described mechanisms (Fernstrom & Goldblatt, 2013).

BIODEFENCE CONSIDERATIONS

The US and former Soviet Union maintained massive biological weapons stockpiles during the Cold War (Alibek, 1999). Aerosol dispersion of potential biological agents was considered the most effective manner of spreading and delivery. An ideal biological warfare agent would be of a particle size that would allow it to be: (1) carried for long distances by prevailing winds and (2) inhaled deeply into the lungs of unsuspecting victims. The size range of particles that meets both of these conditions is 1 to 5 μm in diameter. Particles in this size range are invisible to the human eye, thus, a cloud of such particles would not generally be detected by those attacked (Ristanovic, 2015). But the production and weaponization of such particles is not easy, and would require specific equipment and technology. Dissemination is also dependent on the surrounding air quality and weather conditions (sun, rain, fog, wind). Knowledge of aerodynamics and other scientific areas is necessary as well as of delivery systems. From the standpoint of military medical personnel, the lack of a fielded detection capability for such a biological "cloud" makes clinical and laboratory diagnostics critical for early diagnosis of the initial casualties of a biological attack (Eitzen et al, 1997).

Offensive biological programmes were officially halted after adoption of Biological Weapons Convention but risky work continued for "defensive purposes". Nowadays, in the modern world, terrorism takes on the scary attributes of the global evil. In addition to the traditional terrorism we are increasingly faced with the so-called post-modern

terrorism or super-terrorism which includes the use of weapons of mass destruction (WMD), i.e. biological, chemical, radiological, and nuclear. Although it is the danger as old as civilization and society as a whole, bioterrorism has today acquired frightening dimensions, due to the development and misuse of science, particularly molecular biology, genetic engineering and biotechnology. Examples of such misuse range from modification of certain properties of microorganisms in order to increase virulence, resistance to antibiotics, vaccines and antidotes, environmental factors, crossing of different microorganisms, creating completely new organisms and potential weapons, acceleration of molecular evolution, production of genetic biological weapons that would be related to a particular nation or population. On the other hand, the national security strategies related to this segment are often an inadequate, undoubtedly because awareness of this kind of threats, risks and challenges is not at a sufficient level (Ristanovic, 2015).

So this problem must be seriously addressed in the light of prevention, including preparing of resources for effective detection and identification of possible biological agents, vaccine development, biosecurity and biosafety considerations. The achievments in aerobiology are particularly important in this field.

CONCLUSION

The airborne transmission of infectious disease is a problem encompassing public health, infection prevention, hospital-acquired multi-resistant infections as well as biodefence. Aerobiology as an active discipline must combine various techniques including computational fluid dynamics, molecular methodologies for identification and quantification of airborne particles concentrations in various settings, and epidemiology to track the spread of disease.

Such information would be of great value in reducing the airborne transmission of infectious particles in all settings including hospitals, office buildings, travel settings and hotels. In the absence of new expensive technologies, high-efficiency filtration remains the most widely deployed technology for this purpose.

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10. ADVANCES IN PM CHARACTERIZATION II

10.1. AN INSTRUMENT FOR THE RAPID QUANTIFICATION OF PM-BOUND ROS: THE PARTICLE INTO NITROXIDE QUENCHER (PINQ)

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Abstract. Reactive oxygen species (ROS) present on, or generated by, particulate matter (PM) have been implicated in PM-induced health effects. Methodologies to quantify ROS concentrations vary widely both in detection and collection methods. However, there is currently an increasing emphasis on rapid collection and measurement due to observations of short half-life ROS. To address this problem, this manuscript details the design and characterization of a novel instrument for the measurement of PM-bound ROS named the Particle Into Nitroxide Quencher (PINQ). This instrument combines the 9,10-bis (phenylethynyl) anthracene-nitroxide (BPEAnit) ROS assay in conjunction with a purpose-built aerosol collection device, the insoluble aerosol collector (IAC). The IAC continuously collects PM regardless of size, or chemistry, directly into a liquid sample with a collection efficiency of > 0.97 and a cut-off size of < 20 nm. The sampling time resolution of the PINQ is one minute, with a limit of detection (LOD) of 0.08 nmol.m^{-3} in equivalent BPEAnit-Me concentration per volume of air. This high sample time resolution and sensitivity is achieved due a combination of the highly concentrated IAC liquid sample, minimized liquid sample volume and the rapid reaction and stability of the BPEAnit probe.

INTRODUCTION

The measurement of oxidative potential is a complex issue in terms of both sample collection and chemical analysis. In order for measurement to take place, PM must, in most cases, be collected into a liquid and mixed with a chemical probe. The degree to which this probe reacts with the sample is then measured in order to ascertain a value related to the oxidative potential. Many different chemical probes have been used for this purpose, with a detailed review found elsewhere (Hedayat et al., 2015). The reason for this diversity of probes is twofold. Firstly, each probe is only sensitive to a specific range of ROS. Secondly, it is not known which ROS contribute to the oxidative potential, or if they contribute equally. As such, the use of the term oxidative potential is contentious in the field of *in vitro* ROS measurement. While these probes measure a certain contribution to the oxidative potential, none are true measures of the total oxidative potential. This does not mean the results are not valuable as there have been good correlations between probe responses and oxidative stress response. However, all results must be considered in the context of the probe and methodologies used, and discussed accordingly.

Beyond chemical probes, there are several properties of ROS and combustion aerosols which complicate quantification. PM-bound ROS react readily with the atmosphere and other surroundings (Fuller et al., 2014). This is a significant issue with standard filter capture techniques, as the concentration of PM-bound ROS can be skewed due to the decay of collected ROS during long periods of collection and storage prior to measurement (Fuller et al., 2014, Zhou et al., 2017). Therefore, methodologies involving either: long periods of collection, or delays between collection and measurement risk severely underestimating the concentration of PM-bound ROS in an aerosol. Additionally, extraction processes to remove PM from filters for analysis can introduce further positive and negative sample artefacts (Miljevic et al., 2014). To address these issues, methodologies have been developed to rapidly collect PM directly into liquid for more accurate quantification of PM-bound ROS.

MEASUREMENT TECHNIQUE COMPARISONS

Ultrafine PM concentrations are heavily dependent upon source proximity and atmospheric conditions (Sabaliauskas et al., 2013) which can lead to significant variations over short time periods and distances. This, coupled with the short half-life of some PM-bound ROS species (Fuller et al., 2014, Zhou et al., 2017), indicates that the concentration of PM-bound ROS is dynamic and prone to significant changes over short distances and times. Therefore, in order to accurately measure and understand the health impacts of PM-bound ROS, monitors must have time resolutions sufficient to accurately quantify these variations.

The time resolution of the discussed instruments varies from widely from 3 minutes to 3 hours. It is clear that the steam collection devices and particle collector-based instruments offer much higher potential time resolutions than that of the LLS-based OPROSI.

Future systems should endeavour to adapt or create new methodologies to allow for the collection of insoluble particles to improve the understanding and toxicity of aerosol oxidative capacity.

MANUSCRIPT FOCUS

This paper discusses the design and testing of a novel instrument called the Particle Into Nitroxide Quencher (PINQ). The PINQ has been developed to address the need for an accurate, repeatable method of measuring the PM-bound ROS present in aerosols. Referencing the current literature on the field, the instrument collection mechanism is based on a steam collection device, with PM collected directly into a miniature liquid vortex containing the BPEAnit ROS assay. The fluorescence increase of the BPEAnit probe is measured using a purpose-built flow-through fluorimeter with a low internal volume and minimal flow-path length to ensure rapid quantification of PM-bound ROS.

PINQ LAYOUT

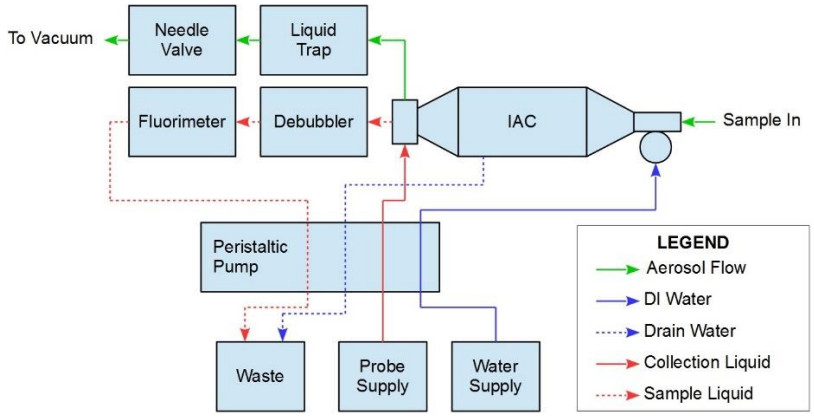

Figure 1. *Diagram of the PINQ system showing all major components and the aerosol and liquid flow paths linking them.*

The flow diagram of the PINQ can be seen in

Figure **1**, including all key components of the system and their corresponding connections through liquid and aerosol flows. The aerosol is collected in a novel instrument called the Insoluble Aerosol Collector (IAC), in which PM is collected continuously into a liquid sample independent of size or chemical composition. The sample solution is then de-bubbled and passed through a purpose-built flow-through fluorimeter to quantify PM-bound ROS.

The standard sample flow rate for the instrument is 16.7 $L.min^{-1}$ (1 $m^3.hr^{-1}$), which is set prior to sampling, using a needle valve connected to vacuum. This has been found to be stable over 24-hour sampling periods. The corresponding steam generator water supply for this flowrate is 1.5 $mL.min^{-1}$. All liquid flows are controlled using a peristaltic pump and so are given in volumetric, rather than mass units, for completeness. The influence of temperature variation on the liquid flow during normal laboratory conditions (20 - 30 ^oC) results in a negligible impact on instrument performance. In more extreme temperature environments, it may be necessary to regulate the liquid reservoir temperatures and correct for variations.

This study is divided into two investigations. The first is the measurement of the PINQ collection efficiency. The second is the characterisation of the PINQ system fluorescence response. Flow diagrams of experimental setups, further methodology details, and calculations can be found in the supplementary material.

PINQ COLLECTION EFFICIENCY

The averaged collection efficiency and corresponding standard error are calculated as:

$$CE_{ultrafine} = 1.05 \pm 0.06$$

The error of the ultrafine collection efficiency is larger than that of the fine collection due to the significantly lower aerosol sample concentration. However, the results are within the error of each other, indicating that the PINQ collects both fine and ultrafine particles with a very high efficiency. This is an expected result for steam collection devices, which will typically collect all particle sizes with equally high efficiency due to condensational growth of particles in the growth chamber well into the ultrafine size range.

The mean collection efficiency was calculated as:

$$CE_{PNC} = > 0.97$$

PINQ CHARACTERIZATION - RESPONSE TIME AND LOD

The averaged values of time delay and mixing time of the PINQ for the eight samples taken and corresponding standard errors were calculated as:

$$time\ delay = 6.3 \pm 0.6\ s$$

$$mixing\ time = 32 \pm 1\ s$$

The time delay of 6.3 s represents a small time correction factor, which does not strongly influence instrument performance. In contrast, the mixing time of 32 s is a key value in determining the limits of instrument time resolution. This value indicates the minimum averaging time which provides independent data points, and is directly proportional to both the liquid sample flowrate, and the internal liquid volume of the liquid sample flow path inside the instrument. An increased liquid sample flowrate above the tested 1 $mL.min^{-1}$ will result in a faster time resolution.

The time resolution of the PINQ is determined by the sum of the total response time, and the time required to average the signal for an accurate measurement. An averaging period of 20 seconds was selected, leading the PINQ to have a time resolution of 1 minute when performing alternating gas and total phase measurements. A total of 234 blanks of 20 seconds averaging time sampled with nitrogen were collected and normalized as equivalent nmol of BPEAnit-Me per cubic meter of air. The limit of detection of the PINQ was determined as three times the standard deviation of these blanks.

$$LOD = 0.08\ \frac{nmol}{m^3}$$

The PINQ has a lower LOD than other online systems with responses normalized per volume of air sampled for two primary reasons. Firstly, the IAC has a very small ratio of liquid sample flow to aerosol sample flow for two reasons. First, the IAC has a very small ratio of liquid sample flow to aerosol sample flow. This ensures a more highly concentrated sample than those of particle collector based systems, which reported LODs between 4 $nmol/m^3$ 10 (Wragg et al., 2016) and 2 $nmol/m^3$ (Zhou et al., 2018). The GAC-ROS system has similar aerosol and liquid flows, resulting in a similarly concentrated samples and hence a closer LOD of 0.12 $nmol/m^3$ (Huang et al., 2016a). The second factor contributing to the lower PINQ LOD is the different ROS probe used. The BPEAnit probe does not auto-oxidise in the same manner as the DCFH probe used by the other system discussed here, resulting in more stable blanks and hence a lower LOD.

SUMMARY

This manuscript's first focus was on the design and characterization of the IAC as a high efficiency aerosol collector for use in the PINQ system. It is defined as a steam collection device, in which the sample aerosol is continuously mixed with a stream of water vapour to generate a supersaturated mixture, growing the particles into large liquid droplets to ensure high efficiency capture independent of initial particle size. The grown droplets are collected continuously into a liquid vortex inside a specially designed vortex collector. This was designed over a simpler

impaction system, as it allows the capture of insoluble in the collection liquid. The vortex collector is also solvent resistant and allows for visual confirmation of the liquid vortex.

The IAC mass collection efficiency was determined to be within error of 1.00 for both fine and ultrafine ammonium sulphate particles. This result indicates that the provided particles seed the liquid droplets, they are collected with a very high collection efficiency. However, hydrophilic particles, like ammonium sulphate, will undergo condensational growth more readily than hydrophobic particles. As the IAC must collect particles independent of their chemical composition for use in the PINQ system. The number of collection efficiency of highly hydrophobic DEHS test particles was also investigated. Using these particles, the number collection efficiency was found to be > 0.97 with a cut-off size of < 20 nm. This result shows that the IAC is capable of collecting particles with a high efficiency independent of particle size and composition.

The PINQ was developed to measure PM-bound ROS using the BPEAnit chemical probe in conjunction with the IAC. A 1 μM solution of BPEAnit in DMSO is used as the sample collection liquid, with particles collected directly into the probe solution inside the IAC vortex collector. The rapid mixing of liquid inside the vortex coupled with the diffusion limited reaction between the probe and any ROS collected ensures the liquid exiting the IAC is fully reacted. The sample liquid is then de-bubbled and put into a specially designed flow-through fluorimeter. Finally, the fluorescence response measured is converted into PM-bound ROS through calibrations performed on known concentrations of BPEAnit-ME, and expressed in $nmol.m^{-3}$.

The PINQ is also sensitive to gas phase ROS. In order to quantify PM-bound ROS it is necessary to account for gas phase contributions by periodically filtering the aerosol sample. Experiments on response time with a standard sample flowrate of 1 $mL.min^{-1}$ indicate that after switching sources the PINQ signal takes ~ 40 seconds to reach equilibrium response. Therefore, with a 20 second sample averaging time the sample time resolution of the instrument is 1 minute when alternating between filtered and unfiltered samples. With this time resolution, the LOD of the instrument was determined to be 0.08 $nmol.m^{-3}$. Both the time resolution and LOD of the instrument are considerably lower than other instruments currently found in the literature, indicating the PINQ is a viable candidate for the quantification of PM-bound ROS.

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

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ABSTRACT

Low-cost particulate matter (PM) sensors can potentially bring PM level monitoring to a much wider audience, thus providing relevant information, at an 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. The aim of this work was to explore the 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 a more inclusive definition: we use the term for either commercially available low-cost instrument or for a prototype that includes bare-bones sensors and supporting electronics.

INTRODUCTION

While clean air can be considered as one of the most basic requirements and conditions for healthy life, the mean annual concentration of fine particles ($PM_{2,5}$), in many European cities according to the European environment agency reports [1], is two or three times higher than that recommended by the World health organization (WHO) [2]. Different individuals in the general population react differently after being exposed to similar levels of air pollution, ranging from almost no health issues to serious respiratory conditions from both short and long-term exposure. Regarding long-term exposure, the seriousness of air pollution can be seen through the fact that the International Agency for Cancer Research within the WHO - IARC frame [3], has classified the air pollution of the environment, as well as the particle pollution, in Group 1 of the carcinogenic substances. Air pollution is also, unfortunately, the highest environmental health risk in Europe [4].

All of the above facts point to the necessity of air pollution monitoring. As the level of air pollution can vary considerably from region to region as well as locally, traditional networks for monitoring cannot give the complete picture about pollution, primarily because of a small number of monitoring stations covering large area of interest. On the other hand, the monitoring of air pollution should not be restricted to outdoor ambient measurements, since people spend the majority of their time indoors. This increases the need for affordable air pollution monitoring, since, as air pollution awareness rises, many interested citizens want to know more about quality of the air that surrounds them.

Standard methods for measuring the main air pollutants (particulate matter and gaseous pollutants) are typically achieved using complex equipment that, despite its high accuracy, brings a number of drawbacks such as a high cost of maintenance (e.g. cleaning, periodic calibrations, parts replacement). This results in low spatial resolution, in both indoor and outdoor settings. Low data resolution, either temporal or spatial, makes realistic insight into the exposure and associated health risks more difficult. Low-cost sensors can potentially improve the situation, but their performance cannot be taken at face value from the data sheets of the manufacturers, instead they must be carefully studied and compared to the laboratory-grade instruments. This paper examines the potential of several low-cost sensors for real-time PM monitoring.

The outline of the paper is as follows. First, we provide a brief discussion on the importance of data quality, the established validation criteria that currently exist for low-cost sensors, and summarize the general types of particulate matter sensors that may be suitable for high resolution monitoring. Then we describe the method and experimental setup that was used in this study. The operating principle of the instruments used is described in detail along with some of the drawbacks of commercially available sensors. Finally, conclusions about the performance of the studied sensors are outlined.

DATA QUALITY, VALIDATION CRITERIA AND TYPES OF PARTICULATE MATTER SENSORS

Recent technological advancements, coupled with simplification and affordability of new measuring systems, give hope for the forward-looking prospects in upcoming air pollution monitoring networks. As well as advances such as an order of magnitude more nodes compared to the traditional regulatory networks, personalized exposure

assessment, air pollution forecasts etc., it should be borne in mind that low-cost sensors, along with their advantages, bring a number of possible disadvantages, one being the looming question of data quality. Metrologically unreliable data originating from low-cost sensors, and the non-official networks which may utilize them, if uncritically provided to the general public and media, are very likely to result in unnecessary concerns and may raise questions about the validity of established governmental monitoring networks. While the involvement of the general public should always be encouraged and is welcome, (e.g. via citizen science projects about air pollution), validation of low-cost sensors should ensure that the results measured in this way will not provide spurious conflicts with the officially provided data. Therefore, the issue of metrological relevance is of utmost importance and data from low-cost sensors must be carefully processed and interpreted, sensors must be calibrated and compared to the lab-grade instruments and only then should data originating from low-cost sensors be made more widely available.

For a number of applications, the data quality of low-cost sensor data should be in accordance with legislation for indicative measurements (DQO - *Data Quality Objectives for indicative measurements*), where European legislation allows measurement uncertainty of up to 25%. Recommendations for validation criteria for measurements of air polluting substances via sensors, with respect to regulatory measurements, in European Union, China and USA are given in Table 1.

Table 1. *Recommendations for validation criteria for measurements of air polluting substances by sensors*

Air pollutant	**Validation criteria**	**European Union**	**USA**	**China**
PM_{10}	Accuracy	/	$R^2 \geq 0{,}9409$	$R^2 \geq 0{,}9025$
	Measuring range	0-1000 μg m^{-3*} 0-10 000 μg m^{-3}**	0-300 μg m^{-3}	0-1000 μg m^{-3}
$PM_{2,5}$	Accuracy	/	R^2: 0,7225-0,9025	$R^2 \geq 0{,}8649$
	Measuring range	0-1000 μg m^{-3*} 0-10 000 μg m^{-3}**	3-200 μg m^{-3}	0-1000 μg m^{-3}
* average value for 24h long measurement ** average value for 1h long measurement				

The quality of data that originate from low-cost sensors is influenced by many factors, some of which are related to the technology choice (stability, selectivity, speed of response, homogeneity of response within the same batch of sensors), while others are related to exploitation cost (power demand of the sensors, manufacturing costs, calibration cost). A very important aspect of low-cost sensor usage is their calibration, which can be done either in laboratory conditions [5] or in the field. Despite the fact that laboratory testing is more repeatable if conducted in controlled atmosphere, field testing (either indoor or outdoor) and calibration is preferred for low-cost sensors since it gives more realistic insight into their performance.

Regarding the current and emerging standards covering the topic of sensors for air pollution monitoring, it is worth mentioning that within the *European Committee for Standardization* - CEN a work group CEN/TC 264 WG42 is developing a standard regarding technical specifications for sensors for gaseous pollutants. It is being proposed that they be divided into three classes. The first two fulfill specifications given in the *Directives 2004/107/EZ and 2008/50/EZ* while the third class does not fulfill a data quality objective but can be used for research purposes and citizen science. Regarding particulate matter monitors, MCERTS (The UK environment agency's monitoring certification scheme), a standard published by UK Environment Agency provides detailed instructions for the certification of PM monitors, albeit more oriented toward in-the-field calibration.

Table 2. *Advantages and possible drawbacks of sensors for PM measurements*

Type of Sensor	**Advantages**	**Possible drawbacks**
Sensor based on light scattering	Small dimensions Relatively cheap	Without additional aerosol conditioning they can't measure fine particles (due to size of particle compared to light wavelength). Limit of operation is about few hundred nanometers for the particle diameter

Type of Sensor	Advantages	Possible drawbacks
		Sensors measure number concentration which can only approximately be converted to mass concentration
Sensor based on light absorption	Higher cost and bigger dimensions Direct link to the climate change aspect of the PM air pollution Continuous measurements	Conversion of light intensity to mass concentration Filter or filter tape is required, and maintenance of filter tape Filter loading effects
Quartz crystal microbalance - QCM based sensor and thin-film bulk acoustic resonator-based sensor (TFBAR)	Direct mass measurement	Highly sensitive to meteorological parameters, which may require input aerosol conditioning

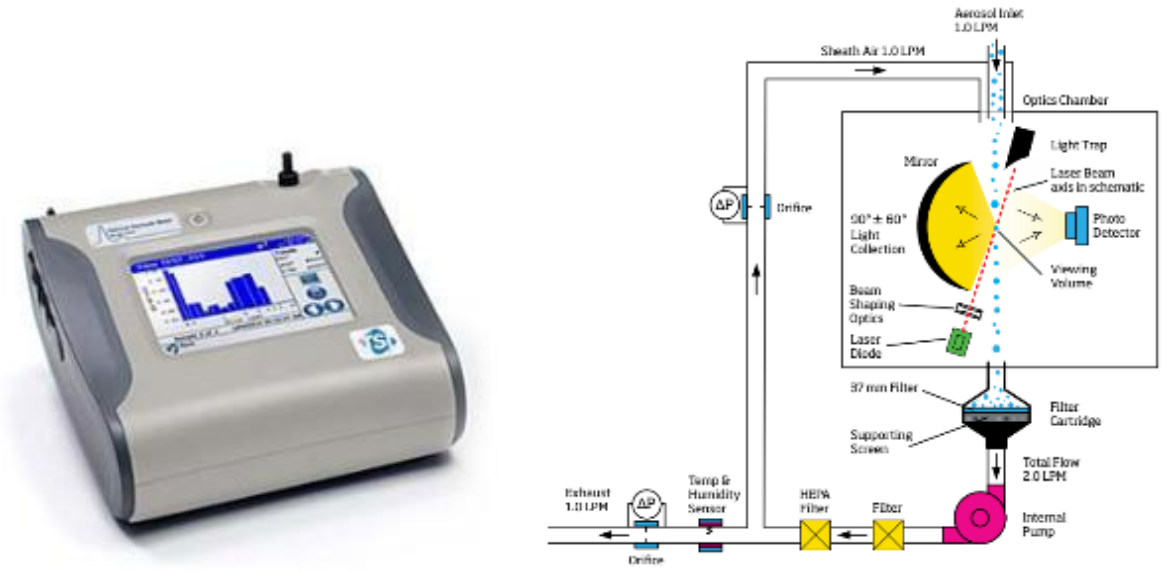
METHOD AND EXPERIMENTAL SETUP

Several low-cost sensors and laboratory-grade instruments were collocated in laboratory office space in Institute Vinca for several weeks from the end of November to the beginning of December 2016. Low-cost instruments included two Sharp GP2Y1010AU0F compact optical dust sensors connected to an Arduino platform, Alphasense CompactOPC sensor and Dylos DC1700 PM unit. Lab-grade instruments included TSI NanoScan SMPS Model 3910 and TSI Optical particle sizer 3330 (17 channels from 0.3um to 10um). However, in this work only the data from the TSI Optical particle sizer were used in order to simplify analysis. All instruments and sensors, except for the Arduino-connected optical dust sensor, sampled aerosol via an internal pump, while the Arduino dust sensor used internal thermal resistor to increase aerosol flow. All instruments that were used in this experiment are based on the scattering of laser light, which enables high temporal resolution. The time resolution of the instruments was set to 1 minute, which for Arduino dust sensor required averaging of about 40 samples per minute.

Both laboratory quality instruments and low-cost instruments, share a lot of similarities: the main differences being in the sophistication of the implementation of the basic operating principle. Therefore, descriptions of the instruments will start with detailed explanations of laboratory-grade instruments, and then will underline the differences for the low-cost instruments. Furthermore, for each analysed sensor/instrument, we will state its potential to be a node in a larger network of devices, and, if appropriate, state data rates needed to enable near-real-time monitoring.

TSI Optical particle sizer OPS 3330

Fig. 1 depicts schematic representation of a measurement system of TSI OPS 3330. The sampled air enters the aerosol inlet at a rate of 1 litre per minute. Suspended particles reach the optical cavity surrounded by clean filtered air (*sheath air),* which directs the sampled air to the laser beam, and additionally protects the optics of the instrument. In this way the necessity for cleaning the instrument is significantly reduced. The sampled air, which contains suspended particulate matter, is irradiated by a laser beam in the cavity, and scattered light is measured using a spherical mirror and a photodetector. In this way, under the assumption of Mie scattering (plane wave scattered by a spherical particle), the particle size and the concentration of particles is determined. Suspended particles may be collected, if necessary, on a gravimetric filter which can then be later used for calibration of the device (by measuring the differential mass of the filters), and chemical analysis of the collected particles or analysis under a microscope.



(a) (b)

Figure 1. *(a) Instrument TSI OPS 3330 and (b) schematics of the main parts of the measurement system. Figures were taken from manufacturer datasheets*

Note that the principle of operation of the instrument has some inherent flaws. For example, the mass concentration of the suspended particles is obtained from the number concentration under rather tight assumptions for particle shape (spherical), particle refraction index and density. If the particle is not spherical (e.g. particle originating from NaCl) or the assumed refractive index is incorrect, an error occurs. However, this is a general drawback of all devices based on light scattering.

This instrument is suitable for controlling air quality in indoor and outdoor environments, for monitoring workplace environments, industrial measurements, as well as, for controlling and monitoring harmful emissions. Using this device, it is possible to test filters (for example, by the ASHRAE 52.2 method), but because of its overall rather sophisticated functionality and cost, this device is not of direct interest for use in a larger sensor network.

This instrument can measure suspended particles of different sizes with diameters in a range of 0.3 to 10 μm, and this range can be divided into 16 channels. The device can measure up to 3000 particles per cubic centimetre. For each measured aerosol sample, the device records both the temperature and the pressure of the inlet air. The device is fully compliant with ISO 21501-01/04 standard (Determination of particle size distribution -- Single particle light interaction methods -- Part 1: Light scattering aerosol spectrometer).

Temporal resolution of the device can be very high, it can even go up to 1 s and the device can be connected to a data acquisition PC using a USB or Ethernet port. With a single battery, the device operates for 10 hours andthe charging time is 4 hours. With two batteries, both the operating time and charging time are doubled.

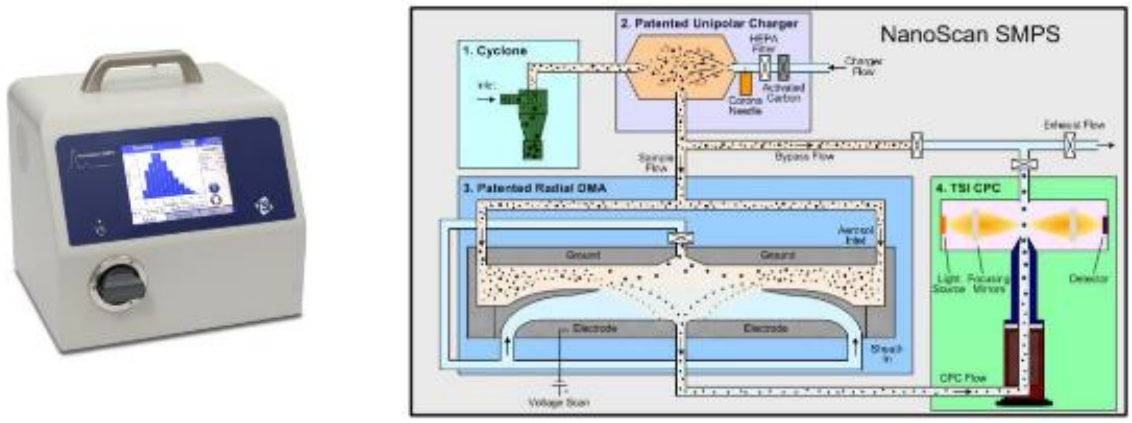
For the estimation of the necessary data flow from the instrument, when used in a larger network of nodes, we can use an estimate based on capacity of the internal memory of the device (internal capacity is about 5 MB and it can be used to store 30,000 measurements). This roughly corresponds to the amount of data of around 40 floating point numbers (4 bytes for a floating-point number is assumed) per measurement, where one measurement includes data from 16 channels (channel boundaries and numerical value of the concentration in the channel), temperature, pressure, sampling duration and sample timestamp.

TSI NanoScan 3910

As stated earlier, devices based on the principle of light scattering from suspended particles have a limit regarding the particle size that they can measure. Smaller particles, with the diameter below the lower range of instruments such as TSI OPS 3330, (i.e. around a few hundred nanometers), cannot be directly detected by the system which only includes an optical cavity, laser and a photodetector.

The estimation of the particle size for devices that use a particle magnification fluid is not carried out in the optical cavity, as was the case with, for example, TSI OPS 3330 (where counting and particle size determination is performed simultaneously). Particles are first classified using, for example, a DMA (differential mobility analyzer) classifier. The DMA classifier is a separate device, or a part of a larger device, that has a polydisperse aerosol as its input (an aerosol having particles of different sizes), and provides a monodisperse aerosol (ideally only particles of a particular diameter) at its output.

A schematic diagram of the principle of operation of the NanoScan 3910 is given in Figure 3b.



(a) (b)

Figure 2. *(a) Instrument TSI NanoScan 3910, (b) schematics of the main parts of the measurement system. Figures were taken from manufacturer datasheets*

As can be seen from the schematic, although the main principles of operation are similar for all instruments based on light scattering, the NanoScan 3910 has a much more complicated measuring system compared to the previously described OPS 3330. This is due to the above-mentioned fact that particles of diameter below 300 nm cannot be detected by purely optical methods. Therefore, the classification of particles is more complicated, and is not based on the analysis of the intensity of the scattered waves (as is for the OPS 3330), but is based on the DMA classifier.

The aerosol first passes through the cyclone (point 1 in Fig. 2), which, because of the particle inertia, prevents larger particles from proceeding further through the measuring system. The aerosol is then further treated (point 2 in Fig. 2) in order to produce the known distribution of aerosol charge, this is a necessary step since the newly-created aerosol does not have known and stable charge distribution. In the model of the instrument being described, this is done by exposing the aerosol to charged ions created from clean air using the needle corona.

This is closely related to the classification method using the DMA classifier (point 3 in Fig. 2), which was mentioned above. In this embodiment, the DMA classifier is a capacitor, in which a DC electric field with a controllable intensity is established, one of the electrodes is modified, it has an opening through which the desired aerosols can go further into measurement system. There is a flow of aerosol surrounded by clean air through the electrodes of the capacitor. The DMA classifier extracts the aerosol particles of certain electrical mobility by establishing a field of appropriate intensity which guides a certain particle size through a hole in the modified electrode. It is clear that the DMA only classifies the particles by size, more accurately by electrical mobility, guiding only the part of the particles that are suitably charged (for example, only a portion of positively charged particles, if the central electrode is negative). Determining the total aerosol concentration is possible only if the particle charge distribution is known, which is not always the case. This is why, before classification and counting of the particles, the aerosol is conditioned to establish a precisely-known charge distribution in the aerosol sample.

As previously mentioned, small particles with diameters below a few hundred nanometres cannot be directly detected by the optical chamber-laser-photodetector system. Therefore, for particles of a diameter from a few nanometres to several hundred nanometres, a physical "magnification" is required to make particles detectable. This magnification is carried out by passing an aerosol sample through a saturated vapour of the working fluid (such as isopropanol, n-butanol or even water), see point 4 in right part of the Fig 2. and then by applying a suitable

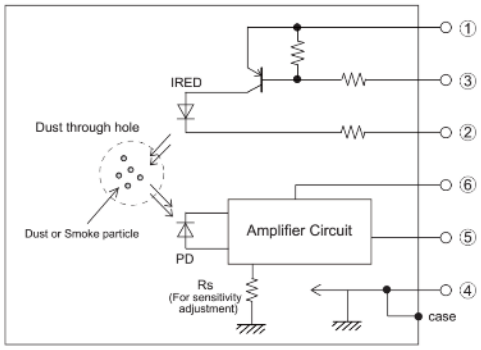
temperature gradient so that the condensation of the working fluid vapour on the aerosol particles occurs. The particles with the condensed vapour of the working fluid on them are now enlarged and can be detected in the optical chamber.

Low-cost PM monitors

The focus of the previous sections was on laboratory quality instruments. Now we will also briefly describe the low-cost sensors that were used in this experiment, note that some of them are not stand-alone devices, but must be, connected to a microcontroller platform.

In Fig. 3 (top left), a Sharp GP2Y1010AU0F sensor is displayed. The infrared light emitting diode (IRED) is used in a detector system, and the sensor output somewhat follows the level of particles in the air. Wavelength data using the sensor are not specified in the manufacturer's specification, but it is known that IRED diodes usually have wavelengths of 770 nm, 870 nm, 880 nm, 940 nm, and 950 nm. In preliminary tests of this sensor, as we will see, it turned out that its output can correlate with some of the channels of laboratory instruments. Sensor performance could be potentially improved by introducing an additional air sampling system (aerosol input, pump flow), because in the basic form, the air flow is made in a rather uncontrollable manner, by using only one heating resistor which stimulates the diffusion of air.

(a)



(b)

(c)

(d)

Figure 3. *a) Sharp GP2Y1010AU0F sensor, b) schematics of Sharp sensor, c) Dylos DC1700, d) Alphasense OPC N1. Figures were taken from manufacturer datasheets*

The DC1700, shown in Fig. 3c, is a laser particle counter, which measures particles in two size fractions, particles of diameter above 0.5 μm and particles of diameter above 2.5 μm. It has temporal resolution of 1 minute, and an internal memory of the instrument can store up to 7 days of continuous measurement. The input aerosol flow is 1 l/min. The manufacturer proposes several typical usages for the instrument. One typical scenario is for the monitoring of workplace air quality. Also, it is possible to gain insight into the effectiveness, or to determine optimal placing, of the air filtration systems. Finally, some users were able to correlate some health issues with the increased level of air pollution, which was tracked using the Dylos monitor.

The Alphasense OPC (*optical particle counter*), is shown in Fig. 3d, and it measures scattered light on individual particles in the air stream which is directed into a specially designed optical chamber (laser wavelength is 658 nm). As was the case for the laboratory-grade instrument, TSI OPS 3330, the particle size is determined from

measurement of the intensity of the scattered light (under the assumptions of Mie scattering) and also particle concentration. As stated earlier, in order to convert the number concentration into mass concentration, a significant number of assumptions must be made, such as particle density and refractive index, with default values being 1.65 g/ml for the density, and $R_i = 1.5 + i0$ for the refractive index. Additionally, for all particles, disregarding their true physical shape, equivalent size is assigned assuming spherical shape (for homogenous spherical particle there is an exact analytical solution of Maxwell equations, known as Mie solution or Mie scattering). The instrument has 16 channels which cover the range from 0.38 to 17 μm.

Most conventional optical counters and sizers have a narrow aerosol inlet in order to precisely guide particles to pass through optical chamber and intersect the laser beam, in that way enhancing accuracy and repeatability of the measurements (see for example Fig. 1 illustrating working principle of TSI OPS330). The disadvantage of this approach is that it requires a stronger pump in order to force the air to flow through narrow aerosol inlet, and filters which help avoid pump contamination and produce clean sheath air to protect the sensitive optics. This increases maintenance and use costs through more frequent filter changes and cleaning of the instrument and more frequent pump replacement. Energy demand of the instrument is increased, which can be a drawback when instrument is battery operated. The Alphasense OPC uses a different approach: pump and air filtration are removed, and by using system of elliptical mirrors and photodetectors the "virtual working volume" is produced in the centre of open optical chamber.

RESULTS

Initial comparisons of the low-cost Alphasense OPC sensor and the laboratory-grade TSI OPS 3330 revealed surprising results. Table (Fig. 4a) summarizes channel cut-off points for the two instruments. A cross-correlation matrix was calculated between all channels of the two instruments, and it is shown in Fig. 4b. By observing the trend of the correlations for the low-cost Alphasense OPC sensor, it can be observed that within one instrument, neighbouring channels are correlated, and that the amount of correlation diminishes relatively quickly when moving away from the observed channel. When comparing channels between the instruments (rectangular region in upper triangular matrix) we can observe very high levels of correlation between (approximately) corresponding channels, with the exception of a few end channels of the Alphasense OPC, which are outside of the range of TSI OPS 3330. Note that correlations between thechannels of the different instruments are somewhat approximate due to different channel boundaries that are setup in the Alphasense OPC firmware. For the (approximately corresponding) channels, cross correlation was about ~ 0.90m, normalized timeseries plots would be in very good alignment, almost indistinguishable. Remaining comparisons will only use the TSI OPS 3330, since the Alphasense OPC would show very similar correlations.

Channels	TSI OPS 3330 [um]	Alphasense OPC [um]
1	0.300 - 0.374	0.38 - 0.52
2	0.374 - 0.465	0.52 - 0.75
3	0.465 - 0.500	0.75 - 1.00
4	0.500 - 0.721	1.00 - 1.25
5	0.721 - 0.897	1.25 - 1.49
6	0.897 - 1.097	1.49 - 2.00
7	1.097 - 1.391	2.00 - 2.99
8	1.391 - 1.732	2.99 - 4.00
9	1.732 - 2.156	4.00 - 5.00
10	2.156 - 2.500	5.00 - 6.50
11	2.500 - 3.343	6.50 - 8.00
12	3.343 - 4.162	8.00 - 10.00
13	4.162 - 5.182	10.0 - 12.00
14	5.182 - 6.451	12.0 - 14.00
15	6.451 - 8.031	14.0 - 16.00
16	8.031 - 10.00	16.0 - 17.23
17	>10.00	NA

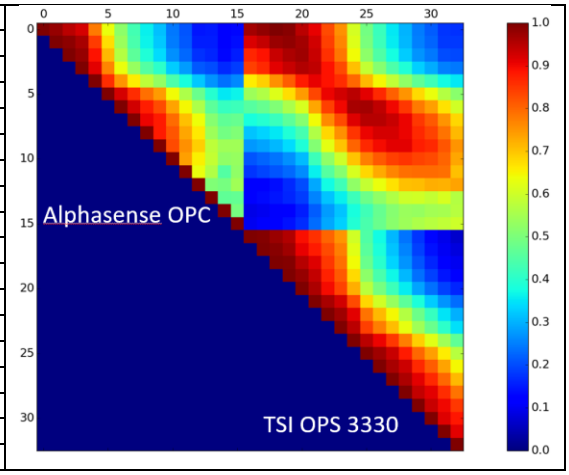


Figure 4. *Cut off points for particle diameter [um] for TSI OPS3330 and Alphasense OPC channels*

Fig. 5 shows comparisons between remaining low-cost sensors and the TSI OPS 3330. Sharp sensors were connected to the Arduino platform and functioned very reliably, both in terms of up time and consistent recording of measured values. Among themselves, Sharp low-cost sensors, had an extremely high correlation of about ~0.98. Compared to the laboratory-grade instrument, they correlated best with the first channel of the TSI OPS 3330 ~0.75 and the correlation coefficient steadily declined when compared to the remaining channels.

Low-cost Dylos instrument outputs data in two channels, small particles (above 0.5um) and larger particles (above 2.5um). Dylos small particles correlate best with the 4th TSI OPS 3330 channel (0.5-0.721um) with a correlation of approximately ~ 0.60 (partial time series of normalized signals is shown in Fig. 6a). Dylos large particles correlate best with 10th TSI OPS 3330 channel (2.156 - 2.500) with correlation of approximately ~ 0.978 with OPS 2.156um.

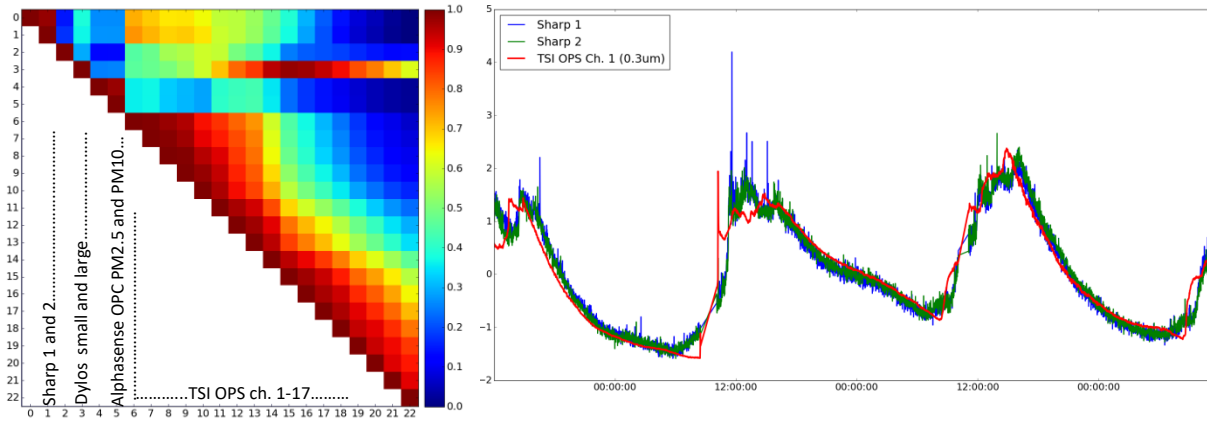


Figure 5. *(a) Cross-correlation matrix of normalized measurements: Sharp 1, Sharp 2, Dylos - small particles, Dylos - large particles, TSI OPS channels 1-17, total of 21 individual signals (b) Normalized Arduino and TSI OPS 3330 ch. 1, from 2016-11-29 12h to 12-02 11h.*

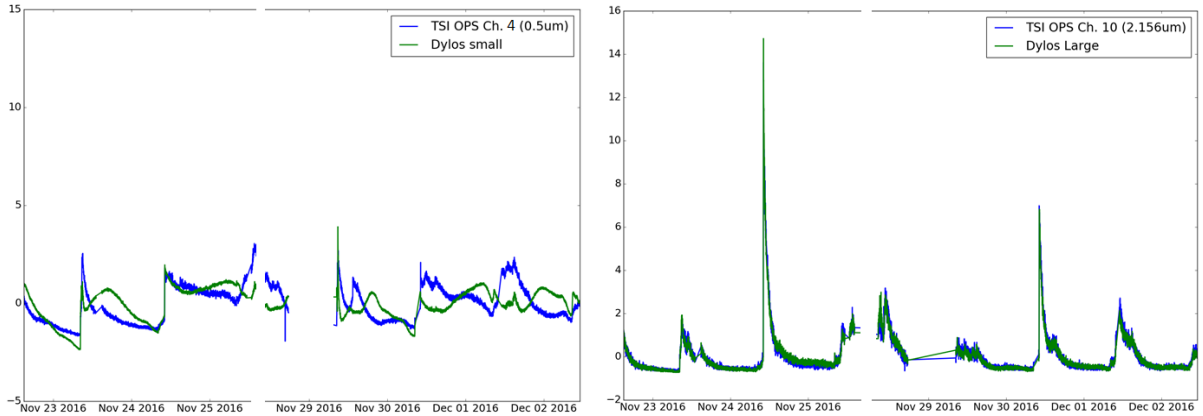


Figure 6. *Overlapped time series of normalized signals from TSI OPS 3330 and Dylos DC1700 (a) OPS Ch. 4 vs Dylos small (b) OPS Ch. 10 vs. Dylos large*

CONCLUSION

Low-cost sensors showed the 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 measurements in 0.3um - 1.4um range. The Dylos low-cost sensor also showed decent results, in contrast to the Sharp sensors it measures two fractions, addressing larger particles with much greater accuracy compared to the lab-grade instrument. The Alphasene OPC was hands-down the most surprising of all sensors, with almost laboratory-grade results. Normalized values were compared and real word deployment would require separate calibration of each sensor, due to differences in absolute levels among signals.

ACKNOWLEDGMENTS

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10.3. ARTIFICIAL INTELLIGENCE MODELS WITH MULTIVARIATE INPUTS FOR CALIBRATION OF LOW-COST PM SENSORS - PROOF OF CONCEPT AND PRELIMINARY ANALYSIS

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ABSTRACT

This paper presents the results of testing of preliminary calibration models for improving the measurement properties of low-cost sensors for $PM_{2.5}$ and PM_{10} particle fractions that were embedded in the AQMESH devices. A multi-dimensional approach was applied for calibration of low-cost sensors. Artificial neural networks (ANNs) were used for modelling dependence between input and output signals. Linear regression (LR) and multivariate linear regression models (MLR) were also developed and compared with ANN models. The evaluation of the established models was performed with standard statistical metrics, R and RMSE. Performance metrics were evaluated during two campaigns in Belgrade at automatic monitoring stations Zeleno Brdo (ZB) and Stari Grad (SG) that belong to the State Network of Air Quality Monitoring in the Republic of Serbia. MLR models had the following median values of the statistical parameters. At ZB (SG) measuring stations for the $PM_{2.5}$ and PM_{10} fractions, R and RMSE had following values: R=0.67 (0.81), R=0.75 (0.85) and RMSE=1.14 (4.28), RMSE=3.41 (7.52). ANN models showed better results compared to the MLR models with the following values: R=0.83 (0.90), R=0.86 (0.88) and RMSE=1.03 (3.25), RMSE=2.71 (6.82). This demonstrates that ANN models could potentialy improve measurement results of low-cost particle sensors in different environmental conditions.

INTRODUCTION

Particulate matter (PM) levels, and their content, in ambient air have been recognized as an extremely important factor that may cause negative effects on human health and the 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). To prevent some of the negative health effects associated with PM, particulate matter mass is regulated.

In order to examine the PM exposure and health effects as reliably as possible, monitoring systems need to be expanded. For the collection of data with high spatial and temporal resolution, it is especially important that novel devices have small dimensions, are easy to operate and have affordable calibration and maintenance procedures. In recent years, small portable systems for the detection of particle concentrations are increasingly being used to support standard measuring stations. This is possible due to the development of new sensors that are characterized by their small size and relatively low price. Due to a significant reduction in investment costs per unit, these sensors are enabling a high spatial and temporal measurement resolution complementing the standard measurement stations.

One of the main problems with using low-cost sensors for respirable particles, is the reliability of the measurements which should be in accordance with legislation and standards (EC, 2008). Sensors manufactured for the market should show stability and reproducibility during operation for a certain period of time. This is often not the case because of errors during production, some structural changes, phase shifts, contamination caused by chemical reactions, etc. Sensor calibration under controlled laboratory conditions is insufficient as the impact of many environmental parameters, such as interfering gases and meteorological parameters can not be taken into account. Calibration in the field is necessary.

Sophisticated calibration can significantly improve the measurement results. Calibration is usually done by simple Linear Regression models (LR), with an assumption of linearity between the sensor and reference response.

With multivariable environmental conditions, this is typically insufficient and sometimes it is necessary to develop models which use a higher number of parameters. Multivariate Linear Regression (MLR) and Artificial Neural Networks (ANN) models are good candidates. This paper presents comparative results of testing LR, MLR and ANN calibration models used in the interest of improving the measurement properties of low-cost sensors for $PM_{2.5}$ and PM_{10} particle fractions that were embedded in AQMESH devices.

MATERIALS AND METHODS

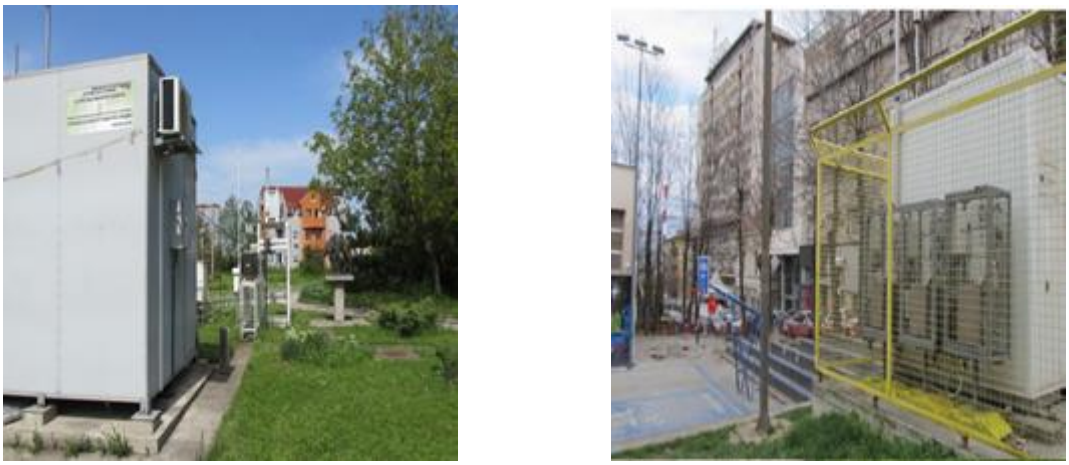
Presentation of automatic measurement stations and low-cost measurement equipment

Throughout 2015, we performed two consecutive data collection campaigns by using AQMESH v. 3.5 units co-located with reference/equivalence PM monitors. The AQMesh units (Environmental Instruments Ltd, UK, http://www.aqmesh.com/) were battery operated stationary platforms that measured four gases (CO, NO, NO_2 and O_3) and $PM_{2.5}$ and PM_{10} particulate matter concentrations.

The PM sensor embedded in this system used an optical scattering method for measurements, with the ability to discern 32 channels corresponding to different particle diameters. The conversion from number to mass concentration was done using an approximation of the particle's spherical shape. Data from sensors were sent to the server for visualization. Data from gas sensors were sent to the server every 1h, while the $PM_{2.5}$ and PM_{10} fractions measurement resolution were 15 min.

The experiment was conducted in co-operation with the Serbian Environmental Protection Agency (SEPA). During the study, 25 AQMESH platforms were co-located next to the two reference monitoring stations belonging to SEPA: (1) Belgrade Zeleno Brdo (21/04/2015-07/07/2015) and (2) Belgrade Stari Grad (14/07/2015-16/10/2015).

AMS Belgrade Zeleno Brdo (20° 31' 18" N, 44° 47' 11" N) could be classified as a background station in a suburban area, located at an altitude of 243 m.a.s.l. On the other hand, Belgrade Stari Grad (20° 27' 32" N, 44° 49' 16" N) is a background station in the urban area of the city, at an altitude of 97 m.a.s.l. Pictures of these stations are presented in Figure 1.



(a) (b)

Figure 1. *Automatic measuring station (a) Zeleno Brdo and (b) Stari Grad.*

Presentation of calibration algorithms

Linear regression (LR) and Multivariate linear regression (MLR) can be considered as one of the most simple statistical modeling approaches. However, despite being simple, they can be, in many situations, be quite usefull. One way to think about linear models is in terms of Taylor series where only linear terms are taken into acount. Thus, MLR (and LR for univariate case) models can, in approximation, model any functional dependance between input predictors and desired target. However, validity of such model and its accuracy will reduce once we are too far from the mean values of the input predictors, i.e. if we use the predictive model outside its initial scope.

Artificial neural networks (ANNs) can be used to model more complicated functional dependencies between input predictors and target. In this paper, feed-forward ANN models with one hidden layer were used. In the hidden layer 10 neurons were used with a sigmoid transfer function, a linear function was used at the output layer. For ANN models, three training algorithms were used: (1) Levenberg-Marquardt algorithm (LM), (2) Resilient backpropagation algorithm (RB) and (3) Conjugate Gradient Powell-Beale algorithm (CGPB).

The performance of each model developed, was tested using common statistics parameters that are shown in Table 1.

Table 1. *Performance statistics for developed models.*

Test	Symbol	Formulation
Correlation Coefficient	R	$\frac{\sum_{i=1}^{n}(x_i-\bar{x})(y_i-\bar{y})}{\sqrt{\sum_{i=1}^{n}(x_i-\bar{x})^2(y_i-\bar{y})^2}}$
Root Mean Squared Error	RMSE	$\sqrt{\frac{\sum_{i=1}^{n}(x_i-y_i)^2}{n}}$

RESULTS AND DISCUSSION

Before model development, we investigated measurement stability of PM sensors in 25-AQMESH v. 3.5 platforms. This was done to verify if some of the sensors were either malfunctioning, or were truly obtaining zero measurements during the campaigns. The simplest way to do this was to visualize the correlation matrix between the sensor's measurements. Figure 2. shows correlation matrices between 25 low-cost sensors for $PM_{2.5}$ and PM_{10} particles during ZB and SG campaigns respectively. Figure 2 a) and c) show the results for the ZB campaign. Figure 2. b) and d) are the results for the SG campaign: Here it can be seen that there was a malfunctioning problem for the sensor located on platform 20. During the first campaign the sensor from platform 12 also showed a greater disagreement with other sensors. From Figure 2. it can be noted that a higher correlation was detected in the first campaign, the second campaign correlation matrix shows greater anisotropy.

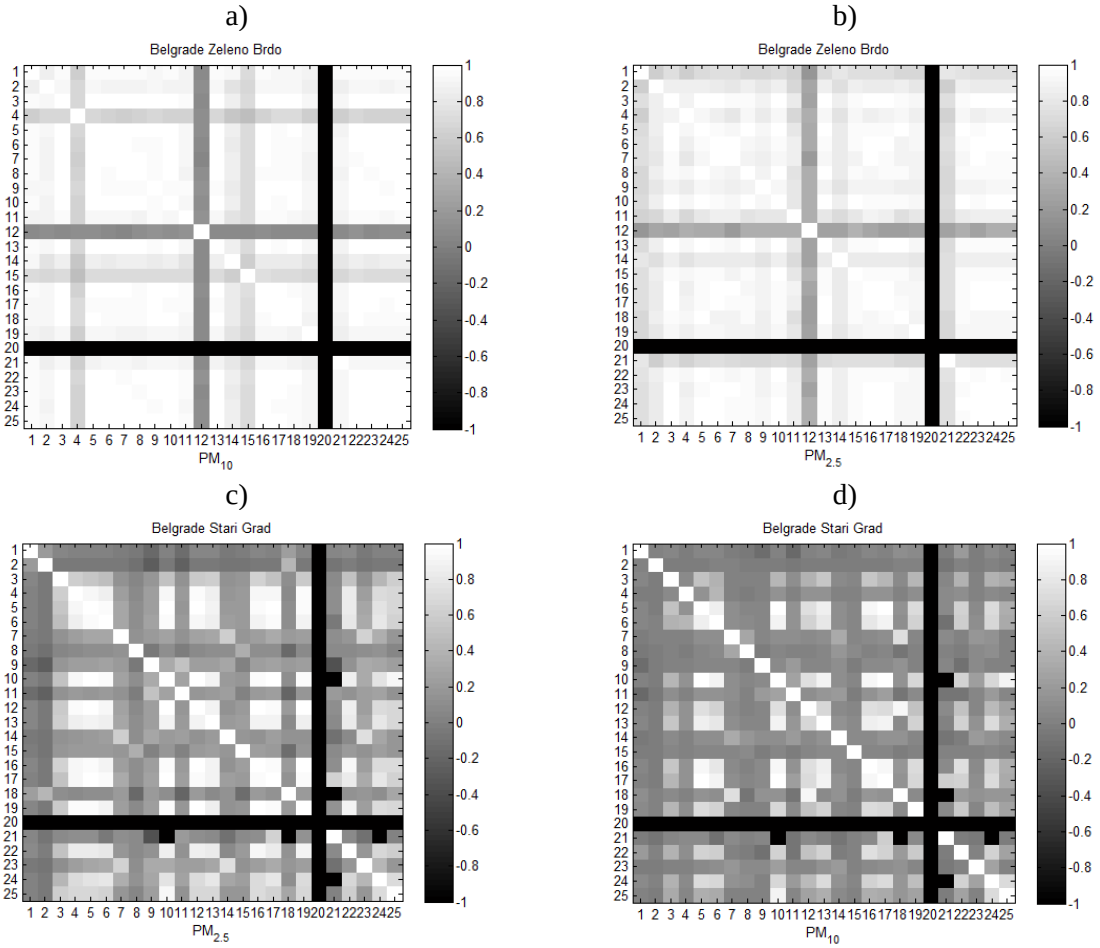


Figure 2. *Pearson correlation matrix between AQMESH v. 3.5 sensors (a) $PM_{2.5}$ during ZB, (b) PM_{10} during ZB, (c) $PM_{2.5}$ during SG, (d) PM_{10} during SG.*

Note that from Figure 2. it can be seen that some points of the matrix have -1 correlations. This is an indication that the sensors did not have measurements at the same time intervals during the campaign. Better values for the first campaign can be explained by the ageing of the sensor.

Table 2. *Partial mutual information between reference measuring variables from ZB (left side) and SG (right side) campaigns.*

	$PM_{2.5}$	**PM_{10}**	**$PM_{2.5}$**	**PM_{10}**
CO	0.00	0.00	0.03	0.05
NO	0.00	0.00	0.00	0.00
NO_2	***0.15***	***0.11***	***0.10***	0.00
O_3	***0.14***	***0.19***	0.00	0.00
$PM_{2.5}$	0.00	0.00	0.00	***0.16***
PM_{10}	0.00	0.00	0.00	0.00
p	0.04	0.05	***0.11***	***0.12***
rH	***0.31***	***0.32***	***0.14***	***0.12***
T	0.09	***0.15***	0.08	***0.26***

The next, and one of the most important steps, in the MLR and ANN model development is the deteremination of an appropriate set of input vectors. ANN models can be used in situations where the relationship between inputs and outputs are suspected to be non-linear in nature. Therefore, for determination of the input data set in model-independent approach, other analytical methods for determining non-linear relations are used.

This can be done by the analysis of partial mutual information (PMI) of possible data sets, or with the calculation of Spearman coefficients. In this paper, for MLR and 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 of mutual information (Vlachos & Kugiumtzis, 2010, Kugiumtzis, 2013).

PMI score indicates the information flow of time series X to time series Y conditioned on the rest time series in Z. The PMI measure values are stored in the matrix, where the value at position (*i, j*) indicates the effect from *i* to *j* (row to column). Thi PMI score for possible input variables is shown in Table 2. for ZB (left columns) and SG (right columns) campaigns. Significant values for PMI are marked bold italic in Table 2. These highlighted parameters guided the choice of supporting predictors in our models. Three different type of models were developed. The first model used only meteorological variables, the second used chosen gases and the third was a combination of the previous two established models. This is summarized in the Table 3 below. Based on the results of statistical metrics, it was found that the third model with a larger number of input parameters showed the best results. Hence, in the following text we only present results for this model. Note that the all calibration models follow the same pattern, where we have one input parameter that we want to calibrate ($PM_{2.5}$ and PM_{10} output from low cost sensor) and a number of supporting predictors, which are also input parameters for the calibration model. Thus, for example, for M1 calibration model for PM_{10} the total number of inputs is 4 (3 supporting predictors and 1 low cost input for calibration), and for M3 the total number of inputs is 7 (3 supporting predictors from M1, 3 supporting predictors from M2 and 1 low cost input for calibration).

Table 3 *Supporting predictors used for $PM_{2.5}$ and PM_{10} calibration models.*

	PM2.5	**PM10**
M1	p, rH and T	p, rH and T
M2	NO2 and O3	PM2.5, NO2 and O3
M3	M1 and M2	M1 and M2

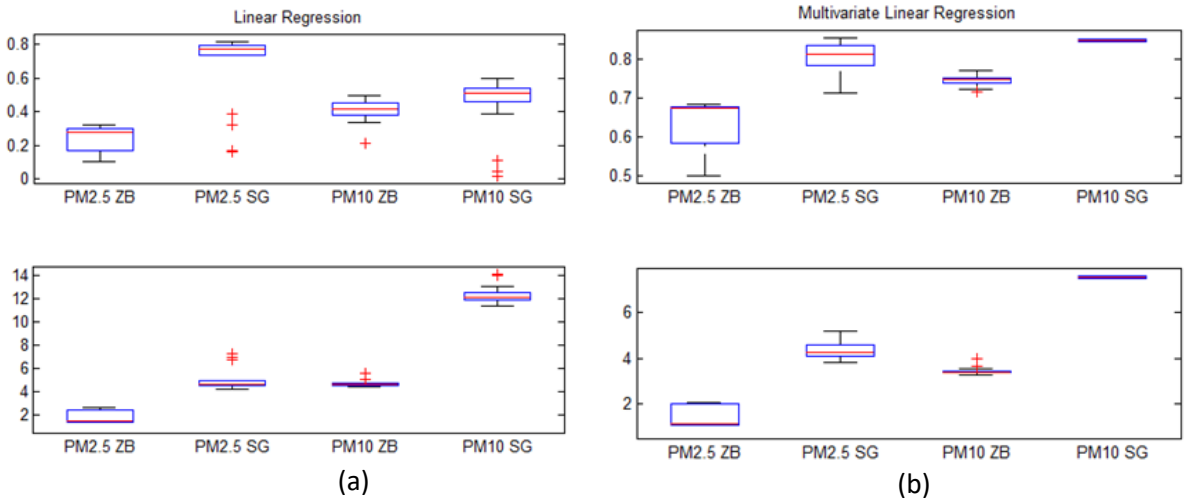


Figure 3. *Box plot for the correlation coefficient R and RMSE between reference and (a) LR and (b) MLR calibrated low cost sensors for 25 platforms in two campaigns.*

While we have made final list of predictors that will be used, before proceeding with the further analysis of calibration models, one must always consider which predictors are actually available, by considering total amount of valid measurements the low-cost sensors provided. If the low cost sensors don't have sufficient data, or if the quality of the data is not satisfactory, the use of such inputs in calibration models is not desirable. Since in this paper we only consider proof of concept of the method for calibration of low cost PM sensors, we opted to use the same predictors for all 25 platforms. To minimize variability in the final calibration models between the different platforms we used the data from *reference instruments as support predictors*. Thus, the variability in the performance for different platforms comes only as a consequence of the single low cost sensor performance. Note that this approach severely limits the practical usefulness of such calibration models, however, it still gives insight into calibration procedures, choice of species of input predictors, types of possible calibrations and similar. Furthermore, since practical usefulness of studied calibration models was not paramount, and consequently precise estimates of model performance, i.e precise predictive power of the calibration models, were not needed, training/test split of the input data was not done. This way, Monte Carlo variation due to training/test split, which can be a significant factor, is avoided.

Figure 3. show box plot diagrams of the R and RMSE tests for LR (a) and MLR (b) models. R is shown in the upper subplot, while the RMSE is on the lower subplot. From Figure 3. it can be noted, that during the second campaign we obtained better results, which can be explained by increased sensor sensitivity in an environment with higher concentration of pollutants. When comparing results from Figure 3 a) and b) (for LR and MLR, respectively), it may be noted that the median of both statistical tests and for both fractions were increased by using the MLR model. The best R results were obtained for $PM_{2.5}$ on SG, while RMSE is the smallest for $PM_{2.5}$ on ZB. The existence of few outliers in statistical tests for LR model were also noted, however, when using MLR models these outliers disappeared. So, we can conclude that the multi-dimensional approach could improve measurements even for sensors with lower R with respect to the referent measurements. The interquartile ranges for both calibration methods are very similar, which can be quantitatively confirmed if the width of the box plot is estimated.

Now we proceed to the most complex model of calibration based on the ANN model. Statistical results for this calibration method are shown on Figure 4. From Figure 4. it can be noted that the examined training algorithms, LM, CGPB and RB, give similar results, which are significantly better when compared to MLR and LR methods. The LM training algorithm has the best results of statistical tests in comparison with CGPB and RB algorithms. Also, the LM ANN model shows the lowest interquartile range. This is an indication that LM ANN models can calculate different nonlinear relations of parameters under different measuring conditions.

Finally, Figure 5. show measurements from the reference stations, raw, LR, MLR and ANN calibrated measurements from one randomly chosen platform during two campaigns. From Figure 5. it can be easily seen that the results obtained by using neural networks are much closer to the reference measurements in comparison to LR and MLR models

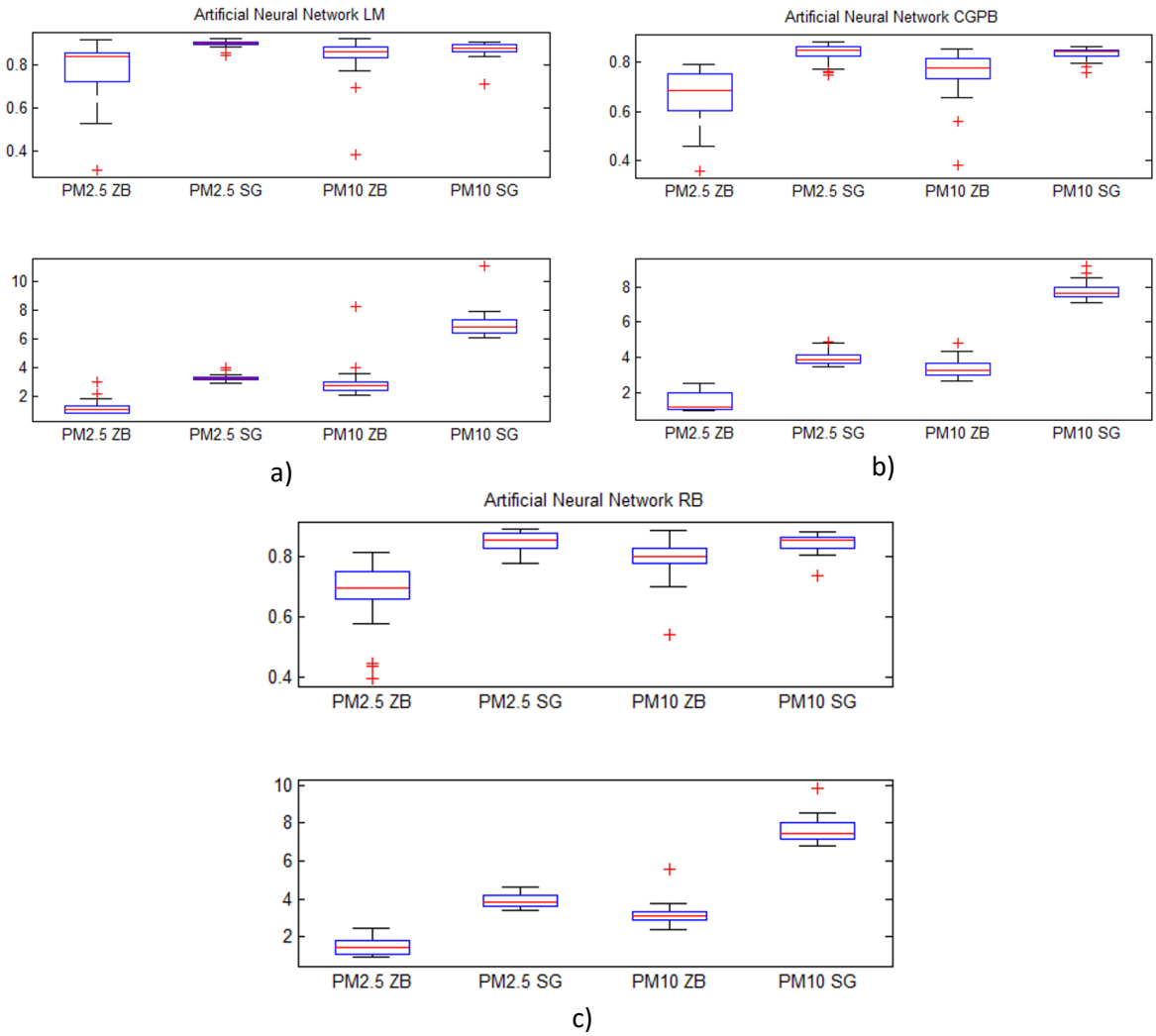
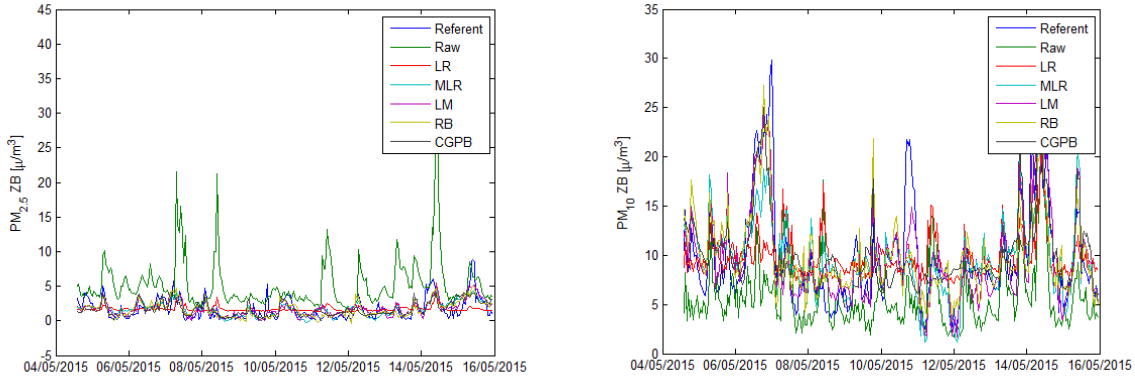
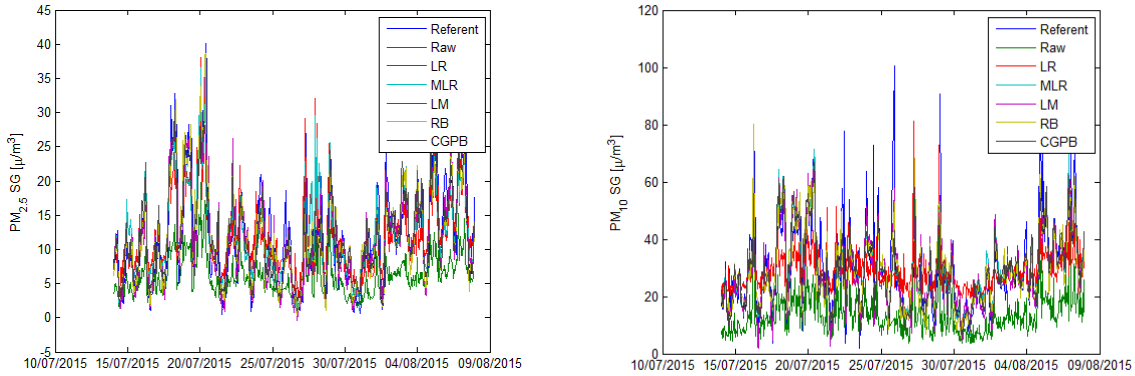


Figure 4. *Box plot of correlation coefficient R and RMSE between reference and ANN (a) LM, (b) CGPB and (c) RB calibrated low-cost sensors measurements for 25 AQMESH platforms in two campaigns.*





(c) (d)

Figure 5. *Referent, raw, LR, MLR, LM, RB, and CGPB calibrated measurements for $PM_{2.5}$ and PM_{10} fractions during campaigns at AMS Zeleno Brdo and AMS Stari Grad.*

CONCLUSION

The aim of this study was the examination and comparison of different signal processing techniques that could be potentially used in the calibration of low-cost sensors for air pollution monitoring. Special attention was paid to the conventional multivariate linear regression method for calibration. This method was compared with artificial neural networks models which have been developed with three different training algorithms: LM, RP and CG.

Based on the results of the statistical tests for the established models, it was found that neural networks, due to significantly larger number of model parameters, showed better results compared to more simple, linear regression model. Specific choices used in this paper regarding number (and type) of supporting predictors, can significantly limit the direct usefulnes of the proposed calibration scheme. However, final results of the statistical tests can be used as an inspiration for further research, which would be more stringent in terms of total number of inputs in the calibration model and demanding less in terms of data quality from the supporting predictors. In the current proof of concept calibration method, number of supporting predictors is unpractically large and error in supporting predictors needs to be low in order to reduce the error in the final calibration model output The LM neural networks have shown the best results compared to RB, CGPB neural networks and multivariate linear regression method.

ACKNOWLEDGEMENTS

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10.4. ANALYSIS OF PARTICULATE MATTER AND SMALL ION CONCENTRATION IN THE INDOOR ENVIRONMENT BASED ON A BALANCE EQUATION

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ABSTRACT

The purpose of this work was to explore the relationship between particulate matter (PM) and small ion (SI) concentration in a typical indoor environment. Changes in SI concentration are due to several factors. Firstly, SI are constantly created in pairs by ionizing radiation that exists in the environment. They are also continually destroyed in a process of recombination. Additionally, SI can attach to PM. Because of this, a change in PM concentration directly results in a change in SI concentration. The SI balance equation can be used to quantitatively describe the above-mentioned processes. We will interpret the results obtained from measuring a wide range of relevant air quality parameters in a typical indoor environment, occupied on workdays, within the framework of balance equation.

INTRODUCTION

The importance of indoor air quality cannot be overstated, especially due to the fact that most people spend large part of their day indoors (in industrialized countries this may exceed 90%). For some age groups, such as the elderly population, this can even easily amount to 100 percent. Concerns about possible health effects are illustrated by the fact that, regardless of indoor or outdoor setting, elevated exposure risks can exist even at relatively low concentrations. Furthermore, while indoor and outdoor conditions are certainly linked (e.g. via a simple ventilation process), some air pollutants are more prominent outdoors (e.g. gaseous pollutants, sulphur dioxide or ozone) while some are typically more prominent indoors (e.g. formaldehyde, carbon monoxide or nitrogen oxides and radon) [1]. In addition to gaseous pollutants, the concentration of airborne particulate matter also raises concerns since, in many European cities according to the European environment agency reports [2], it is two to three times higher (outdoors) than that recommended by the World Health Organization (WHO). This can easily be worse in an indoor environment, especially in view of serious health effects that may result from long-term exposure to an elevated concentration of particulate matter [3].

In this paper we focus on a smaller subset of air pollution phenomena which includes concentrations of radon, small ions (SI) and particulate matter (PM). It is important to note, that while the health effects of radon [4] and particulate matter [3] are well known, the health effects (some authors even state possible benefits, or at least perceived benefits) of small ions are less obvious, see for example [5]. Nevertheless, since all three quantities are linked via the balance equation, even though the health effects are only firmly established for radon and PM, it is justified to consider all three simultaneously.

Let us briefly consider the physical processes that are involved in changes in SI concentration. Firstly, SI are constantly created, in pairs, by ionizing radiation that exists in the environment. There are several natural sources of ionizing radiation that are responsible for air-ion production in the lower troposphere, cosmic rays, radon and terrestrial gamma radiation. Ionization from cosmic rays comprises approximately 20% of the total surface ionization rate. Remaining 80% arises from natural α and β emitters in the air and soil, although air-ion pair generation near the ground varies mostly with the concentration of ^{222}Rn and its progenies. The half-life of ^{222}Rn is 3.82 days and the decay product is an alpha particle with energy 5.49 MeV. The decay of ^{222}Rn generates a large number of nitrogen and oxygen molecular ions (order of magnitude ~ 10^5) per each α-particle. As a consequence, the near-ground ionization rate caused by background ionization, is about 10 ion pairs/cm^{3}s in continental areas. Within microseconds of the ionization process, primary ions evolve through the process of hydration to form small cluster ions, also known as small air ions or nano-air ions. This class of air ions can survive much longer, up to 100s, depending predominantly on air pollution and air density [6].

To summarize, small air ions are electrically charged clusters consisting of several molecules in which ordinarily neutral atmospheric molecules/atoms have gained or lost electrons. While particulate matter can also be charged, it is composed of a much larger number of molecules and is thus up to several orders of magnitude larger in diameter compared to small ion clusters.

SI are also continually being destroyed in a process of recombination, producing neutral molecular clusters. In addition to the process of recombination, SI can attach to PM. Because of this, a change in PM concentration directly results in a change in SI concentration. A significant portion of PM in the urban environment is a result of human activities, where smaller particles are typically associated with the process of combustion occurring in vehicles, industrial activities, biomass burning, and similar, while larger particles are typically due to construction and demolition activities, entrainment of outdoor dust and similar. The SI balance equation can be used to quantitatively describe the above-mentioned processes.

The outline of this paper is as follows. First, we provide a detailed explanation of the small ion balance equation and derive the link between small ion concentration, volumetric production rate and particulate matter concentration. Then we describe the method that was used in the indoor measuring campaign, in which all relevant parameters appearing in the balance equation are measured either directly or via an important proxy. We will show that under a quasi-steady state approximation, it makes sense to use the linear regression model to describe the interdependence between concentrations of larger aerosol particles of various diameters and small ion concentrations. Finally, conclusions about several linear models that were derived are given along with directions of future work.

BALANCE EQUATION AND QUASI STEADY STATE

The small air ion concentration ($n_{\pm}$) is determined by the following balance equation

$$\frac{dn_{\pm}}{dt} = q - \alpha n_{\pm} n_{\mp} - n_{\pm}\beta Z \tag{1}$$

where q is the volumetric production rate, Z is the aerosol number concentration, α coefficient accounts for the losses of ion-to-ion recombination and β represents an effective ion-aerosol attachment coefficient, which is the integral over the size distribution of aerosol particles. The balance equation can include additional terms. If electrostatic deposition (occurring mainly in indoor air) is included in a model, there is an additional right-hand side term $-\delta^{\pm} n^{\pm}$, where δ is an electrostatic deposition rate coefficient of the air ions.

If we assume $n_{+} \approx n_{-}$ (note that in reality $n_{+} \approx 1.12 n_{-}$ which is due to the different mobility of positive and negative small ions, but that constant can be absorbed into α coefficient), the balance equation reduces to:

$$\frac{dn_{-}}{dt} = q - \alpha n_{-}^2 - n_{-}\beta Z\,. \tag{2}$$

In a quasi-steady state, the differential equation reduces to quadratic equation:

$$\alpha n_{-}^2 + n_{-}\beta Z - q = 0\,. \tag{3}$$

Since concentration of small ions must be positive, only the positive branch is the solution:

$$n_{-} = \frac{\beta Z\left(\sqrt{1+\frac{4\alpha q}{\beta^2 Z^2}} - 1\right)}{2\alpha} \tag{4}$$

If we use the Taylor expand term in parenthesis, under the assumption that α is very small, and we obtain:

$$n_{-} \approx \frac{q}{\beta Z}\,. \tag{5}$$

Since β represents an effective ion-aerosol attachment coefficient, which is the integral over the size distribution of aerosol particles, we can expand the above term as:

$$n_{-} \approx \frac{q}{\sum \beta_i Z_i}. \tag{6}$$

This result can also be more readily derived starting from the balance equation if we neglect the quadratic term present in (1). Since our campaign was situated indoors, the electrostatic deposition rate coefficient could also be included, and the balance equation now reads (under the assumption of a quasi-steady state):

$$\frac{dn_{-}}{dt} \approx 0 \approx q - n_{-}\left(\beta Z + \delta^{-}\right) \tag{7}$$

and after expanding βZ term we obtain:

$$n^{-} \approx \frac{q}{\sum \beta_i Z_i + \delta^{-}} \tag{8}$$

or more conveniently

$$\sum \beta_i Z_i + \delta^{-} \approx \frac{q}{n^{-}}. \tag{9}$$

The form of the above equation suggests linear regression is a justified modeling approach if we want to model the interdependence between the concentration of larger aerosol particles of various diameter and small ion concentration. The physical meaning of the coefficients in linear regression (β_i) are an ion-aerosol attachment coefficient and the intercept term corresponds to the electrostatic deposition rate coefficient of the air ions (δ^{-}). Note however, that in a non-laboratory type of campaign, one cannot precisely control the aerosol distribution and there may be a significant correlation between individual channels corresponding to different particle sizes, which makes calculation (and interpretation) of the regression coefficients as attachment coefficients largely approximate.

A few notes about the physical nature of the ion-aerosol attachment coefficient are relevant. Ions attach differently to neutral and charged particles. In the case of neutral particles, the attachment of small ions can be described using diffusion theory

$$\beta_{\text{diffusion}} = 4\pi r_{\text{particle}} kT\left(B_e / e\right). \tag{10}$$

where B_e is electrical mobility, r_{particle} is radius of the particle, T absolute temperature, e is elementary charge, and k is the Boltzmann constant. In the case of charged particles, diffusion is still a factor, but an additional term is needed to account for the movement of ions due to the electrostatic field of a particle

$$\beta_{\text{charged}} = \beta_{\text{diffusion}} + \left(eB_e / \epsilon_0\right). \tag{11}$$

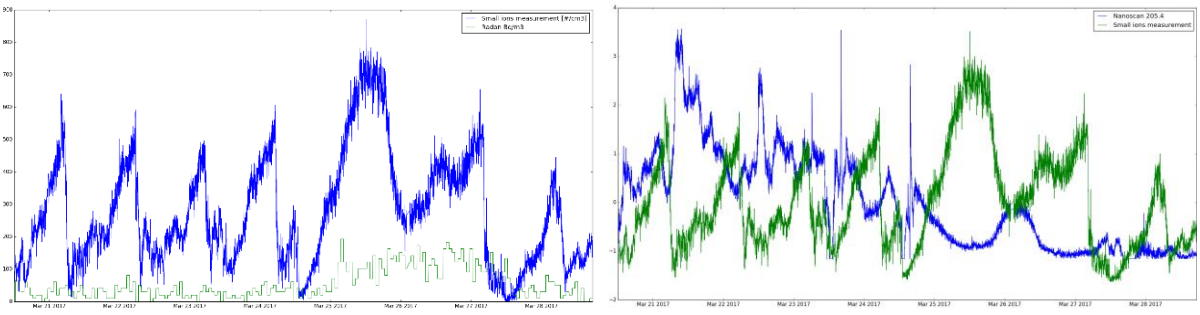
As a result, the approximate physical picture of the attachment process is not simple, and can further depart from real physical processes since during experiments we will certainly encounter multiply charged particles, a non-steady state regarding charge distribution of large aerosols etc. The (simplified) theory also suggests that the attachment coefficient would be larger for particles of a larger diameter.

METHOD AND RESULTS

A wide range of relevant air quality parameters were measured in the indoor environment, occupied on workdays, in March 2017. The measurements included SI measurements using a Gerdien-type air ion detector (Kolarz, 2012), PM concentrations in a 10nm to 10um 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, the radon concentration level was measured hourly using a Radon Scout. The collected data describes all relevant processes: 2 minute SI concentration measurements describe a steady state, radon

concentration gives insight into the rate of volumetric ion pair generation and 1 minute PM measurements give insight into main loss mechanism for SI.

Initial exploratory data analysis shows that there is a correspondence between the increase in radon concentration and the increase in ion concentration, shown in Fig. 1a.



(a) (b)

Figure 1. *Initial exploratory data analysis a) Radon concentration vs. small ion concentration b) Normalized TSI NanoScan data from 205.4nm channel vs. normalized small ion concentration*

We opted not to use radon data as a proxy for the volumetric production rate, due to a large temporal resolution of radon data and since the rolling average would introduce a lag presenting an adverse effect on the calculation of correlations of other variables with radon data. Instead we assumed that the volumetric production rate is constant and that the change in SI concentrations is mainly due to a variation of PM concentrations. Justification for such simplification can be found in Figure. 1b, where normalized TSI NanoScan data from 205.4nm channel vs. normalized small ion concentration is shown. As can be seen from Figure. 1b, roughly speaking, increases in PM concentration are matched with decreases in SI concentration, and vice versa. It is worth mentioning that this effect is most clearly seen for the channel shown in Figure. 1b, despite the fact that theoretical considerations regarding the attachment coefficients given in previous section suggest an increase in the attachment of ions to particles with an increase in particle diameter. However, this effect could be also due to non-controlled PM size distribution which is expected in non-laboratory conditions.

The relationship between SI concentration and PM concentrations was derived using a quasi-steady-state approximation of the SI balance equation. As stated earlier, the form of this relationship suggests that the use of linear regression in modelling is a 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 a significant cross correlation, the ordinary least squares approach was not a reliable method, producing unphysical results. To ensure the regression coefficients had physical meaning we used a non-negative least squares solver [7], and aggregation of channels into total counts and typical PM fractions. Results are shown in Figure. 2a.

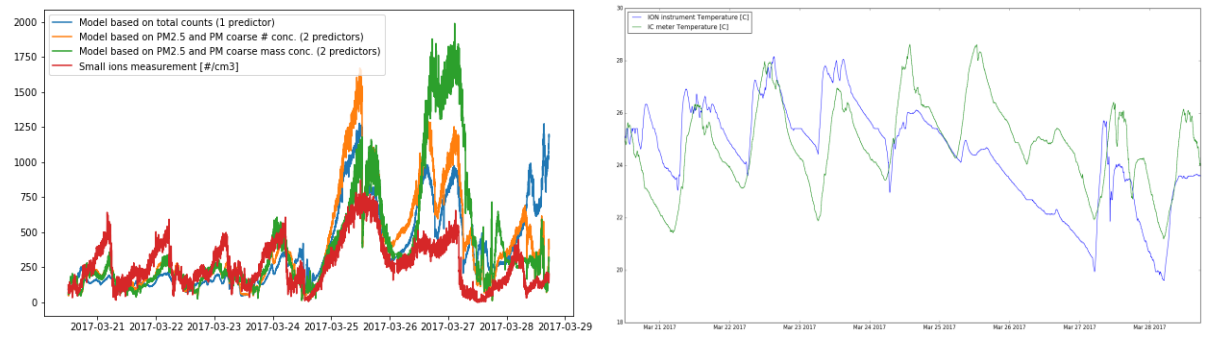


Figure 2. a) Comparison of small ion measurements and 3 models based on total counts and PM fractions b) Additional temperature measurements from IC meter and a Gerdien-type air ion detector

CONCLUSION

All models show daily variations of small ion concentration; however, it seems that models are prone to overestimation, occurring in periods of low particle counts. An additional possibility for larger discrepancies could be temperature variation asseen in Figure. 2b, which is not accounted for in the model. Future work may incorporate additional parameters into modelling, such as temperature, and also introduce more complex models, based on the machine learning approach, where a choice of predictors would be based on the underlying physics. Also, more complex models would not require neglection of the quadratic term, thus potentially, improving the results. However, direct physical interpretation of model parameters in this case could be lost. In the case of a model based on total counts, the attachment coefficient is estimated to be 8.45e-06 $cm^3\ s^{-1}$. Note, however, that interpretation of the regression coefficients as attachment constants is somewhat approximate since there is a significant correlation between individual channels, corresponding to different particle diameter.

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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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ABSTRACT

Air quality information from high-end instruments is currently supplemented, and even challenged, by data and information based on low-cost sensor systems. Low-cost sensor systems, including particulate matter sensors/monitors (LCS-PM), can be deployed in larger numbers because of their lower costs, but questions remain regarding the quality of data they produce. The available LCS-PM offer opportunities for applications that support new atmospheric services and potentially facilitate the involvement of citizen scientists in the process of air quality data collection. Commercially are individual LCS-PM sensors available for 10-100 EUR, and ready-made sensor systems may cost as little as 100 EUR. Majority of LCS-PM sensors/monitors that are available on the market work on the light scattering principle. They are cheap and simple, have low power requirements, and quick response time. In this paper, we give an overview of published and own results of testing inter and intra LCS-PM variability of a widely used OPC Alphasense model, both in control test atmosphere and in field conditions. We also give examples of successful use of LCS-PM in a distributed sensor network, for different cases of mobile monitoring as well as for application in agriculture for pesticide drift investigation.

KEY WORDS: particulate matter, air pollution, low-cost sensors, performance evaluation, air quality monitoring,

INTRODUCTION

International Agency for Research on Cancer (IARC) designated outdoor air pollution as a Group 1 carcinogenic substance. Respirable particulate matter (RPM) mixture, particles 10 microns or less in diameter (PM_{10}), was evaluated separately and also classified in the Group 1 [IARC, 2013]. According to World Health Organization [WHO, 2018.], particulate matter in ambient outdoor air, is more toxic and affects more people than gaseous pollutants. This makes PM a key contributor to adverse health effects of air pollution in outdoor and indoor environment. It adversely affects human health in numerous ways, including by development of chronic diseases or even contributing to premature death. In addition, PM plays a significant role in modifying global climate. Particle mass concentration (PMC), particle number concentration (PNC), size distribution and content varies across space and time, in relation to sources of particles in each study location and its surroundings, and to the transformations that occur in the atmosphere. WHO guidelines, European standards and plans for monitoring in national and local air quality networks specifically address two size fractions of particles, fine particles smaller than 2.5 μm ($PM_{2.5}$), and sum of fine and coarse particles (PM_{10}).

Clean air is considered to be a basic requirement for human health and well-being. WHO guideline states that annual mean particulate matter with a diameter of less than 2.5 micrometers should not exceed 10 $\mu g/m^3$. $PM_{2.5}$ includes a number of harmful pollutants, and it can penetrate deep into the lungs and the cardiovascular system, posing risks to human health. WHO [2016] estimated that 92% of the world's population lives in places where the annual mean fine particulate matter in the air exceeds the guideline. This is also the situation 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 recent years, 85% of exceedances of air pollutants registered by the Serbian Air Quality State Network were attributed to PM pollution. In 2017, more than 2/3 of sites that belong to national and local monitoring networks registered mean annual values of PM_{10} above limit (40 $\mu g/m^3$) value. Data were collected with automatic monitors (thirteen stations) and using gravimetric method collecting daily samples (twelve stations) [SEPA, 2018]. In addition, in 2017, SEPA reported $PM_{2.5}$ levels from eight locations in the seven cities in Serbia. At one location, the $PM_{2.5}$ level was above annual limit value (25 $\mu g/m^3$). At all locations, $PM_{2.5}$ levels were above annual guideline recommended by WHO.

Currently, information on AQ and related hazards, including PM, is mostly generic, and seldom perceived as personally relevant. In order for individuals to consider air pollution and its harmful effects as something personally relevant, the information should be personalized. For example, one could offer information about indicative level of air pollutants in microenvironment along the daily route, and explain how this is personally relevant. By using affordable personal monitors or by establishing a dense network of monitoring units, in which low-cost sensors

(LCS) for various air pollutants, including PM fractions (LCS-PM) are embedded, AQ monitoring gains novel and innovative tools ready for future challenges.

The national networks monitor and measure particulate matter by methods with prescribed accuracy and precision, using high-end monitors and sophisticated quality assurance and quality control systems. This ensures comparability of measurements across geographical areas and meteorological and climatic conditions, but seldom provides high temporal and spatial resolution of air quality information necessary for personalized information. Lately, miniaturization and improved information and communication technologies result in the availability of low-cost sensors, and the use of lower-cost sensor systems is increasing every day. On the market there are available low-cost PM sensors (that cost in range 10-100 EUR) and sensors kits (assembled sensor systems that cost up to 600 EUR and even more, or do-it-yourself kits), from different respectable producers (e.g., see Figure 1). The main characteristics of available sensor systems were compared in Jovašević-Stojanović et al. [2015] and [Rai et al. 2017].

LCS-PM are suitable for deployment in large numbers in terms of the cost of a single unit, but questions remain regarding the quality of data produced. There is no doubt that LCS-PM sensors may increase spatial and temporal monitoring resolution and cover large variety of application in a cost-effective manner, but there are doubts regarding their reliability, accuracy and precision. In this paper, we summarise some of useful and attractive applications of LCS and discuss properties of measured data (in laboratory and field conditions).

Airviz Inc. – Speck	Air Quality Egg	Dylos - DC1700	Shinyei	PurpleAir PA-II (Plantower PMS5003 sensor)	OPC-N2, Alphasense
$140	$250	$ 475	$ 1000	$200	$310

***Figure 1**. LCS-PM kits and their purchase prices in USA (published at by AQ-SPEC, http://www.aqmd.gov/aq-spec/evaluations/summary-pm)*

LABORATORY AND FIELD STUDIES OF LCS-PM

Majority of low-cost PM sensors models that are on the market work on the light scattering method (schematic diagram of LCS-PM in Figure 2). This type of PM sensor is cheap and simple, has low power requirements, and quick response time [Wang et al., 2015]. A light source illuminates the particles and the scattered light from the particles is measured by a photometer. The amount of light scattered is roughly proportional to PNC concentration with diameters greater than ~0.3 μm, while particles with smaller diameter cannot be detected by this method as they do not scatter.

The most important simplifications that lead to reducing the particle sizing and counting capabilities of the LCS-PM in comparison with standardized devices that work on same principle are:

- absence of a sheath flow to keep the aerosol sampled in a confined beam
- the using of a fan to draw the sample flow through the sensor

Studies show that reliability of data collected with LCS-PM in case of lower concentrations is more questionable [Kelly et al., 2017]. For wide use of each of LCS-PM device we need to know:

- Operational characteristics such as a possibility of failure caused by aging due to accumulation of particles inside the measuring chamber
- Meteorological conditions during the LCS-PM operation
- Intramodel variability, i.e. reproducibility between units of the same type of LCS-PM

- Relationship between reference instrument and LCS-PM (linear responses are preferable due to simplicity of calibration procedure)
- LCS-PM response in ambient conditions with high relative humidity, as the response of a sensor declines under the influence of very high air humidity.

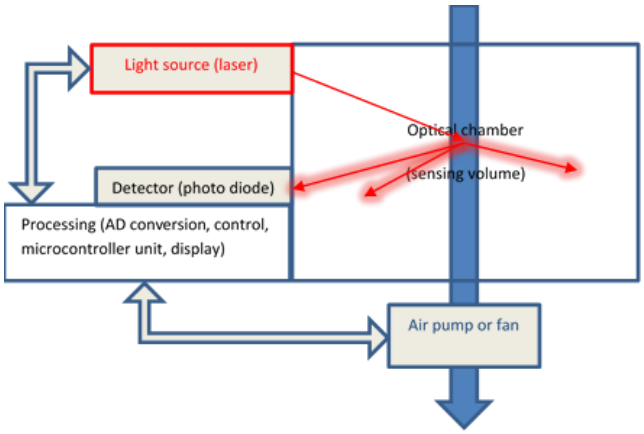

Figure 2. *Schematic diagram of the principle of operation of LCS-PM*

The first generation of LCS-PM was able to detect the amount of opacity (the amount of light not transmitted by the sample), while newly developed sensors detect PM_1, $PM_{2.5}$ and PM_{10}. Specifications of some sensors state that they may measure particles in different particle sizes. However, there is a lack of and disparity in the scientific literature on performance assessment and calibration procedures for PM low-cost sensors. That makes it difficult to evaluate the quality of data obtained in different studies and to make comparisons between them [Rai et al, 2017], Jovašević-Stojanović et al. [2015]. In addition, test results for the same sensor may be very different between the tests performed in the laboratory, in indoor ambient air or in the outdoor field conditions. For measurements in the laboratory we need to established a control test atmosphere and to generate artificial aerosol of known characteristics [Papapostolou et al., 2017]., which given the large heterogeneity of particulate matter is very difficult.

To illustrate the differences, we evaluated our data and data published in different studies, all generated using Alphasense OPC LCS-PM devices. Till now Alphasense developed three version of device: OPC-1, OPC-N2 and OPC-N3. OPC-N1 appeared first and next version, OPC-N2 and OPC-N3, are with small improvements. These OPCs employ a low-power micro fan that is sufficiently strong to draw an air flow through the device, with typical sample flow rates being around 220 ml/min Bezantakos et al. [2018]. The OPC-N2 uses a laser beam at 658 nm as the light source and scattering angle od 30˚ [Zhang et al, 2018] . The resulting scattered light is focused using an elliptical mirror toward a dual-element photodetector. The firmware of the OPC-N2 is considered proprietary information and includes default settings for the refractive index of particles and 1.65 gcm^{-3} for particle mass density. The unit detects particles with diameters within the range of 0.38 μm to 17μm, and classifies them into one of 16 size bins. The device software calculates values of PM_1, $PM_{2.5}$, and PM_{10} at a one-minute temporal resolution based on the particle size distribution using default particle mass density value as it is calibrated by the manufacturer using polystyrene spherical latex (PS) particles with a known diameter, refractive index, and density [Alphasense, 2015].

In the office indoor environment, we have compared older version Alphasense OPC-N1 to TSI OPC 3330 device and obtained the same results as in the low-cost sensor datasheet [Appollo, 2014], Figure 3.

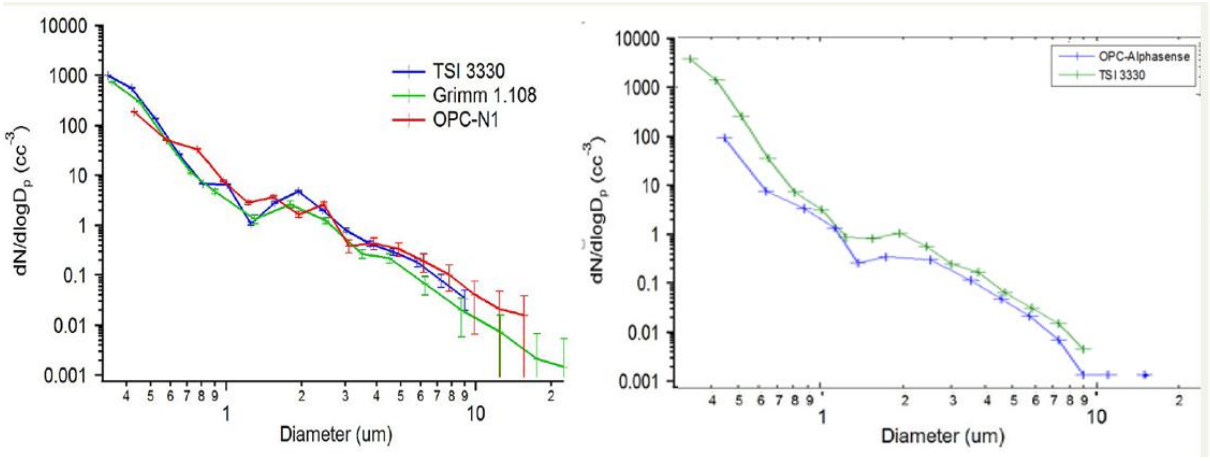

Figure 3. *Correlation between the Alphasense OPC-N1 and TSI 3330 in the indoor ambient air*

Sousan et al [2016] for the first time test detection efficiency of Alphasense OPC-N2 in control test atmosphere, chamber with three different aerosol compositions, NaCl generated polydisperse aerosol, welding fume and Arisona Road Dust - ARD. The number concentrations measured with the OPC-N2 agreed fairly well to those measured with the GRIMM the portable aerosol spectrometer - PAS-1.108 (0.3-20 microns in 15 channels) and two reference instruments for coarse particles, but underestimated number concentrations for sub-micrometer particles. Mass concentrations from both OPCs were highly linear with the reference instruments, coefficient correlation R^2>0.94.

As light scattering is affected by particle refractive index, Zhang et al [2018] tested the performance of OPC-N2 for different aerosol composition in laboratory conditions. They showed strong linear relationships between the SMPS (reference instrument) and OPC-N2 counts, $R^2 \geq 0.99$, for all four artificial aerosols in the range of 380-580 nm where OPC-N2 and SMPS counting may be compared. Detection efficiency of OPC-N2 in comparson with SMPS was 103%, 42%, 55% and 16% while testing on $NaNO_3$, $(NH_4)_2SO_4$, sucrose, and adipic acid artificial aerosol, respectively.

In the study of Bezantakos et al. [2018], two Alphasense OPC-N2 were tested using monodisperse PS spheres (NIST Traceable PS Microspheres, Magsphere Inc.) of six different nominal sizes: 0.8, 1.0, 2.5, 5.1, 7.2, and 10.2 μm. For PM fractions above 1 μm, under conditions relevant for indoor environment, the PNC of both Alphasense OPCs was comparable to that of the reference instrument with differences less than 40%. Under the same conditions for fraction of PS particles of a nominal size of 0.8 μm, it was observed that Alphasense OPCs overestimated the PNC by a factor of two and even more. The sizing accuracy of the Alphasense OPCs under indoor environment conditions was within experimental uncertainty and within 5% of the nominal size of the PS particles used for generation test atmosphere in the chamber. The counting and sizing performance of both Alphasense OPC devices were uninfluenced down to 5^{o}C and 0.7 atm. In one of devices, a systematic degradation of its sizing accuracy occured at temperatures below 5^{o}C due to impurities in its optics system.

An EPA field study [2017] reported little to no agreement, $R^2 < 0.10$, between OPC-N2 sensor collocated for 1 month next to GRIMM EDM 180 monitor. The OPC-N2 was integrated into a prototype UN multi-pollutant sensor pod. $PM_{2.5}$ and PM_{10} mass concentrations were compared to reference values at time averaging intervals between 5 minutes to 24 hours.

During successive field campaigns in late spring and summer in 2015 at two automatic monitoring stations in Belgrade, Jovašević-Stojanović et al. [2016] obtained little or no agreement for mass concentration of twelve AS510, Atmospheric Sensors nodes with integrated OPC-N2 sensors, compared with GRIMM EDM 180 monitor. During the first champaign at urban background site, the correlation between each of twelve low-cost devices and one GRIMM reference monitor, measured as R^2, was in the range 0.27-0.72 and 0.25-0.49 for $PM_{2.5}$ and PM_{10} respectively. During the second campaign at another sampling site, R^2 between the GRIMM EDM 180 monitor and each one of the twelve AS510 nodes varied between 0.00-0.12 ($PM_{2.5}$) and 0.00-0.05 (PM_{10}). 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 needed. Table 1 summarizes recently published data from field collocation studies between LCS Alphasence OPC model and higher grade and reference monitors. The large variability between different studies is challenging to explain.

SCAQMD evaluated three OPC-N2 units and three units of improved version of OPC-N2 model [SCAQMD,2015, SCAQMD,2015] showing low to moderate intramodel variability and overall good correlation with reference and equivalence devices, BAM and GRIMM monitors. OPC-N2 and OPC-N3 usually largely underestimated $PM_{1.0}$ data although were correlated well with the reference monitors. $PM_{2.5}$ and PM_{10} data obtained with LCS-PM OPC-N2 and OPC-N3 were closer to the corresponding values obtained by the reference devices.

Table 1. *Ranges of R^2 for LCS-PM Alphsense OPC versus reference monitors in the different field studies*

Reference	Sensor type free-standing, or integrated in unit	Reference or instrument with known parameters, (comments in parenthesis)	Period of data averring	Number of LCS – PM units	R^2		
					PM_1	$PM_{2.5}$	PM_{10}
Crilley et al [2018]	OPC-N2	TEOM	1h	4		0.70-0.74	0.64-0.68
		GRIMM , PAS-1.108	1h	4		0.71-0.74	0.66-0.69
		TEOM (RH< 85)	1h	4		0.79-0.80	0.82-0.83
		GRIMM PAS-1.108 (RH< 85)	1h	4		0.88-0.90	0.83-0.84
Badura et al. [2018]	OPC-N2	TEOM	24h	3		0.53-0.69	
		TEOM	1h	3		0.43-0.59	
EPA[2017]	OPC-N2, UNEP	GRIMM Federal Equivalence Monitor	5min-24h	1		< 0.1	< 0.1
Jovašević et al [2016]	OPC-N2 Atmosperic sensor	GRIMM EDM 180 (sampling site AMS Zeleno brdo)	5 min	12		0.27-0.72	0.25-0.49
		GRIMM EDM 180 (sampling site AMS Stari Grad)	5 min	12		0.00-0.12	0.00-0.05
SCAQMD [tested 2015]	OPC-N2	GRIMM reference instrument	5min	3	0.62-0.82	0.65-0.79	0.45-0.57
			1h	3	0.67-0.82	0.66-0.80	0.46-0.60
			24h	3	0.55-0.81	0.64-0.88	0.58-0.85
		BAM MetOne reference instrument	1h	3		0.38-0.67	0.42-0.53
			24h	3		0.73-0.90	0.66-0.92
SCAQMD [tested 2018]	OPC-N3	GRIMM reference instrument	5min	3	0.77-0.81	0.58-0.66	0.49-0.52
			1h	3	0.78-0.82	0.60-0.69	0.48-0.53
			24h	3	0.88-0.90	0.69-0.76	0.22-0.26
		BAM MetOne reference instrument	1h	3		0.41-0.48	0.28-0.29
			24h	3		0.75-0.81	0.67-0.70
Feinberg et al. [2018]	OPC-N2	GRIMM EDM 180	5 min	3		0.01-0-17	0.04-0.16
			1h	3		0.01-0.20	0.04-0.46
			12h	3		0.00-0.26	0.02-0.48
			24h	3		0.00-0.26	0.03-0.55
Mukherjee et al. [2017]	OPC-N2	SMPS C5.402(GRIM 11-R) APS (TSI)		3	0.38-0.45	0.40-0.43	0.80-0.84

In the study of Badura et al. [2018] that evaluates OPC-N2 and selected other sensors, it was observed that the raw outputs from some LCS-PM may significantly overestimate the $PM_{2.5}$ concentrations, with a factor of 2.5–5. It may

be due to the fact that sensors are calibrated by the manufacturer using particles with optical properties quite different from the monitored air. For this reason, calibration (or recalibration) of PM sensors should be made at each microenvironment prior to the measurements. The most common method of such calibration is based on the use of the data from the collocated with reference or equivalent instruments.

Under circumstances where the relative humidity approaches 100 %, there is the possibility of mist or fog droplets to be detected as particles, and the Alphasense OPC-N2 seems to significantly overestimate particle mass during such high humidity conditions [Manikonda et al. 2016]. Crilley et al. [2018] developed a correction factor for the Alphasense OPC-N2 for relative humidity >85%.

Mukherjee et al. [2017] examined the characteristics of two types of LCS-PM, where one of them was OPC-N2. During the filed campaign, the PM concentrations were influenced by wind-blown dust events and regional transport. The drift over time of the Alphasense OPC-N2 (12 weeks in the field) was attributed to a potential build up of dust inside the sensor and on the fan. Selected LCS-PM were collocated with two reference instruments, the GRIMM 11-R, optical particle counter monitor, and BAM. Both types of LCS-PM showed high degree of intra correlation (R^2 = 0.8–0.99), and a moderate degree of correlation with the reference instruments (R^2 = 0.6–0.76). Sensor measurements were influenced by the meteorological conditions and the aerosol size distribution.

The above results all indicate that testing the performance of sensors in real-world conditions necessary to make sure that sensors provide data of sufficient data quality.

EXAMPLES OF SUCESSFUL APPLICATION OF LCS-PM

Distributed sensor network

National and local monitoring networks are limited to few sites within a large geographical region. This limits the ability to contribute in characterizing the pollutant variability and sources within the complex urban topography [Zamora et al., 2019]. High costs of operating a monitoring network of reference monitors include cost of monitors themselves, their running and maintaining, as well as rigorous quality procedures. This is a limiting factor for the ability to increase spatial and temporal coverage of high quality of air pollution monitoring data. However, human exposure depends on proximity to local emissions sources such as traffic intensity on the route where people move, domestic heating and district heating sources in the area when they spend time, as well as, on finer scale meteorology (microenvironment). In order to identify population at risk or vulnerable groups of population, to control relevant emissions that contribute to exposures, and for the health protection, we need information with higher temporal and spatial resolution. Many studies demonstrate that LCS-PM can provide a good spatial and temporal coverage of measurements, although the data quality may be considered only as indicative (as defined in legislation). Only a few studies were done where LCS-PM were used to enhance spatial-temporal coverage of pollution by PM. Gao et al [2015] used Portable University of Washington Particle (PUWP) monitors simultaneously deployed at eight sites across Xi'an alongside gravimetric $PM_{2.5}$ monitors. They have shown that PUWP monitors were able to identify a potential $PM_{2.5}$ hotspot of sustained higher concentrations compared with the city average $PM_{2.5}$ levels.

English et al [2018] and Wong et al. [2018] presented a so called community monitoring network (CAMN). This community-led air quality network involves engaging community members to be citizen-scientists performing siting, monitoring and data collection of air pollution. That network consists of 40 monitors, with modified Dylos Pro 1100 monitor, designed to give better information about air pollution to community residents, to support research activities, to guide public policy, and to improve public health.

Zikova et al [2017] and Masiola et al. [2018] deployed outdoors over two winter sampling campaigns twenty-five units of Speck (Airviz Inc., Pittsburgh, PA, USA) LCS-PM. They aimed at collecting data to estimate spatial variability of urban and suburban $PM_{2.5}$ across the metropolitan area of Monroe County. The Speck monitors provided an opportunity to deploy a denser monitoring network compared to a situation with one central monitoring site providing high-accuracy PM data. The technique and methodology proved to be useful for identification of local high concentrations within a wider area or to provide high spatial resolution monitoring data within a smaller area. Outputs of the project were hourly spatial distributions of PM in the county provided at midnight, 6 a.m., noon, and 6 p.m., averaged over the two periods. When these PM maps were compared with hourly traffic count maps representing typical morning and evening rush hour peaks, it is visible that road traffic is one of the more influential PM sources. The PM concentration decreases during night-time proved the limited effect of domestic heating. $PM_{2.5}$ data collected from twenty-three locations across the area were used as input data for Land Use Regression models (LURs). For each hour of the day and weekdays/weekend days, detailed maps were created

using a deletion/substitution/addition algorithm. During weekday and weekend models selected average 21 and 19 predictors respecivitly, with adjusted R^2 average about 0.7

These studies show that LCS-PM are useful to provide input data with sufficient spatial resolution for real-time particulate pollution mapping, hotspots identification and early warning detection system of high concentration PM events.

Applications of LCS-PM for indoor and outdoor hot spots detection

The small size of LCS-PM sensors enables mobile applications such as monitoring by pedestrians, bicycles, vehicles and even flying drones (unmanned aerial vehicle). Measurements while moving can serve as input data to map the dynamics of PM pollution: searching for hot spots of emissions, evaluating the exposure of air pollutants on individual level, or improving the temporal and spatial resolution of monitoring information.

Budde et al. [2013], upgraded smartphones to become PM dosimeters, and have recently presented FeinPhone, a phone-based device Budde et al. [2019]. This is a fine dust measurement system that uses the camera and flash LED available on off-the-shelf smartphones, as both a light receptor and an emitter of a passive clip-on dust sensor. By using a camera instead of a single-pixel photodiode as a light receptor, in combination with image processing algorithms, they offered solution that capture and count the light scatter traces from individual particles, giving additional information on the size spectrum of the observed particles. This system gives promising results while measuring coarse fraction of respirable particulate matter, ($R > 0.9$) in comparison with high-quality APS/SMPS devices, and can successfully capture PM_{10} levels under realistic conditions.

Báthorya and Palotas [2019] used Winsen optical sensors for PM monitoring to design monitoring system that recorded and transmitted temperature, relative humidity, pressure, $PM_{2.5}$ and PM_{10}. In addition, the system has a GPS sensor and can be used to identify hot spots of $PM_{2.5}$ and PM_{10} along a route in both, rural and urban area.

Firla et al. [2019] used LCS unit, developed by Warsaw University of Technology, to measure PM_1, $PM_{2.5}$, PM_{10}, temperature and humidity aiming to measure air quality on the North and Baltic seas and ports. Ships sails on routes with both a high and small intensity of maritime traffic. The data collected with LCS-PM confirmed differences in PM levels between areas of North Sea and Baltic Sea, and identified an increase in PM concentrations in places with frequented shipping routes, demonstrating the usability of LCS-PM. This study also identified at least two areas where passing ships caused a significant increase of PM concentrations, quantified to be 18–28 $\mu g/m^3$ for PM_{10} and 15–25 $\mu g/m^3$ for $PM_{2.5}$.

Application of LCS-PM in agriculture

The off-target movement of pesticides, so call pesticide drift, is a major source of pesticide exposure, particularly among agricultural workers. Drift can also contribute to exposure of bystanders. Drift risk is also related to spray droplet size, in particular to the percentage of fine spray droplets. Traditionally, sampling and estimation of pesticide drift have been performed using passive samplers distributed at treated area, accompanied with meteorological data. Recently published studies present a novel method of drift characterization using LCS-PM monitors to estimate the spray drift potential of a traditional airblast sprayer (axial fan airblast-AFA), and two more modern devices, a multi-headed fan tower-MFT and a directed air tower-DAT. Blanco et al [2019a and 2019b] have used several of the most popular LCS-PM, Dylos DC1100 Pro devices to collect PM above and below the canopy at five distinct locations. Distance measurements, spray times and meteorological observations were merged with Dylos particles number concentration and then used for the calculation of PM concentrations.

The novel method of drift estimation using LCS-PM was generally in agreement with results of a study performed using a traditional method with passive sampling done during the same spray events [Kasner et al., 2018]. The Dylos monitors detected a larger difference between the DAT and AFA sprayer than the passive sampling. Measurements performed with PM collected in real-time and coupled with meteorological data contribute to better understanding of how changes in wind speed and direction impact drift. Such an analysis is not possible with passive sampling. Assessment of pesticide drift using LCS-PM could significantly reduce the number of occupational pesticide drift exposures among workers on neighbouring farms. A similar procedure may be developed for routine monitoring of pesticide drift.

CONCLUSIONS

The major advantages of the low-cost particle sensors/monitors are low price, portability and comparative ease of use. There is no doubt that LCS-PM sensors may increase spatial and temporal monitoring resolution and variety

of use in a cost-effective manner, but there are doubts regarding data accuracy and precision which generally needs to be assessed as part of each deployment.

Response of LCS-PM based on light scattering method varies with aerosol size distribution, composition and optical properties. At this time, there is no single calibration model or correction model that can enable accurate performance for all particle sources over wide range of indoor and outdoor microenvironments. This challenge implies the need for more research, and the need to inform citizens about advantages and limitation of using such monitors.

Despite the shortcomings of the instrumentation, the LCS-PM were successfully used for the purpose of demonstrating particle gradients within given areas and for source identification for traffic and local heating, and for spatial characterization of harmful exposure from pesticide application. This shows the potential of the devices.

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