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Particulate Matter: Research and Management

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Milena Jovašević-Stojanović
and Alena Bartoňová, eds.

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CONFERENCE TOPICS

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 rationale stems from the fact that particulate matter is the air quality constituent that currently is responsible for most instances of non-compliance with air quality directives in Europe. Particulate matter, arising both from primary emissions and as a result of secondary formation in the atmosphere, is also one of the least well understood issues.

The 1st WeBIOPATR Workshop was held in Beograd, 20.-22. May 2007. The workshop was attended by more than 70 participants presenting 35 contributions, and received media attention (newspaper article and TV coverage on national TV). In addition to providing information about latest research in Serbia and internationally, the workshop has contributed to communication within the research community in Serbia, and between the research community and the responsible authorities (Ministry of Health, Ministry of Environment, and the Serbian Environmental Agency).

The 2nd WeBIOPATR workshop was held in Mecavnik, Serbia, 28.8.-1.9. 2009. It has attracted over 40 participants, including participants from the neighboring countries and EU. The participants discussed air quality issues, research needs and management tools and strategies currently used in Serbia. The workshop also had a section on health issues related to particulate matter, recognizing that the legislation is based on health considerations, and that the PM are an important health determinant in adults and in children. Proceedings are available at http://www.nilu.no/index.cfm?ac=publications&folder_id=4309&publication_id=24659&view=rep. Selected extended contributions are published in CHEMICAL INDUSTRY & CHEMICAL ENGINEERING QUARTERLY Vol: 16 No 3 (2010).

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

The 4th event, WeBIOPATR2013, was held in Beograd 2.-4. October 2013. It covered the traditional PM research and management issues as well as topics that aim to encourage citizens to contribute to environmental governance. Ways to provide the citizens and authorities with a range of tools and services related to the environment including PMs, and developing participatory sensing methods and tools utilizing smaller and less expensive monitoring devices and advanced ITC technologies, were one of the foci. The book of abstracts can be downloaded at http://www.vin.bg.ac.rs/webiopatr/3rd-workshop/. Selected extended contributions were published in CHEMICAL INDUSTRY & CHEMICAL ENGINEERING Vol 21, No 1/II (2015).

This proceedings contains 38 papers and abstracts 6 of all presentations of the WeBIOPATR-2015 workshop and conference, the fifth event of the series. In all, 9 invited keynote lectures, 18 oral presentations and 15 poster presentations are presented by speakers from 12 countries, the most from Serbia but also from countries all over the Europe and Australia. We hope that this event will continue to be an important forum for the Serbian scientists and other professionals to meet and discuss, and for the Serbian professional community to meet with professionals dealing with similar issues elsewhere.

We hope that next event, that will be 10 years after the first one, will continue the success from the past. We wish to again provide the professional community from Western Balkans region with a suitable meeting platform, and the global professional community with an arena where we can draw on each other's experiences and scientific insights.

Milena Jovašević-Stojanović and Alena Bartoňová

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1. SCIENCE AND POLICY

1.1 IMPROVING HEALTH GUIDANCE THROUGH INCLUSION OF SCIENTIFIC KNOWLEDGE - FOCUS ON PM AMBIENT AIR POLLUTION

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ABSTRACT

Air quality is the largest contributor to the burden of disease caused by environmental factors. In the WHO European Region in 2012, exposure to air pollution accounted for almost 600 000 premature deaths, out of which 482 000 could be attributed to ambient air pollution. In addition to well-recognized health impacts of air pollution, the evidence is growing for other health effects, such as reduced foetal growth and pre-term birth in children exposed prenatally, as well as impacts of perinatal exposure on health in adult life. Air pollution is a complex mixture of gaseous and particulate pollutants originating from a variety of sources. Of major concern is fine particulate matter (PM2.5), associated with health effects, both for long-term and short-term exposure.

The available scientific evidence provides convincing arguments for taking actions, including a range of legal instruments, to reduce emissions and improve air quality. In 2015, for the first time World Health Assembly adopted a resolution on air quality and health. WHO has been reviewing the scientific knowledge on health aspects of air quality to support policy-makers in developing air quality standards and other policy and management tools. The WHO air quality guidelines provide health based guideline values for selected air pollutants. The recent WHO project to review the evidence on health aspects of air pollution supported the scientific conclusions of the WHO air quality guidelines, and indicated that some effects occur at air pollution levels lower than those used to establish the guidelines. While protection of human health is a powerful driver for air quality policies, WHO guideline values remain more stringent than most air quality standards, such as those in the EU. The upcoming update of WHO air quality guidelines will provide reinforced scientific arguments for taking decisive actions to improve air quality and reduce the burden of disease associated with air pollution in Europe.

Keywords: Air pollution – Health impacts, World Health Assembly Resolution, Evidence Based, Policy, Air Quality Guidelines, Air Quality and Health Policy

HEALTH IMPACTS OF AIR POLLUTION IN EUROPE AND GLOBALLY

Air quality is the single most important environmental factors contributing to the burden of disease. Both, ambient air pollution and air pollution from household use of solid fuels have been convincingly associated with increased mortality and morbidity worldwide, with large regional differences. WHO estimated that globally, 3.7 million persons died prematurely in 2012 due to the effects of ambient air pollution; mainly due to ischemic heart disease (40% of all attributable deaths), stroke (40%), chronic obstructive pulmonary disease, COPD (11%), lung cancer (6%), and lower respiratory tract infections (3%), diseases which ranked among the top ten causes of death in the world (WHO, 2012). In the WHO European Region, exposure to air pollution accounted for almost 600 000 premature deaths, out of which 482 000 were attributed to ambient air pollution (WHO, 2012). Besides human suffering, the associated economic burden is substantial: the staggering figure of more than 1.4 trillion US dollars was the estimated economic cost of premature death due to air pollution in the WHO European Region (as of 2010) (WHO Regional Office for Europe/OECD, 2015). Furthermore, as estimated in the Global Burden of Disease project, occupational exposure to particular matter, gases and fumes is responsible for 205 000 deaths globally, out of the total 717 000 deaths attributable to occupational risk factors in 2013 (Forouzanfar et al, 2015). In addition to well-recognized impacts of air pollution on cardiovascular and respiratory diseases, including lung cancer, the evidence is growing for other health effects, such as reduced foetal growth and preterm birth in children exposed prenatally, as well as impacts of perinatal exposure on health in adult life (EEA/JRC, 2013; WHO, 2013). Air pollution is a complex, highly variable mixture of gaseous and particulate pollutants, which originate from different sources, and is the result of many physico-chemical processes in the atmosphere, often involving long range transport of specific pollutants. However, while exposure and health

impacts of air pollution are largely a multi pollutant process, a single-pollutant approach is predominant in research, setting health-based air quality guidelines and legislation, reflecting our limited understanding of the effects of mixtures, as well as interactions with other stressors, such as noise. The evidence from health studies on interactions of air pollutants is very scarce, largely due to a lack of data and methodological limitations (WHO, 2013).

HEALTH RELEVANCE OF PARTICULATE MATTER

Among air pollutants, of major concern is fine particulate matter (PM2.5), associated with health effects, both for long-term and short-term exposure. PM2.5 shows the most consistent associations with mortality and morbidity, such as lung cancer, hospitalizations for cardiovascular and respiratory diseases, acute and chronic bronchitis, and restrictions in daily activity. The recent review of the evidence reconfirmed the effects of both, short- and long-term PM2.5 exposure on mortality and morbidity and provided a better insight into physiological effects and biological mechanisms; exposed new links for long-term exposure to PM 2.5 and atherosclerosis, adverse birth outcomes and childhood respiratory diseases, as well as emerging evidence on possible links between long-term PM2.5 exposure and neurodevelopment and cognitive function, and diabetes (WHO, 2013). The International Agency for Research on Cancer (IARC), which is a specialized agency of the WHO, classified outdoor air pollution as carcinogenic to humans (Group 1) (WHO IARC, 2013).

While many sources contribute to air pollution with particulate matter, residential heating with solid fuels receives increasing attention in Europe. In parts of the Region, the fraction of total PM2.5 emissions due to residential heating with solid fuels is increasing, partly due to higher biomass fuel use and partly due reduction from other sources. Furthermore, use of solid fuels for heating is expected to continue, as a result of climate policies that favour biomass burning. Both short-term and long-term exposures to wood and coal smoke are harmful to respiratory and cardiovascular health, and appear to act the same way as PM from other sources. The contribution of residential heating to outdoor PM2.5 in Europe has been increasing: between 1990 and 2010, it roughly doubled in Central Europe (from 11% to 21%), and in Western Europe (from more than 5% to almost 12%), and increased in Eastern Europe (from 9.6% to 13%). For comparison, globally this contribution remains stable at some 3%. The estimated burden of premature deaths due to this exposure was higher in 2010 than in 1990 (WHO Regional Office for Europe, 2015).

WORLD HEALTH ASSEMBLY RESOLUTION ON AIR QUALITY AND HEALTH

In 2015, the World Health Assembly (WHA), the decision-making body of the WHO, for the first time adopted a resolution on "Health and the Environment: Addressing the health impact of air pollution" (WHO, 2015). It highlighted the need to reinforce the efforts of member states and WHO to protect people from the health risks posed by air pollution, and urged member states to raise public and stakeholder awareness on the health impacts of air pollution, provide measures to reduce or avoid exposure, and facilitate relevant research, along with developing policy dialogue, strengthen multisector cooperation at national, regional and international levels and take effective steps to reduce health inequities related to air pollution. This resolution explicitly recognizes the role of regularly updated WHO air quality guidelines (AQGs) in providing guidance to facilitate effective decision making, and recommendations for clean air to protect human health (WHO, 2015).

WHO REVIEWS OF THE SCIENTIFIC EVIDENCE OF AIR QUALITY AND HEALTH

WHO has been reviewing scientific knowledge on health aspects of air quality to reliably support policy-makers when developing air quality standards and other policy tools, and considering various options for air quality management. A range of the reviews addressing specific sources (WHO Regional Office for Europe, 2005), populations, or other aspects of health risks of air pollution (WHO Regional Office for Europe, 2003, 2006, 2007, 2008) have been made available to experts and policy makers. Recently, the two projects (REVIHAAP and HRAPIE) provided the review of the evidence on health aspects of air pollution (WHO Regional Office for Europe, 2013) and health risks of air pollution in Europe (WHO Regional Office for Europe, 2013a), offering the science-based answers to a set of policy relevant questions in support to the revision of the EU environmental policy. The overall results supported and strengthened the scientific conclusions of the WHO air quality guidelines (WHO, 2006), and indicated that some effects occur at air pollution concentrations lower than those used to establish the guidelines.

The most prominent is WHO work on the series of air quality guidelines (AQGs), which serve as a reference tool to help decision-makers in setting standards and goals for air quality that ultimately protect human health. The first edition of the WHO AQGs was published in 1987, covering 28 air pollutants (WHO Regional Office for Europe, 1987). The latest '*WHO Air Quality Guidelines, Global Update 2005*', focuses on the so-called classical air pollutants (PM, ozone, nitrogen dioxide and sulphur dioxide), and includes a section on application of AQGs for policy development and risk reduction, followed by a comprehensive risk assessment of the classical air pollutants, that in addition to numerical guidelines, in most cases proposed interim targets above the guideline value to promote steady progress towards meeting WHO guidelines (WHO Regional Office for Europe, 2006).

Considering the conclusions from the recent projects, such as the REVIHAAP, and responding to the WHA resolution from May 2015, WHO has initiated efforts towards the update of the global WHO air quality guidelines. Involving international community of experts, and stakeholders, an update of WHO air quality guidelines will be based on a comprehensive and objective assessment of the available evidence, taking account of technological feasibility, economic development and other factors. The guideline development process coordinated by WHO, follows a rigorous, internationally recognized set of standards and methods, published in the WHO Handbook for Guideline Development (WHO, 2014), to ensure that the guidelines are free from biases and meet public health needs.

WHO AIR QUALITY GUIDELINES AND ENVIRONMENTAL POLICY IN EUROPE

The available scientific evidence provides convincing arguments for taking actions, including a range of legal instruments, to reduce emissions and improve air quality. In the European Union (EU), air quality legislation refers directly to WHO air quality guidelines: '*…to protect human health and the environment […] emissions of harmful air pollutants should be avoided, prevented or reduced and appropriate objectives set for ambient air quality taking into account relevant World Health Organization standards, guidelines and programmes*'(EU, 2008). While protection of human health is a powerful driver for air quality policies, WHO guideline values remain more stringent than most air quality standards, such as those in the EU. For example, as assessed by the European Environment Agency, in 2013, about 9 % of the urban population in the EU-28 was exposed to PM2.5 levels above the target value threshold, whereas approximately 87 % was exposed to concentrations exceeding the stricter WHO AQG value for PM2.5 (EEA, 2015). The new Clean Air Package for the EU, if fully implemented, is expected to deliver substantial health and ecosystem benefits by 2030, far outweighing the costs of pollution abatement; for example, it is anticipated to prevent 58 000 premature deaths annually (EC, 2013). Still, this will not be enough; as concluded in the recent state of the environment report by the European Environment Agency, '*additional measures are needed if Europe is to achieve the long-term objective of air pollution levels that do not lead to unacceptable harm to human health and the environment*'(EEA, 2015a), in line with the long-term aspirations of the EU Environment Action Programme to 2020 (EC, 2013a).

CONCLUSION

The continuous WHO efforts to systematically review the scientific evidence on air quality and health with the view of supporting policy-makers and the upcoming update of WHO air quality guidelines are expected to further reinforce the scientific arguments to facilitate development of advanced environmental policies and for taking decisive actions to improve air quality and reduce the burden of disease associated with air pollution in Europe.

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REFERENCES

1. EC, 2013. European Commission: The Clean Air Policy Package. Available: http://ec.europa.eu/environment/air/clean_air_policy.htm (accessed 12 December 2015)

2. EC, 2013a. Decision No 1386/2013/EU of the European Parliament and of the Council of 20 November 2013 on a General Union Environment Action Programme to 2020 'Living well, within the limits of our planet'. Available: http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32013D1386&from=EN (accessed 4 December 2015).
3. EEA, 2015. Air quality in Europe — 2015 report. EEA report No 5/2015. European Environment Agency, Copenhagen
4. EEA, 2015a. The European environment — state and outlook report. European Environment Agency, Copenhagen
5. EEA/JRC, 2013. Environment and human health. Joint EEA-JRC report. EEA Report No 5/2013. European Environment Agency, Copenhagen
6. EU, 2008. Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe. Available: http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2008:152:0001:0044:EN:PDF (accessed 4 December 2015).
7. Forouzanfar MH, Alexander L, Anderson HR, et al GBD 2013 Risk Factors Collaborators, 2015. Global, regional, and national comparative risk assessment of 79 behavioural, environmental and occupational, and metabolic risks or clusters of risks in 188 countries, 1990-2013: A systematic analysis for the global burden of disease study 2013. The Lancet, 386: 2287–2323.
8. WHO 2012. Burden of disease from ambient air pollution for 2012. Available: http://www.who.int/phe/health_topics/outdoorair/databases/AAP_BoD_results_March2014.pdf?ua=1 (Accessed 14 December 2015)
9. WHO 2015. Sixty-eighth World Health Assembly. Health and the environment: Addressing the health impact of air pollution. Available: http://apps.who.int/gb/ebwha/pdf_files/WHA68/A68_R8-en.pdf (accessed 12 Deecember 2015)
10. WHO IARC, 2013. Outdoor air pollution a leading environmental cause of cancer deaths. IARC Press release nr 221. 17 October 2013. Lyon. Available: http://www.iarc.fr/en/media-centre/iarcnews/pdf/pr221_E.pdf (Accessed 14 December 2015)
11. WHO Regional Office for Europe /OECD 2015. Economic cost of the health impact of air pollution in Europe: Clean air, health and wealth. World Health Organization, Copenhagen
12. WHO Regional Office for Europe 2007. Health risks of heavy metals from long-range transboundary air pollution. Joint WHO/Convention Task Force on the Health Aspects of Air Pollution. World Health Organization, Copenhagen
13. WHO Regional Office for Europe 2013a. Health risks of air pollution in Europe – HRAPIE project. Technical report. World Health Organization, Copenhagen
14. WHO Regional Office for Europe 2015. Residential heating with wood and coal: health impacts and policy options in Europe and North America. World Health Organization, Copenhagen
15. WHO Regional Office for Europe, 1987. Air quality guidelines for Europe. World Health Organization, Copenhagen
16. WHO Regional Office for Europe, 2003. Health risks of persistent organic pollutants from long-range transboundary air pollution. Joint WHO/Convention Task Force on the Health Aspects of Air Pollution. World Health Organization, Copenhagen
17. WHO Regional Office for Europe, 2005. Health effects of transport-related air pollution. World Health organization, Copenhagen
18. WHO Regional Office for Europe, 2006. Air quality guidelines global update 2005: particulate matter, ozone, nitrogen dioxide and sulfur dioxide. World Health Organization, Copenhagen
19. WHO Regional Office for Europe, 2006. Health risks of particulate matter from long-range transboundary air pollution. Joint WHO/Convention Task Force on the Health Aspects of Air Pollution. World Health organization, Copenhagen
20. WHO Regional Office for Europe, 2008. Health risks of ozone from long-range transboundary air pollution. Joint WHO/Convention Task Force on the Health Aspects of Air Pollution. World Health organization, Copenhagen
21. WHO Regional Office for Europe, 2013. Review of evidence on health aspects of air pollution- REVIHAAP project. Technical report. World Health Organization, Copenhagen
22. WHO, 2014. WHO handbook for guideline development, 2nd edition. World Health Organization, Geneva.

1.2 COMMUNICATING PM POLLUTION ISSUES FOR DECISIONS AND THE PUBLIC – SOME EXPERIENCES FROM RESEARCH PRACTICE

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ABSTRACT

Current particulate matter levels are often above the limit values, and measures to reduce air pollution are increasingly requiring the cooperation of the public. This requires communication of complex scientific issues. How are the scientists and researchers responding to this challenge?

In the HENVINET project (www.henvinet.eu), we developed an online expert evaluation tool based on Drivers-Pressures-State-Impact-Response (DPSIR) operational framework. The DPSIR framework proved useful for systematization and communication, for common understanding of the scope of the assessment, recruitment of experts for the evaluation, and linking to policy/decision making.

The CITI-SENSE project (www.citi-sense.eu) addressed public involvement. Using low-cost sensor based devices to assess air quality, we developed case studies in nine European countries, investigating how these devices can be used by and for the public, to provide insight and information. This presentation illustrates some of the challenges and approaches to communication and involvement of the public from our field work.

INTRODUCTION

Particulate matter (PM) pollution is not a new issue in environmental policy making. PM are a systemic issue, involving environmental but also political, social and economic systems. An authoritative study linking PM to health issues (Pope et al, 1995) were among the first who have clearly demonstrated the need to address high atmospheric PM levels. Since then, both national and international bodies have been working with increased focus towards measures to reduce this kind of pollution. Twenty years later, the issues are as pertinent as ever (EEA 2014; Fagerli et al, 2015).

What has however changed is the general public's interest and involvement. The literature on science communication recognizes three models of communication, published by Ziman (1992) and later put in historical perspective by Weigold (2001) or Schiele (2008). The deficiency model (effective communication of science would help the non-scientists to become more literate about what scientists know), the rational choice model (what do people need to know in a culture shaped by science), and the context model (what do people want to know in their particular circumstances). Schiele (2008) argues that while the deficiency model was shaping science communications up to about 1980's, it is now the context model that brings us best advances. This can be seen e.g., in the increase of citizen science.

Today, owing also to the changes brought by the legislative processes, PM seems to be firmly present in the public domain (Eurobarometer 2013). Not least, high pollution episodes are newsworthy, in China (Washingtom Post, 2015) and elsewhere[1], or occasional high pollution episodes in a number of European countries including Poland[2] or Norway[3]. Owing also to the legislative focus, such occurrences are well noticed.

Translating research into policy has long history. As an example, Larigauderie and Mooney (2010) can be quoted: "When asked what were the obstacles for a better use of scientific knowledge in decision making, decision makers mentioned a difficulty to access scientific results, issues with independence and quality of science, and a general lack of relevance of existing data for policy work. Scientists, on the other hand, expressed a desire for their work to be more relevant, but admitted a lack of awareness about policy needs and processes. … time has come for scientists to educate themselves about policy work in order to become 'responsive to the knowledge needs of society'…. Scientists can no longer hope that their work will somehow be used by policy makers. They should try to understand how policy works at local, national or international levels, dialog with

[1] http://www.forbes.com/sites/katiesola/2015/12/18/smog-beijing-air-quality/
[2] http://news.yahoo.com/echoing-beijing-poles-sound-alert-rampant-smog-143905955.html
[3] http://www.bt.no/nyheter/lokalt/Ekstreme-luftmalinger-i-Bergen-3188164.html

users of information to develop together an understanding of knowledge needs, and try to adapt and focus their work to these needs."

In Europe, we have enjoyed an excellent example of science communication to the policy-making domain since the 1980's. The acidification of Scandinavian lakes during late 1960's and early 1970's gave rise to the Convention on Long Range Transboundary Air Pollution[4] CLRTAP, with a support system for science-policy interface[5]. Here, the required elements for evidence-based policies are all in place: research and scientific basis development, observational systems, assessment systems and policy making.

Much literature has been published on the science communication for decision making, studying all aspects of this process. Lang et al (2012) have identified the three main phases of this process: A: collaborative problem framing and building a collaborative research team, B: co-creation of solution-oriented and transferable knowledge through collaborative research, and C: (Re-)integrating and applying the co-created knowledge. In the CLRTAP example, the co-creation is in practice being done in an open system which encourages stakeholders to bring to the table new information and knowledge, that is then subjected to a discussion, creating a consensus result.

Based on these experiences, and often without the full benefit of a trans-disciplinary research team, how can scientists bring this work forward? Two examples from our own research practice can illustrate our efforts.

NETWORKING TO SUPPORT INTER-DISCIPLINARITY IN ENVIRONMENTAL HEALTH RESEARCH: THE HENVINET[6] EXPERIENCE (2006-2010)

The societal relevance of atmospheric particulate matter is related to the known health effects associated the air pollution. The scientific community has two roles: to point out relevant risks, and to deliver research results for ongoing policy making. HENVINET aimed to create tools to facilitate the necessary interdisciplinary dialogue. HENVINET targeted mainly the scientific community; attempts were made to engage with decision-makers, but a systematic relationship was beyond the scope of the project. The role of several types of stakeholders was clearly recognized in the project, and a methodology was devised for their engagement.

The knowledge transfer (Keune et al, 2012) involved three main phases: knowledge evaluation, policy interpretation, and reporting, as seen in Figure 1. In all steps phases, we have used the DPSIR (Drivers-Pressures-State-Impact-Response)[7] framework as an organizing principle, with emphasis on pressures, state and impact. Following the WHO (2002), exposure was part of the Impact element. A full diagram was developed for asthma and allergies as a health endpoint (Henvinet, 2012; Forsberg et al, 2012) and then a number of sub-diagrams were derived for specific issues. Figure 2 gives an example of an evaluation framework for particulate matter. Expert evaluation of knowledge was then performed by volunteering experts, in a framework relating to the elements of the diagram. The results and their policy implications were summarized in a policy brief. The final policy brief was submitted to selected decision makers for their feedback. The independence of the experts and the ability to identify the origin of all the information were most important to the decision makers.

This project, with its wide interdisciplinary basis and significant involvement of the WHO European Centre for Environment and Health colleagues as both users and developers of the platform, has led to a degree of understanding of the process that can bridge science and policy. Our concept of a common platform for science and policy included brokering mechanism for contact between scientists and decision makers, information on decision support tools in a form of searchable database, tools for communication based on the causal diagrams, and project results. We have monitored the access to this platform while the project was active. Most use was registered when a certain issue was on a political agenda (in our case, process of legislation development for one of the studied issues). This has highlighted again that for decision making support on European level, we need to carefully monitor the legislative process, and time our outputs to coincide for requested inputs to such processes.

[4] http://www.unece.org/env/lrtap/lrtap_h1.html
[5] http://emep.int/index.html
[6] https://ec.europa.eu/research/endocrine/pdf/henvinet_final_report_summary.pdf
[7] http://ia2dec.pbe.eea.europa.eu/knowledge_base/Frameworks/doc101182

CITIZEN OBSERVATORIES AS A MEANS OF COMMUNICATING ON ENVIRONMENTAL ISSUES

The CITI-SENSE project (2012-2016, http://co.citi-sense.eu) aimed to develop citizen's observatories (Liu et al, 2014) that would enable citizens to participate in environmental decision making, and that would contribute to environmental monitoring and the Global Earth Observing System of Systems. The project relied heavily on enabling technologies, i.e., sensors for monitoring ambient and indoor air quality including particulate matter, radon and noise, and information technologies allowing seamless transfer of data between the data generators and the data users. We developed a visualisation application for air quality, where the user could see in near real time results from the (at the time of operation world's largest) sensor network deployed across Europe, combined with air quality model data and individual subjective perceptions of air quality.

First phase: knowledge evaluation
Literature review
Design causal diagram
Online evaluation causal diagram
First questionnaire - levels of confidence
Analysis results first phase

Second phase: policy interpretation
Second questionnaire policy interpretation
Expert workshop
Analysis results second phase
Third phase: reporting
Evaluation questionnaire
Report
Publication

Figure 1. *Knowledge transfer steps used in the HENVINET project (adapted from Keune et al (2012)).*

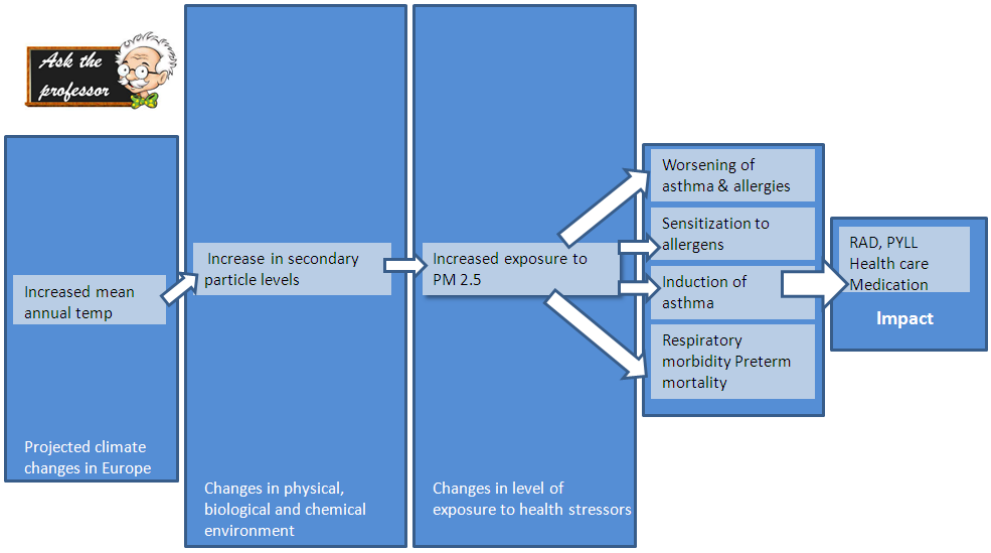

Figure 2. *Example of the causal diagram (adapted from Henvinet (2012)).*

One of the compounds that we have studied was particulate matter. The main challenges included ensuring comparability of the information across technologies. While data from compliance monitoring networks are produced with technologies that have known properties, and in a process that employs rigorous quality assurance and control procedures, we have generated data using novel sensor devices. We investigated a number of devices to learn their properties, e.g., Jovasevic-Stojanovic et al (2015). We have employed a simple calibration as the only systematic quality control measure, and had to develop own approach to assessing the individual sensor performance (Fishbain et al, 2016).

The differences in technologies employed for monitoring, and in quality assurance and control, have major implications for comparability of the results. For this reason, we chose not to communicate data generated by sensor technologies in terms of concentrations, but rather as an "indication of air quality". The "Indication" was created based on a "common air quality index" created by the CiteAir project (CiteAir, 2016), but as we felt it necessary to communicate that there is a difference in data quality between an index based on compliance monitoring and on sensor data, we have called the resulting entity an "APIN", or air quality indication.

In order to provide information to the public, the CITI-SENSE project has created a visualisation web portal that provided both the APIN values for all operational sensors in near-real time, an explanation of the values displayed, and a map for air quality (in the locations where this was available). All the results, codes, literature and other materials are now collected at the web portal http://co.citi-sense.eu, where they are available for anybody to be used, and re-used.

CONCLUSION

Communication of scientific findings, and in this case, results of various types of assessments of air quality, offers many challenges. The user in the end decides if the information was "useful" for them. The scientist however has the duty to provide scientifically and ethically defendable information. Often, the communication is difficult and requires substantial effort to establish dialogue with the users. But, we are learning the mechanisms, and are increasingly literate in the methods and approaches that are designed to help us on the way. Improving the communication process requires attention to many issues, including respect for complexities (in science as well as in decision making, individual or institutional). Developing answers to real world problems in partnership between scientists and stakeholders is the only way to address real-world concerns, and the participatory process is a part of the sought-after solution.

ACKNOWLEDGMENTS

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REFERENCES

1. CiteAir, 2016 available at http://www.airqualitynow.eu/about_indices_definition.php (Accessed 18.10.2016)
2. EEA, 2014. Air quality in Europe. Report no 5/2014, European Environment Agency, Copenhagen.
3. Eurobarometer, 2013. Attitudes of Europeans towards Air Quality. Flash Eurobarometer 360. http://ec.europa.eu/COMMFrontOffice/PublicOpinion/index.cfm/Survey/getSurveyDetail/search/air%20quality/surveyKy/1046 (Accessed 5.10.2015)
4. Fagerli, H., Schulz, M., Gauss, M., Tsyro, S., Jonson, J.E., Benedictow, A., Simpson, D., Valdebenito, A., Griesfeller, J., Semeena, V.S., Wind, P., Olivié, D., Aas, W., Hjellbrekke, A.-G., Solberg, S., Tørseth, K., Yttri, K.E., Mareckova, K., Wankmüller, R., Karl, M., Alastuey, A., Hamburger, T., Posch, M., Tuovinen, J.-P. , 2014. Transboundary particulate matter, photo-oxidants, acidifying and eutrophying components. Oslo, Norwegian Meteorological Institute - MSC-W (EMEP status report 1/2014). http://emep.int/publ/reports/2014/EMEP_Status_Report_1_2014.pdf (Accessed 18.10.2016)
5. Fishbain, B., Lerner, U, Castell, N. Cole-Hunter T., Popoola O., Broday D., Martinez Iñiguez T, Nieuwenhuijsen M., Jovasevic-Stojanovic M., Topalovic D., Jones R.L., Galea K.S., Etzion Y., Kizel F., Golumbic Y.N., Baram-Tsabari A., Yacobi T., Drahler D., Robinson J.A., Kocman D.j, Horvat M.j, Svecova V., Arpaci A., Bartoňová A., 2016. An evaluation tool kit of air quality micro-sensing units. *Science of The Total Environment* (In press). http://dx.doi.org/10.1016/j.scitotenv.2016.09.061.
6. Forsberg B, Bråbäck L, Keune H, Kobernus M, Krayer von Krauss M, Yang A, Bartoňová A., 2012. An expert assessment on climate change and health - with a European focus on lungs and allergies. *Environmental Health*, 11(Suppl 1):S4 (28 June 2012) http://www.ehjournal.net/content/11/S1/S4 (Accessed 5.10.2015)
7. HENVINET (2012) causal diagram for asthma and allergies, http://www.henvinet.eu/language/en-GB/Tools/CauseEffectDiagrams/Astmaandallergy.aspx (Accessed 18.10.2016).
8. Jovasevic-Stojanovic M., Bartoňová A., Topalovic D., Lazovic I., Pokric B. and Ristovski Z. , 2015. On the use of small and cheaper sensors and devices for indicative citizen-based monitoring of respirable particulate matter. *Environmental Pollution* 206:696-704 · September 2015 DOI: 10.1016/j.envpol.2015.08.035.

9. Keune H., Gutleb A.C., Zimmer K., Ravnum S., Yang A., Bartoňová A., Krayer von Kraus M., Ropstad E., Eriksen G., Saunders M., Forsberg B. , 2012. We're only in it for the knowledge? A problem solving turn in environment and health expert elicitation. *Environmental Health*, **11**(Suppl 1):S3 (28 June 2012). http://www.ehjournal.net/content/11/S1/S3
10. Lang, D.J., Wiek A., Bergmann M., Stauffacher M., Martens P., Moll P., Swilling M., Thomas C.J., 2012. Transdisciplinary research in sustainability science: practice, principles, and challenges. *Sustain. Sci* (7 (Suppl 1) 25-43. DOI 10.1007/s1165-011-0149-x
11. Larigauderie A., Mooney H.. 2010. The Intergovernmental science-policy Platform on Biodiversity and Ecosystem Services: moving a step closer to an IPCC-like mechanism for biodiversity *Current Opinion in Environmental Sustainability*, 2:1–6 DOI 10.1016/j.cosust.2010.02.006
12. Liu, H.-Y., Kobernus, M., Broday, D, Bartoňová, A., 2014. A conceptual approach to a citizens' observatory - supporting community-based environmental governance. *Environmental Health*, **13**:107 DOI:10.1186/1476-069X-13-107; http://www.ehjournal.net/content/13/1/107/abstract
13. Pope C.A.III, Thun M.J., Namboodiri, M.N., Dockery D.W., Evans J.S., Speizer F.E, Heath C.W.Jr., 1995. Particulate Air Pollution as a Predictor of Mortality in a Prospective Study of U.S. Adults, *American Journal of Respiratory and Critical Care Medicine*, Vol. 151, No. 3_pt_1 , 669-674. DOI: 10.1164/ajrccm/151.3_Pt_1.669
14. Schiele B., 2008. On and about the Deficit Model in the age of free flow. In: Communicating Science in Social Contexts. In: Communicating Science in Social Contexts - New models, new practices. Donghong Cheng, Michel Claessens, Toss Gascoigne, Jenni Metcalfe, Bernard Schiele, Shunke Shi (Eds): pp. 93-117, Springer Link.
15. Washington Post., 2015. https://www.washingtonpost.com/news/worldviews/wp/2015/12/07/beijing-issues-first-red-alert-for-air-pollution-but-theres-a-silver-lining-in-the-smog/ (Accessed 18.10.2016)
16. Weigold M.F., 2001. Communicating Science. A review of the Literature. *Science Communication*, 23, (2), 164-193, http://www.eea.europa.eu/publications/air-quality-in-europe-2014 (Accessed 5.10.2015)
17. WHO, 2002. Health in Sustainable Sevelopment Planning: the Role of Indicators. Chapter 7. Framework for Linkages between Health, Environment and Development. WHO Geneva. http://www.who.int/mediacentre/events/IndicatorsChapter7.pdf (Accessed 18.10.2016)
18. Ziman J., 1992. Not knowing, needing to know, and wanting to know. In: When science meets the public, edited by D. Lewenstin, pp. 13-20. Washington, D.C, American Association for the advancement of science.

2. SOURCES AND FORMATION

2.1 DOMESTIC HEATING: AN IMPORTANT SOURCE OF PARTICULATE MATTER POLLUTION

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Domestic heating is an important source of particulate matter harmful to human health and the environment. Residential combustion was responsible for respectively 49% and 82 % of the total anthropogenic emissions of primary fine particulate matter (PM2.5) and Benzo(a)pyrene (BaP), in the EU-28 in 2012 (EEA, 2014). The use of solid fuels (mainly biomass, in some country also coal) contributes most to the emission. Such emissions are linked to adverse health effects, especially in urban and sub-urban areas where emissions and population densities tend to be higher. On the other hand, the EU counts on biomass heating to play a very important role in meeting its "20-20-20" targets. The use of solid biomass (e.g. wood and pellets) for domestic heating is often considered as environmentally friendly by the public and authorities, despite its considerable impacts on air quality and health. Solid biomass for heating was the main renewable energy technology in 2012 in the EU-28 accounting for 43 % of all renewable energy source (RES) share. Its use increased by 25 % from 2005 to 2012 in the EU-28 and is expected to increase further and remain the main RES in 2020 (EEA, 2015).

Based on the work published in EEA (2014) and Guerreiro et al (2016), we will present: 1) emissions of PM2,5 and BaP from solid fuel combustion for domestic heating in Europe and their trends; 2) the current status on ambient air concentrations of PM2,5 and BaP over Europe, in relation to the EU target values and WHO guidelines; 3) the estimate of urban and total population exposure to PM2,5 and BaP ambient air concentrations in Europe (Table 1); and 4) an estimate of health effects of current exposure to PM2,5 and BaP. Finally, the need for coordination between air pollution and climate change mitigation policies targeting the residential heating sector at urban, national and European levels will be discussed.

Table 1. Total population exposure and population-weighted concentration for BaP (left) and PM2.5 (right) annual mean in Europe in 2012.

BaP - annual mean, exposed population (%)						BaP popul.	**PM2.5 - annual mean, exposed population (%)**						PM2.5 popul.
< Target value (TV)				**> TV**		weighted conc.	**< Limit value (LV_{2020})**				**> LV_{2020}**		weighted conc.
< 0.12	0.12-0.4	0.4-0.6	0.6-1.0	1.0-1.5	> 1.5	(ng/m^3)	< 5	5 - 10	10 - 15	15 - 20	20 - 25	> 25	($\mu g/m^3$)
11,66	46,73	10,44	10,71	6,82	13,64	0,84	0,8	10,3	47,2	23,7	9,1	9,0	15,6

REFERENCES

1. EEA (2014) Air Quality in Europe - 2014 report, EEA Report No 5/2014, European Environment Agency.
2. EEA (2015) Renewable energy in Europe — approximated recent growth and knock-on effects. EEA Technical report 1/2015, European Environment Agency.
3. Guerreiro, C., Horálek, J., de Leeuw, F., Couvidat, F. 2016. Benzo(a)pyrene in Europe: Ambient Air Concentrations, Population Exposure and Health Effects. Environmental Pollution 214 (2016) 657-667. DOI: 10.1016/j.envpol.2016. 04.081

2.2 PRIMARY AND SECONDARY PARTICULATE EMISSIONS FROM ALTERNATIVE FUELS

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People in urban and semi-urban environments are mainly exposed to a combination of fresh and aged primary emissions and secondary organic aerosols (SOA). The generation of SOA occurs during aging of primary emissions, mainly through oxidation of gas-phase organic compounds that can result either in the formation of new particles or condensation of these compounds onto pre-existing particles. Consequently, atmospheric fate or aging of diesel exhaust has become of a great scientific interest and attracts significant attention from the researchers. In the prospect of limited energy resources and climate change biofuels are becoming a viable alternative to diesel fuel. The effects of alternative biofuels on primary emissions are being extensively studied. A number of studies have shown that biodiesel fuel composition has a significant impact on primary particulate matter emissions. It was also shown that particulate matter produced by the combustion of biodiesels was substantially different from the emissions due to petroleum diesel. Overall, all studies concluded that chemical composition of biodiesel is more important than its physical properties in controlling primary exhaust particle emissions. This suggests that the atmospheric aging processes, including secondary organic aerosol formation, of emissions from different fuels will also be different.

In this study we will present and overview of the role of biofuel composition on the primary particle emissions as well as the role of the fuel composition on the potential to form secondary organic aerosol (SOA). A discussion on the role of atmospheric ageing on the change in the oxidative capacity, and therefore their potential toxicity, of particles emitted by combustion of various biofuels will also be discussed.

2.3 SEASONAL CHARACTER OF EXCEEDANCES OF DAILY CONCENTRATIONS PM_{10} IN REPUBLIC OF SERBIA

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BACKGROUND

Particulate matter PM10 have dominant influence on the air quality in urban areas in the Republic of Serbia. Several papers based on the Report on the State of Air quality in the Republic of Serbia prepared by Environmental Protection Agency confirms this statement (Popović et al, 2015; Radosavljević et al, 2014; Popović et al, 2013). According to the data provided by PRTR operators, absolutely the largest amount of particulate matter originate from the energy sector, (SEPA, 2014).

AIM

The aim of this paper is to present the distinctive trend of daily values of PM_{10} concentrations during the whole year in urban agglomerations, as well as in Uzice and Valjevo, measuring points with the highest concentrations of PM_{10}. Aim of the paper is to compare the trends of PM_{10} and NO_2 in urban agglomerations.

METHODS AND MATERIALS

Trend of daily concentration values during the whole year is given in relative amount – as the ratio of single daily value and the average annual value, in percentages. For more noticeable presentation annual trend is fitted to the polynom of the fifth degree. We used the available data of the results of air quality monitoring in the period 2010 -2014. PM_{10} concentrations were determined by gravimetric and automatic method (used equipment was Tecora skypost and Grimm 180). NO_2 data were determined by automatic method (Teledyne API 200).

RESULT AND DISSCUSION

Annual trend of average daily concentrations in Belgrade, Novi Sad and Nis is shown in Fig. 1. Individual values, by days, are given as the ratio C_Daily / C_Yearly, in percentages, %. Annual trend is fitted to the polynom of the fifth degree.

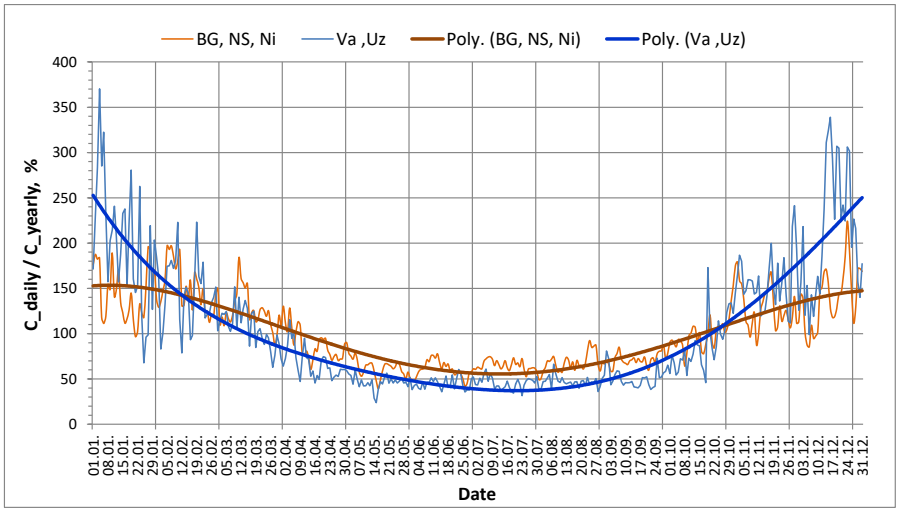

Figure 1. The average annual trend of daily PM_{10} concentration for Belgrade Novi Sad and Nis - brown lines and Valjevo and Uzice - blue lines

CONCLUSION

In urban agglomerations Belgrade, Novi Sad and Nis daily values of PM_{10} have some significant changes during the year. The highest values of PM_{10} during the winter, on the average, are three times greater than the minimum values during the summer. Exceedances of LV of daily PM_{10} values are most likely, on the average, during the period from 5th November till 20th March. In Uzice and Valjevo these changes are more expressive, and period in which, on the average, exceedances of LV could be expected, is longer. Winter values of PM_{10} in Valjevo and Uzice, on the average, are five times higher than the summer values.

Exceedances of LV of daily PM_{10} values in Valjevo and Uzice are most likely, on the average, during the period from 20th September till 30th April. This estimated period, with the most probable appearance of LV exceedances of daily values, is almost twice longer than the equivalent for Belgrade Novi Sad and Nis. NO_2 trend in urban agglomerations Belgrade, Novi Sad and Nis does not have significant fluctuations during the year as the trend of PM_{10}.

REFERENCES

1. Popović, T., Knežević, J., Jović, B., Marić, L., Dimić, B. 2015. Key elements of the basis for the preparation of the National strategy of air protection (in Serbian), Savetovanje "ZAŠTITA VAZDUHA 2015", Key-note lecture, Zrenjanin 2015. (in preparation)
2. Radosavljević, A., Popović, T., Marić, L., Jović, B. 2014. Prekoračenja GV PM10 – stanje kvaliteta vazduha u Srbiji i EU, 10. EnE14/ENV.net, ISBN 978-86-89961-00-3, COBISS.SR-ID 207623436, pp. 12-15.
3. Popović, T., Jović, B., Marić, L. 2013. Substantial influence of PM10 on AQ in Serbia, EnviroChem 2013!, , ISBN 978-86-7132-052-8
4. SEPA, 2014. Izveštaj o stanju životne sredine u Republici Srbiji za 2013. godinu; http://www.sepa.gov.rs/download/Izvestaj2013.pdf

2.4 CARBON MASS CONCENTRATIONS IN SOUTHERN ZAGREB DURING A FIVE-YEAR PERIOD

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ABSTRACT

The purpose of this study was to see how the mass concentrations of elemental carbon (EC) and organic carbon (OC) change across seasons and whether they change over a longer period of measurement. The sampling station was located in the southern part of Zagreb and defined as an urban traffic monitoring station. Samples of PM_{10} particle fraction were collected on quartz fibre filters, pre-fired at 900 °C for three hours. PM_{10} mass concentrations were determined gravimetrically according to the HRN EN 12341 standard. Organic carbon and elemental carbon in the PM_{10} fraction were determined by the thermal-optical transmittance method (TOT), using a Carbon Aerosol Analyzer with a flame ionization detector following a NIOSH-like protocol. Sampling was conducted from 2 January 2009 to 31 December 2013. A slightly negative trend of PM_{10} mass concentrations was observed during the five-year period. The mean mass concentrations of EC and OC for all of the five years were 2.3 μg/m^3 and 11.4 μg/m^3, respectively. Mass concentrations of PM_{10} as well as OC/EC ratio followed the sequence: winter > autumn > spring > summer. Average EC and OC contributions to PM_{10} mass during measuring period were 7 % and 26 %, respectively.

INTRODUCTION

The term particulate matter 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 (Pöschl, 2005). 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. The main anthropogenic sources of particulate matter are factories, power plants, waste incinerators, biomass burning, burning farmland, forest fires, households using wood for space heating and/or food preparation, and traffic exhaust fumes from motor vehicles, construction and dust blown by the wind (Fernandez et al, 2003; Kampa and Castanas, 2008; Rohr and Wyzga, 2012; Watson, 1998). Particulate matter has harmful effects on the environment and human health (respiratory, cardiovascular, nervous system). Particle size determines their deposition in the human respiratory tract. Coarse particulates ($PM_{10-2.5}$, particulate matter with an aerodynamic diameter of less than 10 μm and larger than 2.5 μm) are deposited mainly in the upper respiratory tract, while fine particles ($PM_{2.5}$ and PM_1; particulate matter with an aerodynamic diameter of less than 2.5 μm and 1 μm, respectively) reach in the pulmonary alveoli. The different composition of pollutants in the air, the time of exposure and the fact that people are usually exposed to a mixture of pollutants, not just individual substances, cause a variety of negative effects on human health. Health effects range from nausea and breathing difficulties to skin irritation or even cancer (Donaldson et al, 2005).

The most famous biogeochemical cycle is the carbon cycle in which carbon is exchanged between the biosphere, pedosphere, geosphere, hydrosphere and atmosphere. The main forms of carbon in particulate matter are: elemental carbon (EC), organic carbon (OC) and carbonate carbon (CC) (Chio and Liao, 2008).

EC is a visible component of the PM which is inert, non-volatile and insoluble in the atmospheric environment (Chen et al, 2004), and may be called soot, black carbon (BC) or light-absorbing carbon (LAC) depending on which type of analyses is used for its determination (Chen et al, 2004; Chow et al, 2002; Wilson et al, 2002). EC is investigated because of its potentially harmful effects on human health and the environment. Polluting gases and particles that may have carcinogenic and mutagenic properties absorb on an EC's large specific surface (Lin and Tai, 2001, Husain et al, 2007). EC is the primary pollutant and it is entirely emitted into the atmosphere directly from natural and anthropogenic sources. These sources include the incomplete combustion of fossil and biomass fuels, biomass, industrial processes, forest fires, located in the loess, sand, fossil and ice cores (Chio and Liao, 2008).

Unlike EC, OC is an organic matter fraction that is complex and contains hundreds of organic compounds. These organic compounds may have mutagenic and carcinogenic properties. OC can be a primary and secondary pollutant. Sources of primary OC are natural (photochemical oxidation of gaseous organic precursors, plant spores and pollen, forest fires, volcanic eruptions), (Bice et al, 2009; Castro et al, 1999; Kim et al, 1999; Louie et al, 2005; Na and Cocker, 2005; Van Dingenen et al, 2004) and anthropogenic (combustion of fossil fuels and

biomass, etc.). Secondary OC is formed by the conversion of gaseous pollutants in the air (Cao et al, 2003; Castro et al, 1999; Kumagai et al, 2009; Park et al, 2012).

The purpose of this study was to see how the mass concentrations of elemental and organic carbon change during the seasons and whether they change over a longer period of measurement.

METHODOLOGY

The measuring site was located at the Siget Medical Centre in the southern part of Zagreb, with sampling inlets 4 meters above the ground (Figure 1). This site, defined as an urban traffic monitoring station, is burdened with heavy traffic and is close to offices and schools. Sampling was conducted from 2nd January 2009 to 31st December 2013. In 2009 and 2010, samples were collected only during working days and during 2011-2013, they were collected seven days a week.

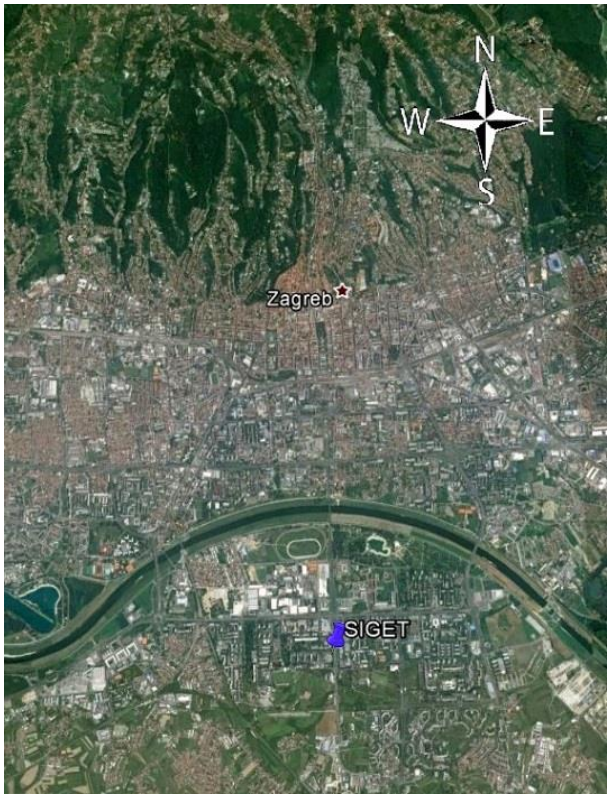

Figure 1. *Position of the urban traffic monitoring site*

The filters (filter diameter: 47 mm; Pallflex Tissuequartz 2500QAT-UP, Pall Life Science) used to collect the samples had to be pre-fired at 900 °C for three hours to reduce carbon content in the filters before sampling. Samples of PM10 particle fraction were collected from approximately 55 m3 of air. Sven Leckel LVS3 (Sven Leck Inginierbüro, Berlin, Germany) reference samplers were used for sample collection and PM10 mass concentrations were determined gravimetrically. Filters were conditioned before and after sampling for 48 h at (20 ± 1) °C and relative humidity (50 ± 5) %, weighed, and after 24 h under same conditions weighed again. 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 as samples. A Mettler Toledo MX 5 microbalance with a golden Faraday cage for removing static electricity and resolution of 10-6 g was used for sample weighing. Organic carbon (OC), elemental carbon (EC) and total (TC = EC + OC) carbon fraction of particulate matter in PM10 fraction were determined by the thermal-optical transmittance method (TOT), using a Carbon Aerosol Analyzer (Sunset Laboratory Inc.) with a He-Ne laser and flame ionization detector (FID) following a NIOSH-like protocol called Quartz (Birch and Cary, 1996; Godec et al, 2012; Quincey et al, 2009). For purposes of quality assurance and quality control (QA/QC) and in order to 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 were in range 96 % - 104 %, average value was 101 % with a relative standard deviation of RSD < 5 %. The detection limits were determined and calculated ($\gamma \pm 3\sigma$) on the basis of an average taken from ten measurements of blank samples (unexposed filters). The detection limits were: 0.02 µg/cm2 for EC, 0.82 µg/cm2 for OC, and 0.83 µg/cm2 for TC. The detection limits expressed in µg/m3 were 0.01 µg/m3 for EC, 0.18 µg/m3 for OC and 0.18 µg/m3 for TC (Godec et al, 2012).

RESULTS AND DISCUSSION

The statistical parameters for PM_{10} and carbon species concentrations at an urban traffic monitoring station during 2009-2013 are shown in Table 1. The average PM_{10} mass concentration for the five-year period was 41.4 µg/m^3, and it was above the limit value (40 µg/m^3 for 1-year period) stipulated by the Regulation on limit values of pollutants in the air (2005) and Directive 2008/50/EC (OG 113, 2005; European Parliament and Council of the European Union, 2008). During the examined years, the daily recommended tolerant values were exceeded several times (Table 2). The mean mass concentrations of EC and OC for all of the five years were 2.3 µg/m^3 and 11.4 µg/m^3, respectively. The average OC/EC ratio for all five years was 5.2, and did not exhibit any trend. All ratios were above 3 indicating the presence of secondary OC in this part of Zagreb. The lowest yearly average OC/EC ratio was spotted in 2009, and the highest in 2013. The lowest daily OC/EC ratio of 1.1 was recorded on 12th October 2009, which indicated only the presence of primary OC in the air during that day. The highest daily OC/EC ratio value of 36.1 was recorded on 20th December 2010.

Table 1. *Statistical parameters for PM_{10} and carbon species concentrations at an urban traffic monitoring station during 2009-2013.*

	PM_{10} µg/m^3	EC µg/m^3	OC µg/m^3	TC µg/m^3	OC/EC
N	1189	1189	1189	1189	1189
$\bar{x}$	41.0	2.3	11.3	13.6	5.2
x_{min}	4.1	0.3	0.8	1.4	1.1
x_{25}	21.8	1.4	4.9	6.8	2.5
median	32.6	2.1	7.4	9.7	3.6
x_{75}	51.9	2.9	13.4	15.9	6.3
x_{max}	234.6	12.1	91.8	96.0	36.1

N - number of samples, $\bar{x}$ - average, σ_x – standard deviation,
x_{min} – minimum measured value, x_{max} – maximum measured value,
PM_{10} – particle matter with aerodynamic diameter less than 10 µm,
EC – elemental carbon, OC- organic carbon, TC - total carbon,
OC/EC - OC/EC mass concentration ratio

Table 2. *Number of exceedances of the daily recommended tolerant values for PM_{10} stipulated by the Regulation on limit values of pollutants in the air for each year separately.*

Year	Tolerant value	100 µg/m^3	150 µg/m^3
2009	45	10	3
2010	57	14	5
2011	57	7	2
2012	68	13	4
2013	62	10	-

Although the yearly averages were above the limit value, a slightly negative trend of the PM_{10} mass concentrations was observed during the five-year period (Figure 2). Unlike the PM_{10} yearly average mass concentration, OC and EC yearly averages did not exhibit a trend. Yearly mean mass concentrations of OC followed the sequence: 2010 > 2009 > 2012 >2013 > 2011 while EC followed: 2009 > 2012 > 2011 > 2013 >

2010. The lowest daily measured concentration of OC was recorded in 2012 and amounted to 0.8 μg/m^3, while the highest was measured in 2010 and was 91.8 μg/m^3. The lowest daily measured concentration of EC was recorded in 2012 (0.3 μg/m^3) and the highest in 2012 (12.1 μg/m^3).

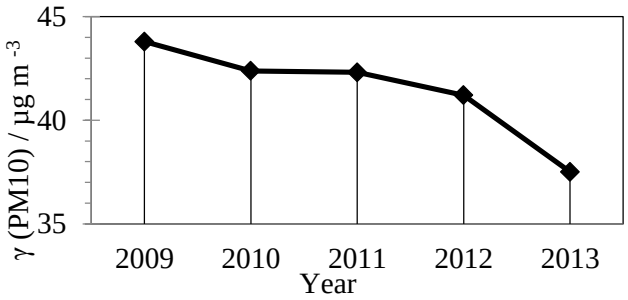

Figure 2. *Yearly averages of PM_{10} mass concentrations from 2009 to 2013 at the urban traffic monitoring site.*

Mass concentrations of OC followed the sequence: winter > autumn > spring > summer (Figure 3). The highest EC mass concentration was recorded during autumn, while the lowest during spring. Significant statistical differences in EC and OC mass concentrations were found between the seasons. As it can be seen from Figure 3, there were great differences in OC mass concentrations in winter and autumn compared to spring and summer. Ho et al, (2006), Sánchez de la Campa et al, (2009) and Terzi et al, (2010) found a similar seasonal distribution of EC and OC mass concentrations in Europe and Asia. Although there are significant statistical differences according to the seasonal distribution of EC mass concentrations, they were equally distributed over all of the seasons. This is exactly the reason why there was a seasonal distribution of OC/EC ratios following series: winter > autumn > spring > summer like and OC mass concentrations. The high OC/EC ratio during winter and autumn suggests the presence of secondary OC. The OC/EC ratio during summer did not exceed 3, which suggests only primary OC is present in the southern part of Zagreb during summer.

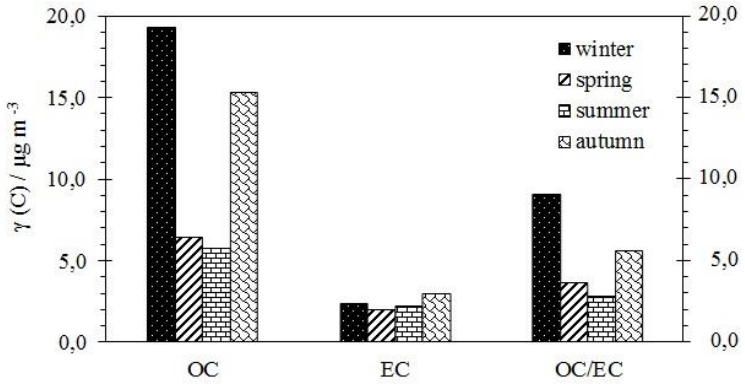

Figure 3*. Seasonal averages of OC and EC mass concentrations from year 2009 to 2013 at the urban traffic monitoring site.*

EC and OC mass contribution to the total PM_{10} mass for each year separately at the urban traffic monitoring station is shown in Table 3. The lowest EC and OC mass contribution was noted in 2011, while the highest was in 2013. EC and OC mass contribution to the total PM_{10} mass for the five-year period is presented in Figure 4. Average EC and OC contributions to PM_{10} mass were 7 % and 26 %, respectively. The highest OC contribution to PM_{10} mass was recorded during autumn and the lowest during spring, while the lowest EC contribution to PM_{10} mass was recorded during winter and the highest in summer period.

CONCLUSIONS

Although the mass concentrations of both EC and OC did not differ during longer periods of measurement, significant statistical differences between the seasons were found in EC and OC mass concentrations. The high OC/EC ratio during all of the years suggests the presence of secondary OC. The EC and OC contribution to the total PM_{10} mass showed seasonal variations.

Table 3. *EC and OC mass contribution to the total PM_{10} mass for each year separately (2009-2013) at the urban monitoring station.*

Year	EC (%)	OC (%)	Rest of pollutants in PM_{10} (%)
2009	7.8	25.0	67.2
2010	6.7	26.3	67.0
2011	6.4	22.5	71.1
2012	6.9	26.1	67.0
2013	8.2	29.6	62.3

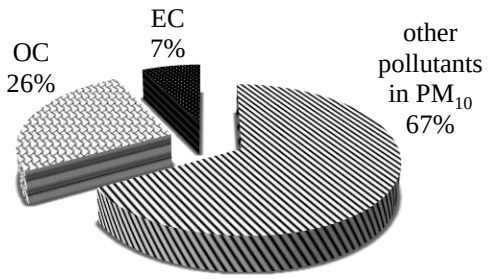

Figure 4*. EC and OC mass contribution to the total PM_{10} mass for the five-year period (2009-2013) at the urban traffic monitoring station.*

REFERENCES

1. Bice, K., Eil, A., Habib, B., Heijmans, P., Kopp, R., Nogues, J., Norcross, F., Sweizer-Hamilton, M., Whitworth, A., 2009. Black carbon: A review and policy recommendations. Woodrow Wilson Sch. public Int. Aff. 80.
2. Birch, M.E., Cary, R. a., 1996. Elemental Carbon-Based Method for Monitoring Occupational Exposures to Particulate Diesel Exhaust. Aerosol Sci. Technol. 25, 221–241. doi:10.1080/02786829608965393
3. Cao, J.J., Lee, S.C., Ho, K.F., Zhang, X.Y., Zou, S.C., Fung, K., Chow, J.C., Watson, J.G., 2003. Characteristics of carbonaceous aerosol in Pearl River Delta Region, China during 2001 winter period. Atmos. Environ. 37, 1451–1460. doi:10.1016/S1352-2310(02)01002-6
4. Castro, L.M., Pio, C. a., Harrison, R.M., Smith, D.J.T., 1999. Carbonaceous aerosol in urban and rural European atmospheres: Estimation of secondary organic carbon concentrations. Atmos. Environ. 33, 2771–2781. doi:10.1016/S1352-2310(98)00331-8
5. Chen, L.W.A., Chow, J.C., Watson, J.G., Moosmüller, H., Arnott, W.P., 2004. Modeling reflectance and transmittance of quartz-fiber filter samples containing elemental carbon particles: Implications for thermal/optical analysis. J. Aerosol Sci. 35, 765–780. doi:10.1016/j.jaerosci.2003.12.005
6. Chio, C.P., Liao, C.M., 2008. Assessment of atmospheric ultrafine carbon particle-induced human health risk based on surface area dosimetry. Atmos. Environ. 42, 8575–8584. doi:10.1016/j.atmosenv.2008.08.027
7. Chow, J.C., Engelbrecht, J.P., Freeman, N.C.G., Hisham Hashim, J., Jantunen, M., Michaud, J.P., De Tejada, S.S., Watson, J.G., Wei, F., Wilson, W.E., Yasuno, M., Zhu, T., 2002. Chapter one: Exposure measurements. Chemosphere 49, 873–901. doi:10.1016/S0045-6535(02)00233-3
8. Donaldson, K., Mills, N., MacNee, W., Robinson, S., Newby, D., 2005. Role of inflammation in cardiopulmonary health effects of PM. Toxicol. Appl. Pharmacol. 207. doi:10.1016/j.taap.2005.02.020
9. European Parliament, Council of the European Union, 2008. Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe. Off. J. Eur. Communities 1–43. doi:http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2008:152:0001:0044:EN:PDF
10. Fernandez, A., Wendt, J.O.L., Wolski, N., Hein, K.R.G., Wang, S., Witten, M.L., 2003. Inhalation health effects of fine particles from the co-combustion of coal and refuse derived fuel. Chemosphere 51, 1129–1137. doi:10.1016/S0045-6535(02)00720-8
11. Godec, R., Čačković, M., Šega, K., Bešlic, I., 2012. Winter mass concentrations of carbon species in PM10, PM 2.5 and PM1 in Zagreb Air, Croatia. Bull. Environ. Contam. Toxicol. 89, 1087–1090. doi:10.1007/s00128-012-0787-4
12. Ho, K.F., Lee, S.C., Cao, J.J., Chow, J.C., Watson, J.G., Chan, C.K., 2006. Seasonal variations and mass closure analysis of particulate matter in Hong Kong. Sci. Total Environ. 355, 276–287. doi:10.1016/j.scitotenv.2005.03.013
13. Kampa, M., Castanas, E., 2008. Human health effects of air pollution. Environ. Pollut. 151, 362–367. doi:10.1016/j.envpol.2007.06.012

14. Kim, Y.P., Moon, K.C., Lee, J.H., Baik, N.J., 1999. Concentrations of carbonaceous species in particles at Seoul and Cheju in Korea. Atmos. Environ. 33, 2751–2758. doi:10.1016/S1352-2310(98)00313-6
15. Kumagai, K., Iijima, A., Tago, H., Tomioka, A., Kozawa, K., Sakamoto, K., 2009. Seasonal characteristics of water-soluble organic carbon in atmospheric particles in the inland Kanto plain, Japan. Atmos. Environ. 43, 3345–3351. doi:10.1016/j.atmosenv.2009.04.008
16. Louie, P.K.K., Chow, J.C., Chen, L.W.A., Watson, J.G., Leung, G., Sin, D.W.M., 2005. PM2.5 chemical composition in Hong Kong: Urban and regional variations. Sci. Total Environ. 338, 267–281. doi:10.1016/j.scitotenv.2004.07.021
17. Na, K., Cocker, D.R., 2005. Organic and elemental carbon concentrations in fine particulate matter in residences, schoolrooms, and outdoor air in Mira Loma, California. Atmos. Environ. 39, 3325–3333. doi:10.1016/j.atmosenv.2005.01.054
18. Park, S.S., Cho, S.Y., Kim, K.W., Lee, K.H., Jung, K., 2012. Investigation of organic aerosol sources using fractionated water-soluble organic carbon measured at an urban site. Atmos. Environ. 55, 64–72. doi:10.1016/j.atmosenv.2012.03.018
19. Pöschl, U., 2005. Atmospheric aerosols: Composition, transformation, climate and health effects. Angew. Chemie - Int. Ed. 44, 7520–7540. doi:10.1002/anie.200501122
20. Quincey, P., Butterfield, D., Green, D., Coyle, M., Cape, J.N., 2009. An evaluation of measurement methods for organic, elemental and black carbon in ambient air monitoring sites. Atmos. Environ. 43, 5085–5091. doi:10.1016/j.atmosenv.2009.06.041
21. Rohr, A.C., Wyzga, R.E., 2012. Attributing health effects to individual particulate matter constituents. Atmos. Environ. 62, 130–152. doi:10.1016/j.atmosenv.2012.07.036
22. Sánchez de la Campa, a. M., Pio, C., de la Rosa, J.D., Querol, X., Alastuey, a., González-Castanedo, Y., 2009. Characterization and origin of EC and OC particulate matter near the Doñana National Park (SW Spain). Environ. Res. 109, 671–681. doi:10.1016/j.envres.2009.05.002
23. Terzi, E., Argyropoulos, G., Bougatioti, A., Mihalopoulos, N., Nikolaou, K., Samara, C., 2010. Chemical composition and mass closure of ambient PM10 at urban sites. Atmos. Environ. 44, 2231–2239. doi:10.1016/j.atmosenv.2010.02.019
24. Van Dingenen, R., Raes, F., Putaud, J.P., Baltensperger, U., Charron, A., Facchini, M.C., Decesari, S., Fuzzi, S., Gehrig, R., Hansson, H.C., Harrison, R.M., Hüglin, C., Jones, A.M., Laj, P., Lorbeer, G., Maenhaut, W., Palmgren, F., Querol, X., Rodriguez, S., Schneider, J., Ten Brink, H., Tunved, P., Tørseth, K., Wehner, B., Weingartner, E., Wiedensohler, A., Wåhlin, P., 2004. A European aerosol phenomenology - 1: Physical characteristics of particulate matter at kerbside, urban, rural and background sites in Europe. Atmos. Environ. 38, 2561–2577. doi:10.1016/j.atmosenv.2004.01.040
25. Watson, J.C.C.& J.G., 1998. Guideline on Speciated Particulate Monitoring, Draft 3. Desert Res. Institute, P.O Box 60220, Reno NV 89506.
26. Wilson, W.E., Chow, J.C., Claiborn, C., Fusheng, W., Engelbrecht, J., Watson, J.G., 2002. Monitoring of particulate matter outdoors. Chemosphere 49, 1009–1043. doi:10.1016/S0045-6535(02)00270-9

2.5 PARTICULATE MATTER AND AIRBORNE POLLEN AS BACKGROUND POLLUTION IN URBAN AREA - EXAMPLE OF RIGA, LATVIA

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ABSTRACT

The main reason for studying air pollution from anthropogenic and biological sources is the negative impact on human health. Pollen has significant impact especially in urban areas with high level of particulate matter.

The aim of this study is to compare daily and inter-seasonal patterns of different fractions of particulate matter, airborne pollen amount in the air and meteorological variables.

Pollen monitoring, as well as monitoring of particulate matter, was performed in the centre of the city of Riga during the time of birch flowering April-May 2014. Both a *Burkard* sampler (for pollen) and a GRIMM dust monitoring station (for particulate matter) was placed at a height of 23m a.g.l. The height was chosen to represent background air pollution in the city. Two-hourly and daily pollution from different sources was analyzed with meteorological variables.

The results have shown differences during night hours, while background air pollution during the day is influenced mostly by local meteorology.

Keywords: Particulate matter, pollen, background air pollution, Riga

INTRODUCTION

The occurrence of pollen allergies is constantly increasing, and pollen-related sensitization has already reached a substantial fraction of European population and is starting to have significant socioeconomic impact (Huynen et al, 2003). Various ways of reducing its impact exist but none have proven to be a universally applicable solution (Ring et al, 2012).

Recent findings (Bergmann et al, 2013; D'Amato, Cecchi, D'Amato, & Liccardi, 2010; Konishi et al, 2014; Morgenstern et al, 2008) partly describe the result of interaction between particulate matter and airborne pollen. According to Berstein (Bernstein et al, 2004), pollen allergy (*polinosis*) is notably higher in people living near high-traffic streets compared with individuals from regions with low-traffic levels. A substantial part of the interaction between particulate matter and pollen is a change in pollen structure caused by the fine fraction of particulate matter (Guedes et al, 2009), as well as splashing of pollen by the finest fraction of PM and allergen emission directly in the air (Konishi et al, 2014). Ribero (Ribeiro, Oliveira, & Abreu, 2008) emphasized that pollen particles are able to absorb a fine fraction of particulate matter and that may influence its allergenicity.

Many studies are focused on single pollutants, but an important point is that there is a wide complex of numerous pollutants of different origin impacting jointly on the human respiratory tract.

The main idea of the current study is to compare the daily behaviour of PM and pollen and evaluate if the bi-hourly fluctuation of air pollution from different sources has the same pattern during the day and if it depends on the same meteorological variables.

METHODOLOGY

Study site

Monitoring of air pollution was performed in central part of Riga city (N56°57'02'', E24°06'57''), Latvia, at a height of 23m above ground level (27m above sea level). The height was chosen to prevent the influence of street canyons and closeness of potential sources (i.e. traffic) on background measurements.

The height above roof level allows:

(i) to avoid direct influence of potential source (in both cases – traffic as well as trees);

(ii) to link and compare air pollution from different sources to meteorology;

(iii) to evaluate the impact of meteorology on air pollution dispersion process.

Sampling

Two different samplers were used for air pollution measurements. First, pollen measurements were taken by using Hirst-type Burkard trap (Hirst, 1954) (Fig.1., Fig.2), produced by Burkard Manufacturing Co. Ltd., UK.

Pollen observation is based on pollen accumulating on sticky plastic tape inside the volumetric instrument. The transparent plastic tape was covered by solution of vaseline and fixed around a drum (Fig.2), which rotated by 7-day clockwork at a speed of 2mm per hour.

Figure 1. *Burkard volumetric pollen – spore trap and GRIMM station at the monitoring site*

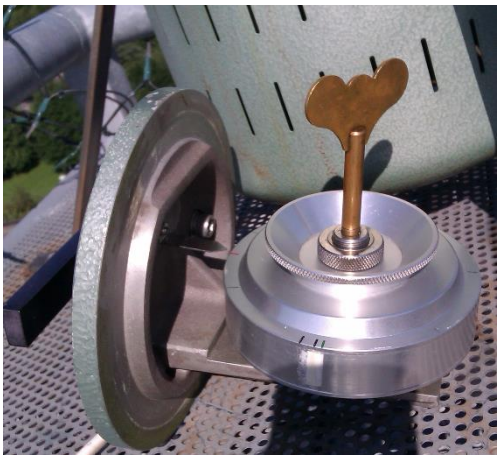

Figure 2. *Drum with the tape for pollen sampling*

A built-in vacuum pump continuously samples air at a rate of 10 L min^{-1} (speed of human breathing) thought a slit against the tape, on which the airborne particles were attached. Daily sections of the tape were mounted with *gelvatol* (polyvinyl alcohol) under a cover glass. Then all pollen spores and other hard micro-particles were determined in slides by the light microscope *"Axiostar*". In each slide 12 vertical lines, which serve every 2 hours were counted. The pollen sum counted by the microscope was converted to concentration (µm /m^3).

The particulate matter data collected by GRIMM pollution monitoring station (Fig.1) for the same period was recalculated to two-hourly data because of the minimal level of pollen data. The GRIMM EDM 365 device (complies with the standards EN12341, EN14907, US-EPA and GOST-R) detects airborne particles from 0,25 to 32 µm (single particle count) without the loss of the semi-volatile compounds (reached by *Nafion* drying). Every single aerosol particle is detected in the optical measurement cell and then allocated to a defined particle size based on the intensity of the scattering light signal. This precise and reliable single particle count allows for a simultaneous measurement of the dust mass fractions PM_{10}, $PM_{2.5}$, PM_1 and also the particle size distribution in 31 size channels. In order to guarantee the precision of the measurements, and to protect the measuring cell from contamination, the constant 1,2 l/min sample air flow is filtered and brought back into the device as rinsing air.

Meteorology

Meteorological data were taken partly from meteorological station Riga-LU which is situated 1km to NW from monitoring place, and another part of the meteorology (atmospheric pressure, relative humidity, wind speed and direction), was measured exactly at the same place as the monitoring of pollution. Hourly values of meteorological variables were recalculated to bi-hourly and included in the analysis.

Analysis

The GRIMM monitoring station allows to measure different fraction of particulate matter. The necessary size fraction (closer to birch pollen) was chosen. The size of airborne pollen is from 10 to 35 microns: birch pollen, analyzed in this study, has the size of 23-25 microns. Thus, PM fractions with the size 18.75µm, 22.5µm and 27.5µm were filtered out of database for analysis. $PM_{2.5}$ and PM_{10} also was used for evaluation of possible correlations between data sets.

Because of the different techniques used for pollen/particulate matter monitoring, normalization of data was necessary to make data sets comparable. Homogenization of 2 data sets (both, for particulate matter and for pollen) was achieved by normalization of bi-hourly values $P_i(t)$ with the sum of observation $(\sum_{t\in i} P_i(t))$ from whole period *i*, at the result we get homogeneous bi-hourly time series $p_i(t)$ (Fig. 3.):

$$p_i = \frac{P_i(t)}{\sum_{t\in i} P_i(t)},$$

Where (t) is bi-hourly time value.

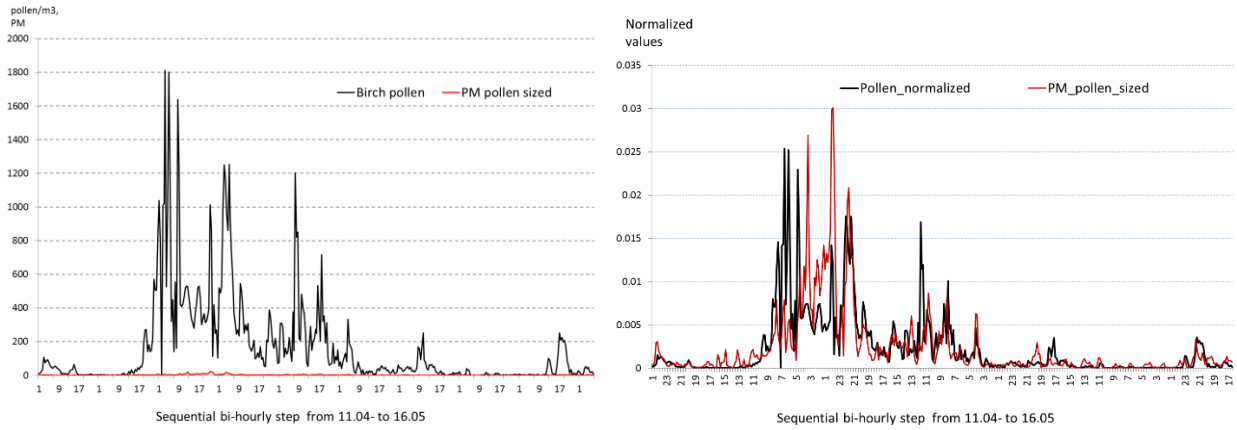

Figure 3. *Absolute (left side) and normalized (right side) values of birch pollen and pollen-sized particular matter*

Simple statistical analysis was performed by using statistical package of R programming language.

RESULTS AND DISCUSSION

There are about 35-47 different pollen types observed every year in the air over Riga. Thus, the high-allergenic pollen for Latvia comes from: alder (*Alnus* Mill.), birch (*Betula* L.), hazel (*Corylus* L.), grasses (*Poaceae*) and mugwort (*Artemisia* L.).

The general pollen season, which starts in March and ends in September, can be divided into four main periods. Three of them – the first, third and fourth are very dangerous to allergenic people.

The start of the pollen season is defined by the first appearance pollen in air which is conveyed by phenological features. The end of the pollen season is defined by pollen disappearance for seven days (phenological and meteorological information is taken in account).

The highest percentage of pollen usually found in the period from the last decade of April to the first decade of May which is related to the birch flowering in Latvia and also to transported pollen from another countries. The most dangerous pollen in Latvia comes from birch tree. Birch produces a large amount of pollen every year and its flowering time is from middle April to second decade of May (Fig.4). The period of pollen appearance in the air is usually called *pollen season*.

It is important that the birch pollen season also consists of several parts (called *peaks*). The first peak at the very beginning of the exact pollen season is usually caused by transported pollen, from the regions where flowering starts earlier due to climatic conditions. The distance for birch pollen transportation by airflow sometimes reaches up to 1000km from the emission place. Because of the long distances covered, transported pollen levels are usually observed as low but noticeable amount of pollen during several (2-7) days (Fig.4).

After the first peak, there is a gap until the start of the flowering season. The start of birch flowering is mostly influenced by air temperature and is sensitive to precipitation and relative humidity. In the case of high air temperature, low humidity and absence of precipitation, very high concentration of pollen are observed (Fig.4). Maximal values are usually observed during 2 weeksat the time of intensive plant flowering at a distance of 30km around the pollen sampler. The pollen season is prolonged by transported pollen from northern regions (Fig.4).

At the time of local flowering, the main factors limiting emission and dispersion of pollen are precipitation, relative humidity and high level of cloudiness.

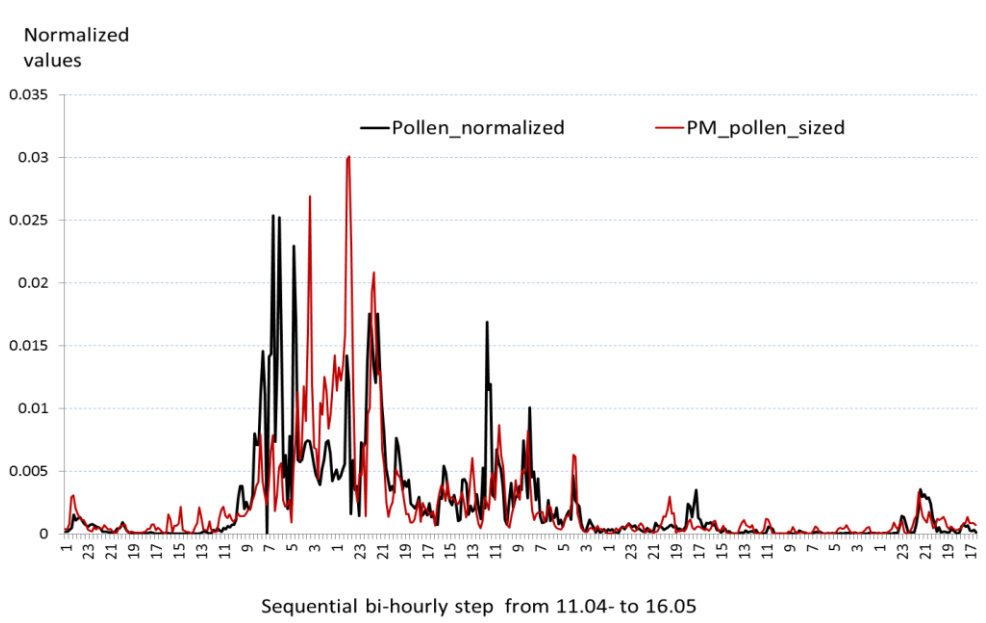

Figure 4. *Changes of normalized values of birch pollen and birch pollen sized particulate matter during birch pollen season 2014 in Riga, Latvia*

Analysis of particles of different origin at roof level shows a lot of similarities between hourly and daily fluctuations of variables during the birch pollen season in Riga. There were several days during the pollen season of 2014 when the PM has higher values then birch pollen. An explanation is stagnant weather conditions. In the case of particular matter this causes an increase in the concentration of air pollution, whereas, in case of pollen, stagnant weather decreases the concentration, because, at least moderate wind is needed to shake birch catkins and release pollen. The Pearson correlation between variables gives coefficient of 0.64 (on 95% confidence interval between 0.57 and 0.68). One of hypotheses of such similarities is that pollen-sized PM are too heavy to be raised up by airflow and GRIMM counted particles, are, mostly pollen except on very windy days.

Comparing particulate matter on different sizes ($PM_{2,5}$; PM_{10}) to birch pollen, we got similarities of fluctuations during whole period (Fig.5), at the same time diurnal variation usually do not have the same pattern. The explanation is based on aerodynamic characteristics and place of origin of the particles.

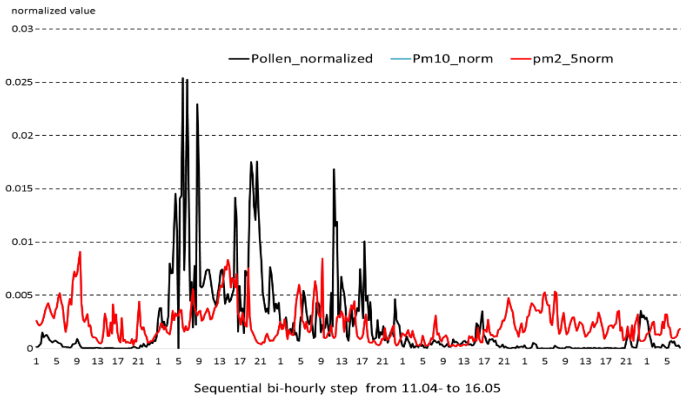

Figure 5. *Behaviour of different size of PM and pollen during the birch pollen season in Riga, Latvia 2014*

Noticeable similarities were found at the daily level of fluctuations of pollen–sized background pollution. Thus, pollen sized particulate matter has very similar seasonal and diurnal fluctuation as pollen (Fig.6). It is explained

by the influence of meteorological situations on the same-sized particles with both biological and anthropogenic origin.

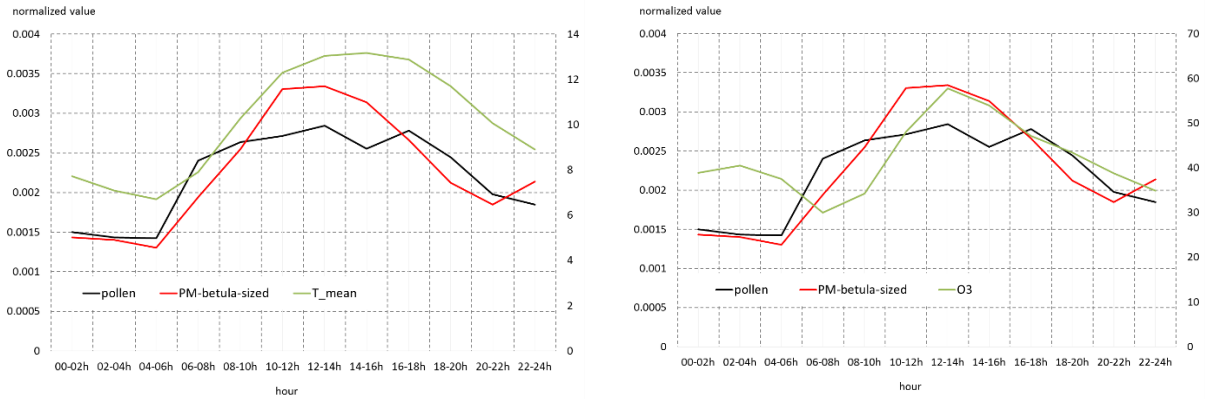

Figure 6. *Diurnal cycle with bi-hourly step of different kind of background air pollution , air temperature and O_3 at roof level in Riga*

The bi-hourly pattern of average measurements from 445 entries was analysed. In case of birch pollen, similar sized particulate matter has very similar behaviour during the daytime. The maximal level of pollution is at mid-day (from 12.00 to 14.00), corresponding with the time with maximum daily temperature of air.

The outcome of linear regression analysis shows that atmospheric pressure is a most important influencing factor of background pollution.

The mean and maximum temperature of the air is important factor during the daytime, and pollution from both sources reaches the maximum corresponding with maximal temperature of air, also because of the influence of temperature on birch pollen emission rate – in April/May, the higher air temperatures promotes earlier and more powerful emission of pollen. The relative humidity of air is limiting factor, which reduced both - the intensity of emission (in case of pollen) and rate of dispersion (in case of pollen and particulate matter).

The same occurs at the seasonal level, when noticeable changes of level of pollution depend on temperature fluctuations.

CONCLUSION

Despite the fact, that pollen and particulate matter have absolutely different origin, structure, function and noticeably different levels of concentration in the air, these might be comparable after minimal modification of data. This is the first study on finding a relationship between pollen and the coarse fraction of particulate matter in Latvia, and it showed that further studies on topic will bring opportunity to predict approximate behaviour of same-sized air pollutants, based on monitoring and the relationship to meteorological situation – either pollen or PM.

Such a similar fluctuation of pollutants led us to conclude that location and the kind of emission source of the pollutant is not the primarily factor influencing the level of background pollution

It is mentioned quite often that the coarse fraction of particulate matter is produced by attrition of smaller particles (Brunekreef & Holgate, 2002), at the same time, it is necessary to note that pollen might be a relevant percent of PM coarse fraction and jointly with anthropogenic PM may cause a number of diseases and impact human health.

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REFERENCES

1. Bergmann, K.-C., Simoleit, A., Wagener, S., Mücke, H.-G., Werchan, M., & Zuberbier, T. 2013. The distribution of pollen and particulate matter in an urban agglomeration using the city of Berlin as an example. Allergo Journal, 22(August 2015), 475–479. doi:10.1007/s15007-013-0430-7
2. Bernstein, J. a., Alexis, N., Barnes, C., Bernstein, I. L., Bernstein, J. a., Nel, A., Williams, P. B. 2004. Health effects of air pollution. Journal of Allergy and Clinical Immunology, 114, 1116–1123. doi:10.1016/j.jaci.2004.08.030
3. Brunekreef, B., & Holgate, S. T. 2002. Air Pollution Health, 360, 1233–1242. doi:10.1016/S0140-6736(02)11274-8
4. D'Amato, G., Cecchi, L., D'Amato, M., & Liccardi, G. 2010. Urban air pollution and climate change as environmental risk factors of respiratory allergy: an update. Journal of Investigational Allergology & Clinical Immunology, 20(2), 95–102; quiz following 102. Retrieved from http://www.ncbi.nlm.nih.gov/pubmed/20461963
5. Guedes, A., Ribeiro, N., Ribeiro, H., Oliveira, M., Noronha, F., Abreu, I. 2009. Comparison between urban and rural pollen of *Chenopodium alba* and characterization of adhered pollutant aerosol particles. Journal of Aerosol Science 40: 81-86
6. Hirst, J. M. 1954. An automatic volumetric spore trap. Annals of Applied Biology, 39(2), 257–265.
7. Huynen, M., Menne, B., Behrendt, et.al (2003). Phenology and Human Health: Allergic Disorders. World Health.
8. Konishi, S., Ng, C. F. S., Stickley, A., Nishihata, S., Shinsugi, C., Ueda, K., Watanabe, C. (2014). Particulate matter modifies the association between airborne pollen and daily medical consultations for pollinosis in Tokyo. Science of The Total Environment, 499 (August 2015), 125–132. doi:10.1016/j.scitotenv.2014.08.045
9. Morgenstern, V., Zutavern, A., Cyrys, J., Brockow, I., Koletzko, S., Krämer, U., … Schäfer, T. (2008). Atopic diseases, allergic sensitization, and exposure to traffic-related air pollution in children. American Journal of Respiratory and Critical Care Medicine, 177, 1331–1337. doi:10.1164/rccm.200701-036OC
10. Ribeiro, H., Oliveira, M., & Abreu, I. 2008. Intradiurnal variation of allergenic pollen in the city of Porto (Portugal). Aerobiologia, 24(3), 173–177. doi:10.1007/s10453-008-9091-5
11. Ring, J., Akdis, C., Behrendt, H., Lauener, R. P., Schäppi, G., Akdis, M., … Rietschel, E. 2012. Davos declaration: allergy as a global problem. Allergy, 67(2), 141–3. doi:10.1111/j.1398-9995.2011.02770.x

2.6 CHARACTERIZATION OF MARINE AEROSOLS AT THE HIGHLY EUTROPHIC SEAWATER ECOSYSTEM ROGOZNICA LAKE IN CENTRAL DALMATIA, ADRIATIC SEA

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ABSTRACT

Physico-chemical characterization of the water soluble marine aerosol (WSMA) fraction was performed on samples collected at the highly eutrophic marine lake Rogoznica lake on the Adriatic coast. Aerosol samples, $PM_{2.5}$, were collected on the glass fiber GF/F filters (φ=47 mm) by low volume sampler (2.3 m^3/h, sampling time: 24 h). In order to get better insights into aerosol characteristics and dynamics between the atmosphere and the lake marine system, the study is designed to comprise seasonal data of marine aerosols as well as the sea surface microlayer (SML) and underlying water samples (ULW, from 0.5 m depth) of the Rogoznica Lake

Organic matter i.e. surface active substances and reduced sulphur species characterization in WSMA, SML and ULW was performed by electrochemical methods in combination with measurements of total and dissolved organic carbon by high temperature catalytic oxidation (HTCO). In parallel samples trace metals by ICPMS measurements were determined.

INTRODUCTION

In the frame of the project funded by Croatian science foundation "The Sulphur and Carbon Dynamics in the Sea- and Fresh-water Environment" (SPHERE) we are studying sulphur (S) and carbon (C) dynamics between different environmental compartments (atmosphere, water, sediment, biota) of the sea- and fresh-water environment. A main focus is on distribution between organic, inorganic, dissolved, colloidal and nanoparticulate fractions. An important part of the project is focused on characterization of marine and freshwater aerosols mainly by electrochemical, chromatographic and ICPMS methods.

The atmosphere is one of the Earth's major C and S reservoirs and an important component of the global C and S cycles. In the perspective of chemical cycling and surface-atmosphere exchange with other compartments, the atmosphere serves as a delivery system to bring material and energy to and take material away from an ecosystem. The exchange processes have a decisive role in global changes and in environmental protection. The boundary layer between the water and the atmosphere defined as the surface microlayer (SML) as upper 1 to 1000 μm of the sea surface is generally enriched in organic substances which are mostly surface active and accumulate in the SML forming surface films (Frka et al, 2012).

Organic matter is an important atmospheric fraction which enters the Earth's atmosphere through primary biogenic emissions from terrestrial and marine ecosystems and anthropogenic sources such as traffic and residential heating (Hallquist et al, 2009). Furthermore, organic matter can transform due to photochemical reactions (that involve UV-VIS radiation, volatile organic compounds (VOCs) and oxidants, primarily ozone and OH radicals) and lead to the formation of secondary organic aerosols (SOA). The composition of the aerosol organic matter and the respective source contributions are far less known than those of the inorganic part (Jacobson et al, 2000). Many of the organics identified in the atmospheric particles are known to be surface active in aqueous solutions contributing aerosol water soluble organic carbon (WSOC) fraction (Latif and Brimblecombe, 2004). Lastly, studies on the composition of airborne marine organic particles have found evidence of carbohydrates (Facchini et al, 2001; Hawkins et al, 2010), amino acids (Kuznetsova et al, 2005), alcohols, fatty acid salts, esters (Gagosian et al, 1981), and marine microorganisms (Aller et al, 2005).

The atmospheric deposition of mineral dust is one of the most important pathways by which trace metals reach the ocean. Recently, it has been recognized that trace metals such as Fe, Mn, Zn, Cu, Co, and Cd are essential for phytoplankton growth (Baker and Croot, 2010). The fraction of atmospherically deposited trace metals especially iron which dissolves in seawater, or becomes available to phytoplankton for growth, is a key determinant of primary productivity in many open ocean regions. The fraction of the trace metals contained in atmospheric deposition which is soluble in seawater and/or available to marine photosynthetic organisms are highly variable in both space and time.

Marine aerosols play a dominant role in the transfer of oceanic material to the atmosphere. Most marine aerosol originates when air bubbles burst at the sea surface ejecting material from the sea surface microlayer (SML) and

bubble surface layers into the air. Concentrations of chemical compounds in these surface layers often differ from their concentrations in bulk water.

The unique, highly eutrophic, and euxinic (anoxic water with free hydrogen sulphide in the water column) marine lake system Rogoznica Lake in central Dalmatia (Middle Adriatic, 43°32'N 15°58'E, Figure 1) was selected as one of the important study sites in the frame of the above mention SPHERE project. Rogoznica Lake is considered as an extreme, naturally eutrophic system which feels all effects of the Adriatic atmospheric and ocean conditions (Ciglenečki et al, 2015). The influence of these conditions due to the lake semi-closed nature might be several times stronger than in other coastal and open sea Adriatic waters. Extremely fluctuating environmental conditions such as high seasonal variations in salinity and temperature, water stratification with strong redox gradient and euxinia, accompanied by high concentrations and variability of nutrients on one side and episodic appearance of holomixis with hypoxia and anoxia conditions on the other side, highly influence the lake ecosystem.

In order to get better insights into aerosol characteristics and dynamics between the atmosphere and the lake marine system, this study is designed to comprise seasonal data of the marine aerosols as well as the sea surface microlayer and underlaying water samples (ULW, from 0.5 m depth) at Rogoznica Lake. Physico-chemical characterization of the water soluble organic matter (WSOM) aerosol fraction, SML and ULW samples were conducted by mainly electrochemical methods for surface active substances (SAS) (Frka, 2012; Ćosović, 1989; Ćosović, 1996; Ćosović et al, 2007; Ćosović et al, 2000) and reduced sulphur species characterization (Ciglenečki and Ćosović, 1997; Bura-Nakić et al, 2009), in combination with measurements of total and dissolved organic carbon (TOC,DOC) by high temperature catalytic oxidation (HTCO). In parallel samples trace metals by ICPMS measurements were determined. The first preliminary results will be presented and discussed.

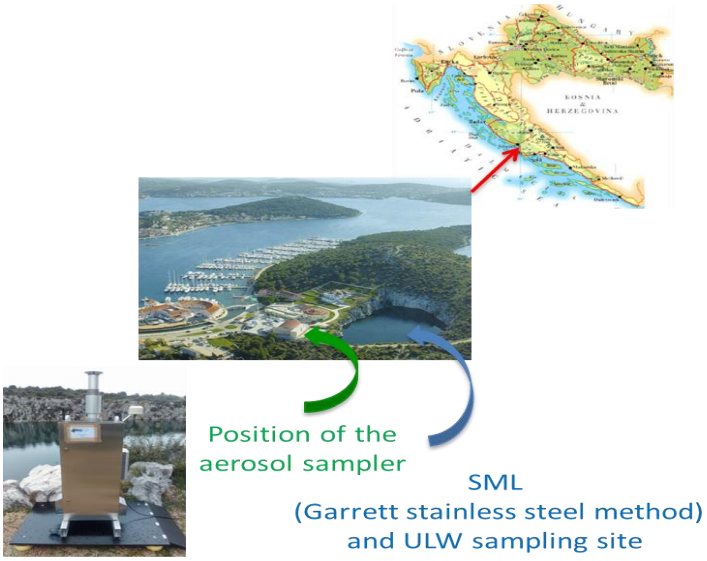

Figure 1. *Map of Croatia with indicated position of Rogoznica lake, shown by air photo and indication of aerosol sampler position, and position where SML is sampled.*

METHODOLOGY

The aerosol samples (aerodynamic diameter <2.5 μm) were collected on the glass fiber GF/F filters (φ=47 mm) by low volume sampler (2.3 m^3/h, sampling time: 24 h). Before exposure, the filters were pre-combusted 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 during winter (January-February in 2015) at the Rogoznica Lake marine system in the central Dalmatia (Middle Adriatic, 43°32'N 15°58'E, Figure 1). Rogoznica Lake can be considered as an extreme, naturally eutrophic system which feels all effects of the Adriatic atmospheric and ocean conditions. The climate is Mediterranean, with warm summer and mild winter periods with average temperatures of 8-10 °C during winter. The whole region is characterized with extensive tourism, and a low impact of industrial activities.

The SML samples were collected by the Garrett screen method using the stainless steel screen and ULW by hand in 1,3 L glass bottles from the lake water column at depth of 0.5 m.

Sample pre-treatment

The water-soluble aerosol fraction was extracted by placing half of the filters in 0.13–0.2 dm^3 of high purity deionised MilliQ water (Millipore Corp.) for 24 h, following the work of Frka et al (12). The extracts were then filtered through 0.7 μm GF/F filters pre-combusted 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} $HgCl_2$.

Filter samples for trace metal analyses were dissolved in acid pre-cleaned plastic bottles filled with 0.5% nitric acid.

Sample analysis

Characterization of organic matter and reduced sulfur species in WSMA fraction and SML and ULW Rogoznica lake samples was performed by a fast, easy-performing and sensitive electrochemical method that has been developing in our group for characterization and measurements of surface active substances (SAS) and different reduced sulfur compounds in natural waters (Frka et al, 2012; Ćosović, 1989; Ćosović, 1996; Ćosović et al , 2007; Ćosović et al, 2000; Ciglenečki et al, 1997; Bura-Nakić et al, 2009; Marguš et al , 2015). Electrochemical 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 platinum coil as the auxiliary electrode. A saturated solution of NaCl was added to the WSMA sample to adjust the ionic strength of 0.55 mol dm^{-3} electrolyte solution prior to the measurement. In the same samples the presence of reduced sulfur species based on acidification step (Ciglenečki and Ćosović, 1997; Bura-Nakić et al, 2009) was characterized by use of cathodic stripping voltammetry.

A sensitive high-temperature catalytic oxidation analyser TOC-VCPH (Shimadzu, Japan) with platinum-coated silica catalyst and a non-dispersive infrared detector for CO_2 measurements was used for WSOC measurements. The sample was acidified with 2 M HCl to pH 2–3 in order to eliminate inorganic carbonates. The concentration of TOC in each sample was calculated as an average of three to five replicates. The average MilliQ blank was found to be around 0.03 mg dm^{-3} with relative high reproducibility (1.6%). Normalized SAS concentration (SAS/WSOC) values were calculated by dividing the concentration of SASs in mg dm^{-3} as the equivalent amount of T-X-100 with the obtained WSOC content in mg dm^{-3} for a particular aerosol sample (Ćosović, 1989; Ćosović, 1996; Ćosović et al, 2007; Ćosović et al, 2000; Marguš et al, 2015). A high resolution, inductively coupled 226 plasma mass spectrometer (ICPMS, Element 2, Thermo Finnigan, Bremen, 227 Germany) was used for trace metal measurements.

RESULTS AND DISCUSSIONS

Our preliminary results indicate that SMLs were enriched with TOC and SAS on average 6.6 and 2.1 times respectively, if compared with ULW samples. Typical voltammetric curves recorded for SAS in aerosol,SML and ULW samples are presented in Figure 2. It is clearly visible by the recorded desorption peak between -1.2 and -1.4 V vs. Ag/AgCl that the same type of the SAS material is present in all studied samples, indicating the same or similar origin of the material. The contribution of dissolved organic carbon to the TOC pool was in the range from 53 to 97% for the SML samples. Concentrations of the aerosol mass in the collected samples fluctuated from around 2.5 to 18.2 $\mu g/m^3$. The average concentration (5.5 $\mu g/m^3$) is comparable to the $PM_{2.5}$ values presented for several regional background sites in Europe. Organic matter represents, on average, approximately 3.8% of the aerosol mass. The average organic carbon concentrations in this study are compared with those from other marine enviromnents over the world.

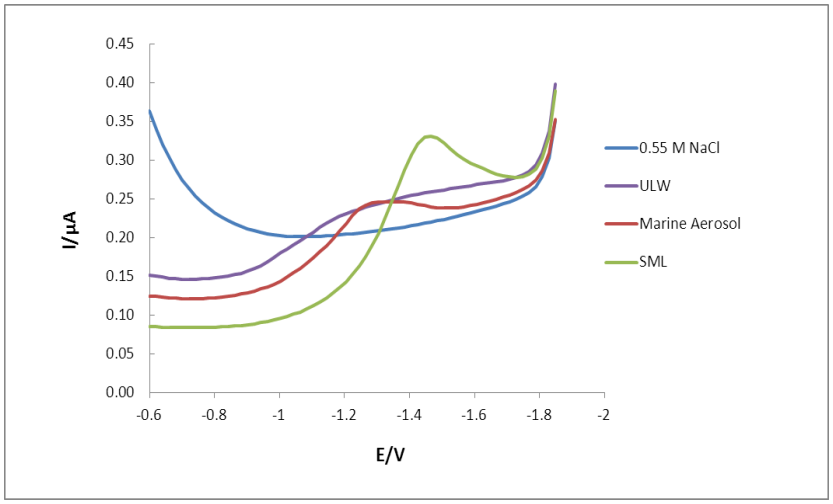

Figure 2. *AC voltammetric curves of aerosol, SML and ULW samples collected from Rogoznica Lake in winter 2015. Concentrations of WSOC and SAS were determined to be 11.48 and 0.344 mg/L in SML; 1.52 i 0.141 mg/L in ULW; and 4 and 0.262 mg/L in marine aerosols. Potential is measured in relation to an Ag/AgCl reference electrode.*

To get more insight to the seasonal variability of predominant surfactant material in the marine aerosols, the obtained SAS concentrations (expressed in equivalent amounts of model surfactant T-X-100, mg/L) were normalized to the dissolved organic carbon content and correlated with normalized surfactant activities obtained for different model organic compounds (Ćosović, 1989; Ćosović et al, 2007; Ćosović et al, 2000) . The SAS/DOC ratio for studied samples shows the dominant presence of a more hydrophilic material in the WSOC fraction of marine aerosol samples with relatively low SAS and DOC content in contrast to the strongly hydrophobic surfactant material recorded in urban aerosols (Vidović, 2014). Detected organic material can preferably be attributed to the so called »HULIS« type of material (Frka et al, 2012). The SAS/DOC ratio for Rogoznica Lake water column samples also shows the dominant presence of the hydrophilic material which can be attributed to humic substances and polysaccharide type of organic matter (Marguš et al, 2015) .

In studied winter WSMA samples as well as in SML and ULW, reduced sulfur species were not detected at higher concentration than 1 nM, which is the detection limit of the electrochemical method used. However after acidification treatment of the SML samples, recovery of the reduced sulfur species was found, indicating the presence of organosulfur compounds which hydrolises in the acidic solution. The same type of the organic material can be usually found in Rogoznica Lake during intensive phytoplankton activity (Ćosović et al, 2000; Marguš et al, 2015) .

Preliminary data on trace metal content in the winter Rogoznica Lake marine aerosols showed concentration of Fe, Pb, V, Ni, Mn, Cu, Cr, Se, As, Mo,Ag and Cd which are similar to trace metal composition and concentration in remote northern tropical Atlantic marine environment, as in the case study on the Cape Verde islands (Fomba et al, 2013). The recorded concentration of these metals is shown in Table I. It is important to emphasise that samples for trace metals were also collected on the glass fiber GF/F filters which showed increased blank concentration for Li, Be, Rb, U, Al, Ti, Zn, Sr and Ba. However blank concentrations for selected reported trace metals were in the acceptable range . In order to find the relation and difference for trace metal concentrations, primarily obtained for Gf/F filters, the summer and autumn sampling of Rogoznica Lake marine aerosols was performed both on glass and teflon filters. The results obtained are still in the process of evaluation and discussion.

Table 1. *Trace metals concentration in Rogoznica Lake aerosol samples*

Element	**Fe**	**Pb**	**V**	**Ni**	**Mn**	**Cu**	**Cr**	**Se**	**As**	**Mo**	**Ag**	**Cd**
ng/filter	**996**	**239**	**206**	**64,4**	**47,5**	**28,90**	**20,50**	**20,1**	**5**	**4,3**	**3,8**	**2,7**
ng/m3	**18,89**	**4,53**	**3,90**	**1,22**	**0,90**	**0.55**	**0,39**	**0,38**	**0,09**	**0,08**	**0,07**	**0,05**

CONCLUSIONS

Physico-chemical characterization of the water soluble marine aerosol (WSMA) fraction collected at the highly eutrophic marine lake Rogoznica lake on the Dalmatian Adriatic coast shows the presence of more hydrophilic material in the WSOC fraction in contrast to the strongly hydrophobic surfactant material recorded in urban aerosols. The presence of reduced sulfur species in winter aerosol, SML and ULW samples was not detected at higher concentration than 1nM by electrochemical methods. However, the existence of organosulfur species that are highly hydrolysable in acidic conditions is indicated. Preliminary data on trace metals content in the studied marine aerosols collected on the glass fiber filters show good comparable results for Fe, Pb, V, Ni, Mn, Cu, Cr, Se, As, Mo, Ag and Cd, which are similar to trace metal composition and concentrations in the remote northern tropical Atlantic marine environment. Increased blank concentrations were observed for Li, Be, Rb, U, Al, Ti, Zn, Sr and Ba, indicating that these metals cannot be measured on the glass fiber filters.

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REFERENCES

1. Aller M.I., Veale E.L., Linden A.M., Sandu C., Schwaninger M., Evans L.J., Korpi E.R., Mathie A., Wisden W., Brickley S.G. 2005. Modifying the subunit composition of TASK channels alters the modulation of a leak conductance in cerebellar granule neurons. J. of neuroscience. 25, 11455-11467.
2. Baker,A.R., Croot, P.L. 2010. Atmospheric and marine controls on aerosol iron solubility in seawater. Mar. Chem. 120, 4–13.
3. Bura-Nakić, E., Helz, G.R., Ciglenečki, I., Ćosović, B. 2009. Seasonal variations in reduced sulfur species in a stratified seawaterlake (Rogoznica Lake, Croatia): evidence for organic carriers of reactive sulfur. Geochim. et Cosmochim. Acta. 73, 3738-3751.
4. Ciglenečki, I., Janeković, I., Marguš M., Bura-Nakić, E., Carić, M., Ljubešić, Z., Batistić, M., Dupčić, I., Hrustić, E., Garić, R. 2015. The impacts of the extreme weather events on the eutrophicated seawater ecosystem (Rogoznica Lake, Adriatic coast), Cont. Shelf Res.108, 144–155.
5. Ciglenečki, I., Ćosović, B., 1997. Electrochemical Determination of Thiosulfate in Seawater in the Presence of Elemental Sulfur and Sulfide. Electroanalysis 9, 775-780.
6. Ćosović, B., Ciglenečki, I. 1996. Surface Active Substances in the Eastern Mediterranean. Croat. Chim. Acta. 70, 361-371.
7. Ćosović, B., Ciglenečki, I., Viličić, D., Ahel, M. 2000. Distribution and seasonal variability of organic matter in a small eutrophicated salt lake. Estuar. Coast. Shelf Sci. 51, 705-715.
8. Ćosović, B., Orlović-Leko, P., Kozarac, Z. 2007. Rainwater Dissolved Organic Carbon: Characterization of Surface Active Substances by Electrochemical Method. Electroanalysis 19, 2077-2084.
9. Ćosović, B., Vojvodić, V. 1989. Voltammetric analysis of surface active substances in natural seawater. Electroanalysis 10, 429–434.
10. Facchini, M. C., Mircea, M., Fuzzi, S., Charlson, R. J. 2001. Influence of Soluble Surfactant Properties on the Activation of Aerosol Particles Containing Inorganic Solute, J. Atmos. Sci. 58, 1465–1467.
11. Fomba,K.W., Muller,K., van Pinxteren,D., Herrmann, H. 2013. Aerosol size-resolved trace metal composition in remote northern tropical Atlantic marine environment: case study Cape Verde islands. Atmos. Chem. Phys. 13, 4801–4814.
12. Frka,S., Dautović, J., Kozarac,Z., Ćosović,B., Hoffer, A., Kiss, G. 2012. Surface-active substances in atmospheric aerosol: an electrochemical approach", Tellus B. 64, 18490-18502.
13. Frka,S., Pogorzelski,S., Kozarac,Z., Ćosović,B. 2012. Physicochemical signatures of natural sea films from Middle Adriatic stations. J. of Phys. Chem. A. 116, 6552-6559.
14. Gagosian, R.B., Peltzer, E.T., Zafiriou, O.C. 1981. Atmospheric transport of continentally-derived lipids to the tropical north Pacific. Nature (London) 291(5813):312-314, doi:10.1038/291312a0
15. Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L. 2009.The formation, properties and impact of secondary organic aerosol: current and emerging issues.« Atmos. Chem. and Phy. 9, 5155–5235.
16. Hawkins, L.N., Russell, L.M. 2010. Polysaccharides, Proteins, and Phytoplankton Fragments: Four Chemically Distinct Types of Marine Primary Organic Aerosol Classified by Single Particle Spectromicroscopy. Advances in Meteorology, Article ID 612132, doi10.1155/2010/612132
17. Jacobson, M.C., Hansson, H.C., Noone, K.J. and Charlson, R.J. 2000. Organic Atmospheric Aerosols: Review and State of the Science. Rev. Geophys. 38, 267–294.

18. Kuznetsova, I.M., Stepanenko, O.V., Turoverov, K.K., Staiano, M., Scognamiglio, V., Ross, M., D'Auria,S. 2005. Fluorescence Properties of Glutamine-Binding Protein from Escherichia coli and Its Complex with Glutamine. *Proteome Res.*, *4* (2), 417–423
19. Latif, M.T., Brimblecombe, B. 2004. Surfactants in atmospheric aerosols. Environ.Sci. & Techn. 38, 6501-6506.
20. Marguš, M., Morales-Reyes,I.,Bura-Nakić, E., Batina,N., Ciglenečki,I. 2015. Anoxic stress conditions explored at nanoscale by Atomic Force Microscopy in highly eutrophic marine environment, Continental Shelf Research 109, 24–34.
21. Vidović, K., Seasonal variation of organic matter properties of atmospheric aerosol over Zagreb, Diploma thesis, University of Zagreb, September 2014, in Croatian, Abstract in English.

2.7 CONCENTRATION AND SOURCE IDENTIFICATION OF PAHS IN GASEOUS AND PARTICULATE FRACTIONS IN SCHOOL ENVIRONMENT DURING HEATING SEASON IN SERBIA

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ABSTRACT

The indoor and outdoor PAH concentrations in total suspended particles (TSP), coarse (PM_{10}) and fine ($PM_{2.5}$) particles, as well as in the gas phase, are reported in this paper. Samples were collected during one week from December 2011 to April 2012, in seven educational institutions in different locations in Serbia. The average total PAH concentrations, including particle (TSP) and gas phases, in educational institutions ranged from 152.76 to 1024.94 ng/m^3 outdoors, and from 133.83 to 973.44 ng/m^3 indoors. Significant differences in the gas/particle partition of PAHs were found between indoor and outdoor air samples. The PAHs diagnostic ratios for gas phase are clearly different than those calculated for PM samples. Diagnostic ratios in combination with PCA indicated that traffic emission and coal combustion were the predominant sources for indoor and outdoor PAHs pollution in Serbian schools during heating season.

INTRODUCTION

European Union (EU) legislation requires the measurement of a number of harmful pollutants, including Polycyclic Aromatic Hydrocarbons (PAHs). Many studies have shown that PAHs have direct impact on human health (Ravindra et al, 2008; Lee et al, 2010). Human exposure to air pollution is dominated by indoor air pollution, which is partly outdoor air pollution that has penetrated indoors and partly pollution from indoor sources. The importance of conducting simultaneous indoor and outdoor measurements emerged, because people spend more than 90% of their time indoors. Indoor air quality is becoming an important issue in recent decades due to its contribution to human health (Mentese et al, 2015; Jantunen et al, 1998). Children are more susceptible to air pollutants than adults and air quality in schools is of great importance for children`s health. Indoor air quality problems in schools may be even more serious than in other categories of buildings, due to higher occupant density and insufficient outside air supply, aggravated by frequent poor construction and/or maintenance of school buildings (Almeida et al, 2011; EPA, 2010).

The main objectives of this work include: investigate the levels of PAHs during the heating season in Serbian schools; their distribution between particulate matter, to be precise between TSP, PM_{10} and $PM_{2.5}$; their partition between the gas and particle-bound phases and identification of sources using the diagnostic ratios and principal component analysis.

METHODOLOGY

Total suspended particles (TSP), coarse (PM_{10}) and fine ($PM_{2.5}$) particles were collected in the indoor air of classrooms of educational buildings and simultaneously in outdoor air in front of the windows on a balcony during December 2011 and April 2012 in Serbia. Seven sampling sites (five primary schools and two kindergartens) were selected to match different types of locations (Fig. 1). One school and one kindergarten (S1 and K1) were located in Belgrade, in a densely populated residential area. All other schools were located in the eastern part of Serbia, close to Bulgarian border. School S3 and kindergarten K2 are located in Bor town, about 1 km from a Copper Smelter Complex. The school S4 is located in Zajećar, next to a high traffic density street in the central zone of the town. Schools S2 and S5 were located in villages close to Bor and Zajećar, in an area of low population density.

The sampling campaigns were conducted simultaneously indoors and outdoors during one week successively in each school in the heating season. Samples were collected using the low volume sampler Sven/LACKEL LVS3 for 24h period. The 16 EPA priority PAHs were quantified in the particulate matter collected on quartz filter (Whatman QMA, 47 mm), and those in the gas phase were collected on polyurethane foam (PUF). The sampling flow rate was 2.3 m^3/h. Before sampling, the PUF plugs were cleaned by extracting them in a Soxhlet with acetone (8 h) and 1:5 mixture of diethylether/hexane (16 h), and filters were baked at 900°C for 4 h to remove organic compounds and reduce blank values.

PAH compounds, namely naphthalene (Nap), acenaphthylene (Ace), acenaphthene (Ane), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benz[a]anthracene (BaA), chrysene (Chy), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenz[a,h]anthracene (DbA), benzo[g,h,i]perylene (BgP) and indeno[1,2,3-cd]pyrene (InP) were analyzed using gas chromatography–mass spectrometry (GC–MS) following the TO-13A method [US EPA TO-13A, 1999] with a DB-5 MS capillary column (30 m x 0.25 mm x 25 μm). The oven temperature program started at 70°C (held 4 minutes), ramp 8°C/min till 310°C (hold 5 minutes). Solvent delay was 5 minutes and time of run was 46 minutes.

The calibration curves for the all 16 PAHs were obtained by spiking seven known quantities of substances, all with an R^2 of the calibration curve above 0.995. Method quantification limit for all PAHs was 0.02 ng/m^3. The detection limits were expressed as 3 times the mean blank concentration.

Diagnostic ratios were calculated to investigate the possible origins of the PAHs. Principal component analysis was also performed to identify the relationships between the determined PAHs, in order to enhance the accuracy of emission source identification. The analysis was carried out using the SPSS 13.0 software.

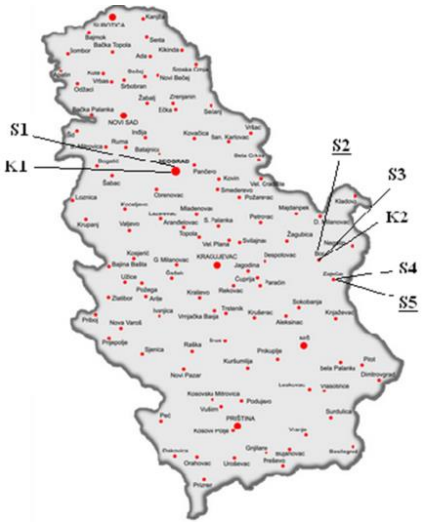

Figure 1. *Map of the Republic of Serbia with the sampling sites marked.*

RESULTS AND DISCUSSION

The average total concentrations of 16 PAHs (sum of particle (TSP) and gas phase PAHs), in educational institutions, ranged from 152.76 to 1024.94 ng/m^3 outdoors, and from 133.83 to 973.44 ng/m^3 indoors (Fig. 2).

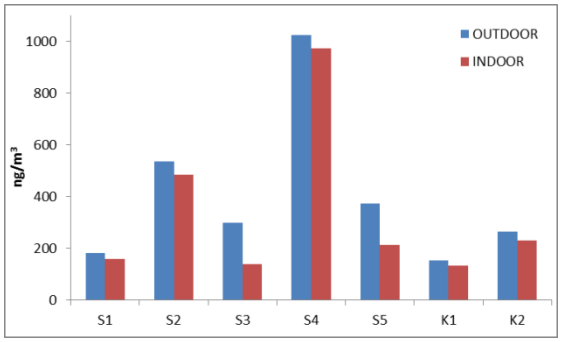

Figure 2. *The average total outdoor and indoor concentrations of 16 PAHs in educational buildings.*

The highest indoor and outdoor concentrations of PAHs, occurred in school S4. The values of individual PAHs at school S4 were higher than in the other schools, mainly due to the high emissions from the traffic and coal-burning boilers for individual heating, because the school is located next to a high traffic density street in the city

centre. The terrace with the outdoor air sampler was located directly above the street at about 3 m above ground level. The location is directly influenced by traffic emissions. There is a large number of coal combustion boilers for domestic heating, which contributes to air pollution level in the winter. In this school the highest presence of 5 and 6 rings PAHs was observed, which are usually asociated with vehicle emission.

The highest total PAH values were associated with the low and medium molecular weight PAHs (with 2,3 and 4 rings) for both indoor and outdoor (Fig. 3). Figure 4 shows an example of PAHs distribution between TSP and gas-phase and particulate fractions in school S4. The distribution is similar in other schools. The volatile PAHs (2 and 3 ring) were most abundant at all schools in the gas phase, both indoor and outdoor, and they are not detected in the particulate-bound phase. These PAHs, which were associated in the gas phase, represent more than 80% of the total of all PAHs, both indoor and outdoor (Fig. 4). Most of the I/O ratios were less than 1.0 which indicated that the indoor PAHs were mostly from outdoor sources, except in schools S4 and S2, for Flu, Phe and Fla (Fig. 3). Higher outdoor PAHs levels were observed probably because of emission from heating combustion sources. The highest outdoor concentration of naphthalene was in school S3. Nap was dominant in outdoor air and it was primarily dominated in industrial flue gases and could be a tracer for industrial combustion (Ravindra et al, 2008). The 4-ring PAHs (Fla, Pyr, BaA and Chy) were present in both phases, while Fla and Pyr were most abundant in gas the phase. They are probably associated with coal combustion (Xie et al 2009).

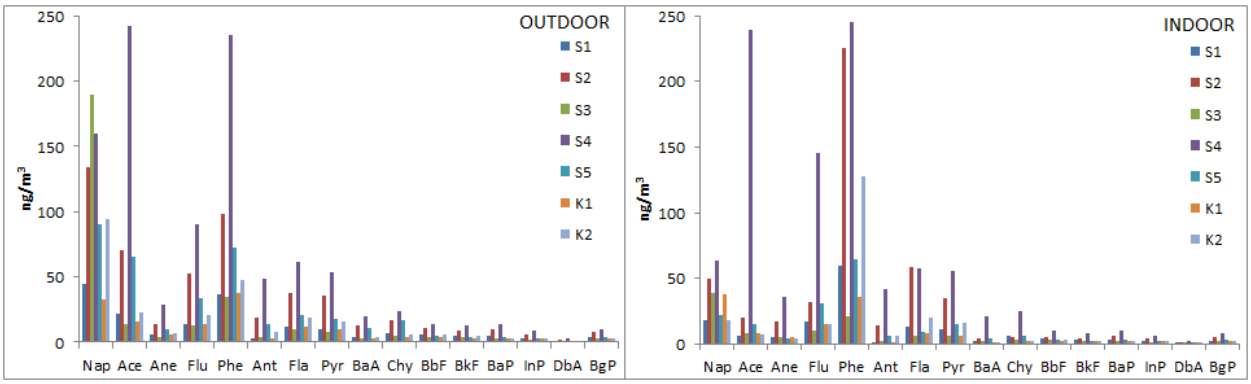

Figure 3. *The total outdoor and indoor values of individual PAHs in educational buildings.*

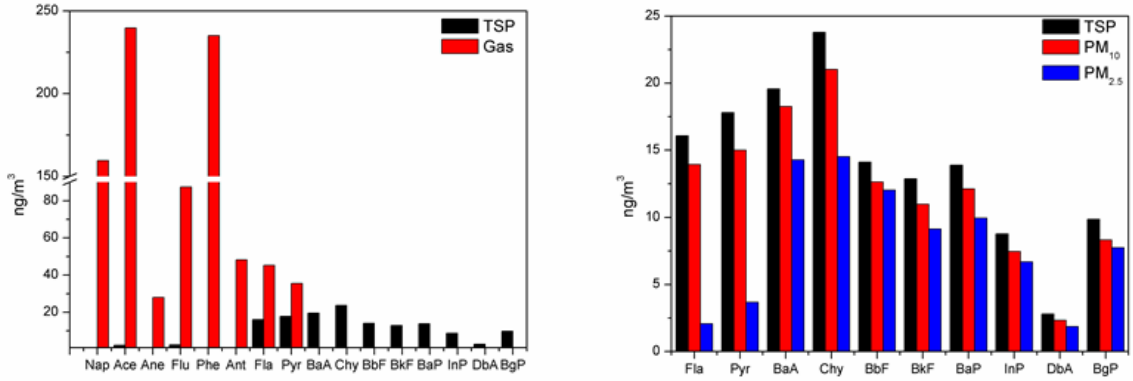

Figure 4. *Distribution of outdoor PAHs between TSP and gas-phase (left) and particulate fractions (right) in school S4.*

Diagnostic ratio (DR) combined with principal component analysis (PCA) were used to identify the origin of outdoor PAHs. In this study, diagnostic ratios were calculated between outdoor gas- and particulate-bound phases of PAHs (Table 1). As the distribution of PAHs between the particle phases was similar in all schools (Fig. 4), the DR is calculated only for the TSP fraction. There are differences when gas and particulate-bound phase are considered separately (Fig. 5).

Table 1. *Diagnostic ratios of PAHs in gas, TSP and total (sum of gas and TSP PAHs) phases*

School	Phase	ΣCOMB/ΣPAHs	Flu/(Flu+Pyr)	Ant/(Ant+Phe)	Fla/(Fla+Pyr)	BaA/(BaA+Chy)
S1	Gas	0.13	0.65	0.08	0.56	0.33
	TSP	0.92	0.13	0.18	0.48	0.40
	Total	0.30	0.59	0.08	0.55	0.40
S2	Gas	0.12	0.68	0.16	0.54	0.39
	TSP	0.94	0.13	0.17	0.46	0.43
	Total	0.27	0.60	0.16	0.52	0.43
S3	Gas	0.05	0.71	0.10	0.60	0.50
	TSP	0.91	0.09	0.26	0.46	0.36
	Total	0.13	0.62	0.10	0.56	0.36
S4	Gas	0.94	0.13	0.43	0.47	0.45
	TSP	0.94	0.13	0.43	0.47	0.45
	Total	0.21	0.63	0.17	0.54	0.45
S5	Gas	0.15	0.68	0.16	0.54	0.37
	TSP	0.94	0.17	0.15	0.47	0.45
	Total	0.23	0.65	0.16	0.53	0.40
K1	Gas	0.16	0.62	0.07	0.56	0.33
	TSP	0.92	0.11	0.18	0.47	0.39
	Total	0.28	0.59	0.07	0.55	0.38
K2	Gas	0.14	0.59	0.15	0.54	0.40
	TSP	0.94	0.19	0.27	0.46	0.38
	Total	0.24	0.56	0.15	0.53	0.38

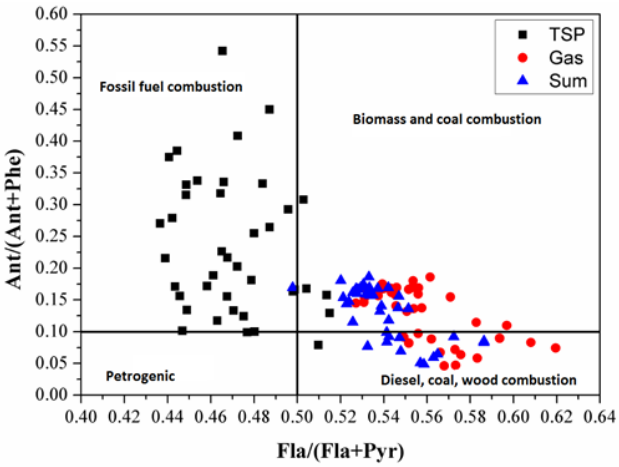

Figure 5. *Distribution of outdoor PAHs between TSP and gas-phase (left) and particulate fractions (right) in school S4.*

The ratios of combustion PAHs to the total PAHs (CPAH/ΣPAH) were higher in particulate-bound phase. These values were close to 1 for particulate-bound phases, which indicated that coal combustion was a potential source of particulate-bound PAHs (Tobiszewski and Namiesnik, 2012). The Flu/(Flu+Pyr) ratios were determined to be < 0.5 at all sampling sites in the particulate-bound phase, which were similar to the values for petrol emissions and this ratio for total and gas phase was > 0.5 at all sites indicated diesel emissions (Tobiszewski and

Namiesnik, 2012). The Ant/(Ant+Phe) ratio higher than 0.1 was associated with combustion processes (Tobiszewski). This ratio was higher for the particulate-bound phase. Similar values were obtained for gas and particulate-bound phases for Fla/(Fla+Pyr) ratio (Tobiszewski, Muendo). The values of BaA/(BaA+Chy) ratio indicated mixedsources of traffic emissions and coal/wood combustion at all sites (Tobiszewski and Namiesnik, 2012; Muendo et al, 2006).

Table 2 shows results of PCA analysis for different outdoor sites and factors with their factor loadings for the individual sum of gas and particulate-bound phase PAHs. The principal components with eigenvalues higher than 1 have been selected. The first factor is responsible for more than 80 % of the total variance, and this factor is heavily weighted by almost all PAHs for schools S2, S3, S5 and kindergarten K1. This seems to be related to mixed sources, which cannot be clearly separated. The first factor has a high loading of BbF, BkF, BaP, InD and BgP, which indicates gasoline emissions in schools S2, S3 and S5 (Ravindra et al, 2008). Also, the high loading of Nap and 3-rings PAHs for first factor indicated traffic emission (both diesel and gasoline) for schools S2, S3, S4 and S5, and kindergarten K2 (Guo et al, 2003; Khalili et al, 1995; Park et al, 2002). The second factor with high loadings factors for 3 and 4-rings PAHs for schools S1 and S4 can be related to coal combustion (Ravindra et al, 2008). Fla and Pyr have been associated with domestic fuel burning. High loadings for Nap and Ace can indicate wood burning and oil fumes (Masih et al, 2012).

Table 2. *VARIMAW-rotated factor loadings of outdoor PAHs (gas+particle) in the PCA.*

PAHs	S1			S2		S3		S4		S5		K1			K2		
	PC1	PC2	PC3	PC1	PC2	PC1	PC2	PC1	PC2	PC1	PC2	PC1	PC2	PC3	PC1	PC2	PC3
Nap			0.948	0.976			0.969		0.880					0.969	-0.816		
Ace		0.852		0.984			0.984	0.776		0.938		0.919					-0.751
Ane		0.852		0.726		0.783		0.956		0.974			0.988		0.776		
Flu		0.975		0.863		0.898		0.943		0.974			0.805		0.935		
Phe		0.880		0.830		0.904			0.812	0.957		0.893			0.789		
Ant		0.870		0.882		0.875			0.727	0.917		0.976			0.971		
Fla		0.927			0.985	0.997			0.785	0.973		0.902			0.960		
Pyr		0.913			0.957	0.981			0.763	0.982		0.931			0.964		
BaA	0.763			0.917		0.751		0.898			0.973	0.889					-0.833
Chy	0.762			0.913		0.791		0.915			0.964	0.710				-0.894	
BbF	0.947			0.915		0.914		0.881		0.980			0.740				0.844
BkF	0.930			0.909			0.763	0.851		0.899		0.824				0.704	
BaP	0.926			0.949		0.730		0.861		0.976		0.867				0.974	
InP	0.922			0.919		0.877		0.785		0.982		0.747				0.842	
BgP	0.917			0.913		0.841		0.701		0.980		0.725				0.906	
DbA	0.800			0.875		0.856		0.919		0.914		0.762				0.785	
Eigenvalue	12,437	2,172	1,076	13,669	1,720	14,305	1,601	13,015	1,744	11,387	1,269	13,069	1,452	1,281	8,644	3,847	2,570
Variance (%)	77,729	13,573	6,724	85,430	10,751	89,407	10,009	81,341	10,899	85,353	14,182	81,684	9,077	8,005	54,027	24,043	16,062
Cumulative (%)	77,729	91,302	98,025	85,430	96,181	89,407	99,416	81,341	92,240	85,353	94,134	81,684	90,761	98,766	54,027	78,069	94,132

CONCLUSIONS

Significant differences in the gas/particle partition of PAHs were found for both indoor and outdoor air samples. The PAH diagnostic ratios for gas phase are clearly different than those calculated for TSP samples. Because of this, the total (gas+particle) concentrations of atmospheric PAHs were used to calculate the diagnostic ratios and PCA analysis. Diagnostic ratios and PCA showed that the studied schools were different. Diagnostic ratios in combination with PCA indicated that traffic emission and coal combustion were the predominant source for outdoor PAHs pollution in Serbian schools during the heating season. The results from this study will help a better understanding ambient environmental sources of PAHs and also provide helpful information about the environmental levels of these harmful substances in schools in Serbia.

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REFERENCES

1. Almeida, S.M., Canha, N., Silva, A., Freitas, M.C., Pegas, P., Alves, C., Evtyugina, M., Pio, C.A., 2011. Children exposure to air particulate matter in indoor of Lisbon primary schools. Atmospheric Environment, 45, 40, 7594-7599.
2. Guo, H., Lee, S.C., Ho, K.M., Zou, S.C., 2003. Particle-associated polycyclic aromatic hydrocarbons in urban air of Hong Kong. Atmos. Environ., 37, 5307-5317.
3. Jantunen, M. J., Hanninen, O., Katsouyanni, K., Knoppel, H., Kuenzli, N., Lebret, E., Zmirou, D., 1998. Air pollution exposure in European cities: The" EXPOLIS" study. Journal of Exposure Analysis and Environmental Epidemiology, 8, 4, 495-518.
4. Khalili, N.rR., Scheff, P.A., Holsen, T.M., 1995. PAH source fingerprints for coke ovens, diesel and, gasoline engines, highway tunnels, and wood combustion emissions. Atmos. Environ., 29, 533-542.
5. Lee, B.K., Vu, V.T., 2010. Sources, Distribution and Toxicity of Polyaromatic Hydrocarbons (PAHs) in Particulate Matter, Air Pollution, Vanda Villanyi (Ed.), InTech, ISBN: 978-953-307-143-5
6. Masih, J., Singhvi, R., Kumar, K., Jain, V.K., Taneja, A., 2012. Seasonal variation and sources of polycyclic aromatic hydrocarbons (PAHs) in indoor and outdoor air in a semi arid tract of Northern India. Aerosol and Air Quality Research, 12, 515-525.
7. Mentese, S., Mirici, N.A., Otkun, M.T., Bakar, C., Palaz, E., Tasdibi, D., Cevizci, S., Cotuker, O., 2015. Association between respiratory health and indoor air pollution exposure in Canakkale, Turkey, Building and Environment 93, 72-83.
8. Muendo , M., Hanai , Y., Kameda, Y., Masunaga, S., 2006. Polycyclic Aromatic Hydrocarbons in Urban Air: Concentration Levels, Patterns, and Source Analysis in Nairobi, Kenya. Environmental Forensics, 7, 147-157.
9. Park, S.S., Kim, Y.J., Kang, C.H., 2002. Atmospheric polycyclic aromatic hydrocarbons in Seoul, Korea. Atmos. Environ., 36, 2917-2924.
10. Ravindra, K., Sokhi, R., Van Grieken, R., 2008. Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation. Atm.Environ., 42, 2895-2921
11. Tobiszewski, M., Namiesnik, J., 2012. PAH diagnostic ratios for the identification of pollution emission sources. Environ. Pollut., 162, 110-119.
12. Unites States Environmental Protection Agency (EPA), 2010. Managing Asthma in the School Environment - Indoor air quality tools for schools, 2010, available from http://www.epa.gov/iaq/schools
13. US EPA TO-13A, 1999. Determination of polycyclic aromatic hydrocarbons (PAHs) in ambient air using gas chromatography/mass spectrometry (GC/MS). In “Compendium of Method for the Determination of Toxic Organic Compounds in Ambient Air”, 2nd edition, EPA/625/R-96/010b, Centre for Environmental Research Information, US Environmental Protection Agency, OH
14. Xie, M., Wang, G., Hu, S., Han, Q., Xu, Y., Gao, Z., 2009. Aliphatic alkanes and polycyclic aromatic hydrocarbons in atmospheric PM10 aerisils from Baoji, China: Implications for coal burning,. Atmos. Res., 93, 840-848.

2.8 UPGRADE OF MICRO-SCALE SITING OF AIRBORNE TOXIC ELEMENTS BY MOSS BAG TECHNIQUE: CROSSROAD, TWO- AND ONE-LANE STREET STUDY

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ABSTRACT

Database of potentially hazardous substances, necessary for estimation of human exposure to air pollutants, is principally deficient because of a limited number of regulatory monitoring stations. In this study, the moss bags were exposed at 48 crossroads, two- and one-lane streets across the city of Belgrade (Serbia) for 10 weeks during the summer of 2014. During the experimental period, traffic flows were estimated at each site by vehicles counting during the rush hours. The concentrations of 39 elements were determined in the moss samples. The most enriched elements were Sb, Cu, and Cr. For the majority of elements, the moss bags identified a common pattern of decrease in the concentration from the crossroad to the one-lane street. A significant correlation (r = 0.65 – 0.70) between the moss concentration of Sb, Cu, and Cr, and traffic flows makes these elements reliable traffic tracers.

INTRODUCTION

Transport sector represents dominant source of air pollution in urban areas. Traffic-related air pollutants, that include particulate matter (PM) associated with toxic elements, are widespread. These pollutants can often be locally-elevated close to urban microenvironments such as major roads, crossroads, junctions, and bus stations. Exceedances in the limit values of the air pollutants have been associated with many hazardous health effects (e.g., EEA, 2013). Epidemiological studies commonly utilise data from one or few stations of regulatory monitoring network to estimate personal exposure to PM air pollution (Brauer, 2010). However, recent research has indicated that monitoring stations may not accurately characterize complexities of the PM spatial dispersion across an urban area (Brauer, 2010). Regulatory network of air quality monitoring have been typically designed to assess regional and temporal air pollution variability. Specifically, for micro-scale siting, sampling sites should be placed at least 25 m from the edge of crossroads and not on the carriageways of roads (Directive 2004/104/EC, Directive 2008/50/EC). Thus, testing of long-term on-road exposure of pedestrians, commuters, cyclists, and workers (e.g., drivers, policemen) to traffic-related toxic elements requires alternative approaches (Brauer, 2010).

Over the past several decades, biomonitoring has been developed as a valuable tool for assessing environmental pollution. Biomonitoring represents usage of living organisms (plants, animals) as a measure of environmental quality. Among the terrestrial organisms employed as plant biomonitors, mosses have been proven as reliable biomonitors of air quality due to their morpho-physiological characteristic. Moss lacks a developed root system and thus obtains nutrients from air. In addition, a high cation-exchange capacity of moss increases adsorbent efficiency (Brown and Bates, 1990). Between the two types of moss biomonitoring, passive (using naturally growing mosses in a certain area) and active (using moss transplants), the active approach has been applied for studies in anthropogenically devastated areas, such as industrial and urban, where naturally growing mosses are scarce or even absent. Since the early work of Goodman and Roberts (1971), the “moss bag technique” was introduced as a method of active moss biomonitoring. The technique involves exposure of anthropogenically unpolluted moss material within mesh bags for monitoring of the presence of pollutants in ambient air, and has been tested in different environments (Aničić et al, 2009a; Ares et al, 2012; Vuković et al, 2013). The moss bag technique gives a reliable picture of pollution patterns in a much more cost-effective way than regulatory monitoring devices, which could not provide dense monitoring network, and also require power supply and maintenance. It also integrates air pollutant levels over longer period than most of instrumental measurements do. Long-period sampling is prerequisite for assessment of cumulative exposure to a certain pollutant, which has hazardous impact on human health.

The purpose of this study was to assess a level of airborne toxic elements close to highly traffic-burdened crossroads, two- and one-lane streets using the moss bag technique. We hypothesized that distance-decline of the

toxic element concentrations exists from crossroads to two- and one-lane streets depending on the traffic burden. The aim was also to assess if the moss bags could reflect this phenomenon.

METHODOLOGY

Moss Bag Preparation

The moss *Sphagnum girgensohnii* Russow was collected from a pristine wetland area located near Dubna, Russia. This area is pronounced to be an appropriate background site in our previous research (Aničić et al, 2009a; 2009b). In the laboratory, the green apical parts of the moss was separated from the rest brown tissue and carefully manually cleaned of soil particles, plant remains, and epiphytes. Subsequently, it was rinsed three times with double-distilled water. Such prepared moss was air-dried and gently hand-mixed to obtain homogeneous material. Approximately 1.5 g of the moss was packed loosely in 7 × 7 cm nylon net bags with 2-mm mesh size. For determination of the moss element content before the bag exposure (initial concentrations), several moss bags were stored at room temperature in the laboratory conditions.

Experimental Set-up and Traffic Flow Estimation

The moss bags were exposed for 10 weeks using plasticized aluminium holders, specifically designed for this purpose. The holders were mounted perpendicular to the lampposts, at open space, at the representative height of 3 – 4 m (Vuković et al, 2013). The holders with moss bags were exposed at 48 sampling sites across the city of Belgrade urban area (44^0 50'- $44^0$44'N, and $20^0$22' - $20^0$32'E at 70 - 250 m altitude) from June 15th to August 15th, 2014. The sets of 3 sampling sites – crossroad, two- and one-lane street, away from each other approximately 300 m, were selected. Three pedestrian zones were chosen to represent urban background sites. The sites were selected in different parts of the city: urban-central and peri-urban zone, and within an urban forest. In addition, for each study site, traffic flows were recorded by video cameras for later off-site counting. The vehicle fleet were classified into categories of passenger cars, buses, trams, trolleys, motorcycles, light and heavy duty vehicles. Traffic flows of each vehicle category were counted for 15 minutes during the rush hours (7:00 – 9:00 am and 4:00 – 6:00 pm) on Wednesday and Sunday in June and July. The average traffic flows during the experimental period were estimated from these counts, using a recommended procedure by the Secretariat for Transport of Belgrade (*personal communication*).

Chemical Analyses

After exposure period, the moss samples were air-dried and homogenised. Approximately 0.3 g of each moss sample (3 subsamples per exposure site) was digested for 45 min in a microwave digester (ETHOS 1, Advanced Microwave Digestion System, Milestone, Italy), at 200°C, with 1 mL of 30% H_2O_2 (Sigma Aldrich, puriss. p.a.) and 7 mL of 65% HNO_3 (Sigma Aldrich, puriss. p.a., distilled by the apparatus for acid distillation – BERGHOF, Products+ Instruments GmbH, Germany). Digested samples were diluted with double-distilled water to a total volume of 50 mL. The concentrations of Al, B, Ba, Cu, Fe, and Zn were determined using inductively coupled plasma-optical emission spectroscopy, ICP-OES (Thermo Scientific iCAP 6500 Duo, Thermo Scientific, UK). The concentrations of As, Cd, Ce, Co, Cr, Dy, Er, Eu, Ga, Gd, Ho, La, Li, Lu, Nd, Ni, Pb, Pr, Pt, Rb, Sb, Sc, Sm, Sn, Sr, Tb, Th, Ti, Tl, Tm, V, Y, and Yb were determined using inductively coupled plasma-mass spectrometry, ICP-MS (Thermo Scientific iCAP Q, Thermo Scientific, UK). To control the quality of the element analysis, the control samples, certified reference materials and analytical blanks, were analysed once every 10 samples. As the certified reference materials, the moss *Pleurozium schreberi*, M2 and M3 (Steinnes et al, 1997) was used.

Data Processing

To assess the element enrichment of the studied moss species, relative accumulation factor (RAF) was calculated based on the moss content of each element after exposure ($C_{exposed}$) reduced and then divided by the element content before moss exposure ($C_{initial}$):

$$RAF = (C_{exposed} - C_{initial})/C_{initial}$$

The data were processed using STATISTICA 8.0 (StatSoft, Inc., Tulsa, OK, USA). The normality of the data was tested by Shapiro-Wilk test ($p < 0.05$). Spearman's correlation was applied ($p < 0.05$) to determine the correlation between the moss elemental concentrations and the traffic flows. To represent graphically abundances of the rare earth elements (REE), concentrations of the REE observed in the moss samples were normalised to those in

different standards North American Shale Composite (NASC) and Post-Archean Australian Shales (PAAS) (Dołęgowska and Migaszewski, 2013).

RESULTS AND DISCUSSION

Spatial Gradient of Moss Element Content: Crossroad, Two- and One-Lane Street

Moss bag technique enables a longer sampling period of airborne pollutants such as toxic elements and better spatio-temporal resolution of sampling sites. These advantages could provide characterization of long-term human exposure to toxic elements, which is more accurate and relevant in the assessment of chronic health effects than daily instrumental measurements. In this study, the concentrations of the most elements in the exposed moss bags of *S. girgensohnii* were above the initial element concentrations in the moss. Markedly high RAF values of Sb, Sn, Sm, Cu, Cr, and Zn (Table 1) in the moss samples imply significantly elevated concentrations of these elements within on-road microenvironments. Moreover, at the crossroads, Pt, which naturally occurs in very low concentrations in mosses, was markedly enriched. Thus far, concerning the moss bag technique application, Pt has only been observed in the moss bags exposed within a road tunnel (Zechmeister et al, 2006) and very scarcely in ambient air in the proximity of bus lines (Rivera et al, 2011).

Table 1. *RAF values in the S. girgensohnii moss bags exposed at sites with different traffic intensity: crossroad, two- and one-lane street, for 10 weeks*

RAF	Element
0 - 5	Al, B, Ba, Co, Dy, Mg, Sr, Tl, Y
5 - 10	As, Cd, Ce, Er, Eu, Fe, Ga, Gd, Ho, La, Lu, Nd, Ni, Pb, Pr, Pt, Sc, Tb, Ti, Tm, Yb
10 - 30	Th, V, Cr, Zn
> 30	Cu, Sb, Sm, Sn

The *S. girgensohnii* moss bags indicated spatial variability in the concentrations of the majority of determined elements. Particularly, concentration gradient of As, Ba, Co, Cu, Cr, Ni, Sb, and V in the moss samples (Fig 1) clearly emphasizes the crossroads as pollution hotspots where pedestrians and commuters are likely to be exposed to highly increased level of toxic elements. At crossroads, a pattern of braking and accelerating driving mode, so called "stop and go", is especially conspicuous. In comparison to constant free-flowing traffic mode, which characterised two- and one-lane streets, "stop and go" mode leads to elevated pollutant emissions from both, exhaust and non-exhaust traffic source (Tsai et al, 2003).

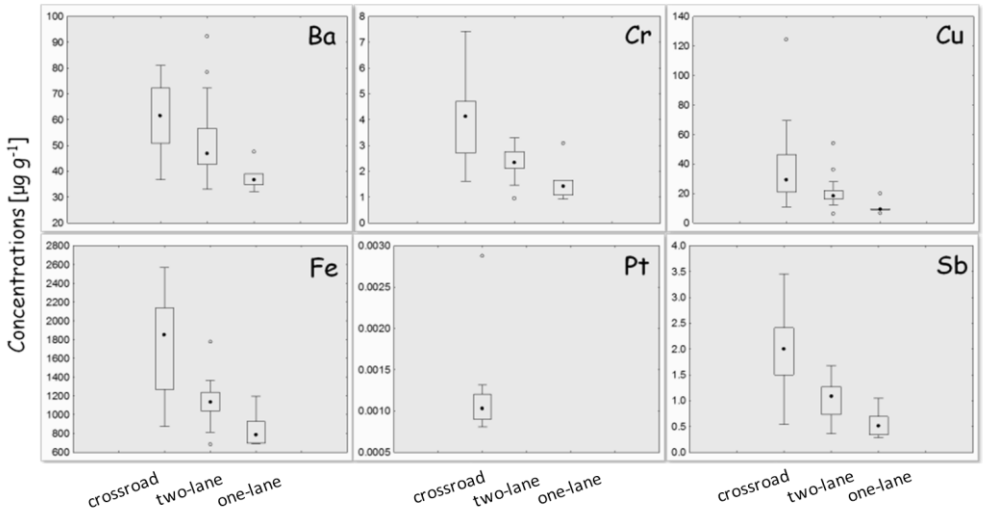

Figure 1. *Concentrations (µg g^{-1}) of Ba, Cr, Cu, Fe, Pt, and Sb in the S. girgensohnii moss bags; * Pt was only detected at the crossroads*

The decrease in the moss shale-normalized concentration of the REE (Figure 2) confirms spatial dependence of these elements on anthropogenic activities, i.e., vehicle movements. Similar order of abundance of the REE was identified, just as it has been pointed out in our previous study (Vuković et al, 2015b). This confirms consistent signature of REE in urban area.

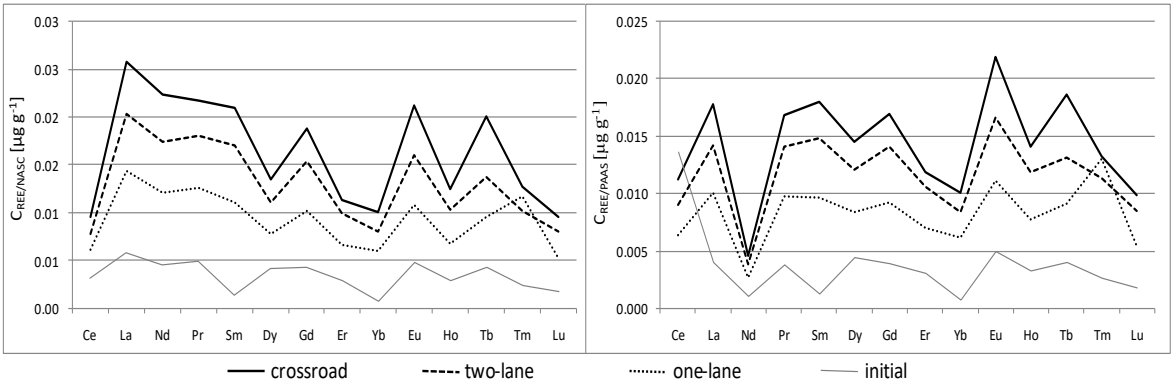

Figure 2. *The median concentrations (µg g^{-1}) of the REE normalized to NASC and PAAS in the S. girgensohnii moss bags exposed at sites with different traffic flows: crossroad, two- and one-lane street; initial – element concentrations in the unexposed moss; the REE order on the x-axis is chosen according to their abundances in the NASC and PAAS.*

The results draw attention for better spatial resolution of regulatory monitoring sites from which data are usually used in epidemiological studies. Note that permitted levels of emission of Cu, Sb, Cr, Pt and rare earth elements such as Sm, in the air has not been regulated yet by legislation (Directive 2004/107/EC), although these elements are recognized as toxic by WHO (2013).

Correlation between Moss Element Concentration and Traffic Flow

Based on the high correlation coefficients ($r > 0.80$) among Ba, Cr, Cu, Fe, Ni, Sb, and V in the moss samples, the common sources of these elements can be assumed. The vehicle movements cause: (i) exhaust emissions from the tailpipe; (ii) non-exhaust emissions due to wear and tear of vehicle parts such as brake, tyre and clutch; and (iii) re-suspension of road dust. Non-exhaust emissions mainly contribute to increased concentrations of Ba, Fe, Cu, and Sb (Gietl et al, 2010) while fuel combustion is the major source of Cr, Ni, V, and Cu (EMEP/EEA, 2013). Given the moderate, but significant correlation coefficient ($r = 0.65 – 0.70$, $p < 0.05$) between the total traffic flows and the concentrations of Cr, Cu, Fe, and Sb in the moss bag samples, these elements could be considered as reliable tracers of traffic-related emissions. Our results support previous findings from the road traffic studies using both terrestrial mosses and moss bags biomonitors (Zechmeister et al, 2005) in which Cr, Cu, Fe, and Sb have been identified to be traffic-originated. Regarding the categories of vehicles, the significant correlation coefficient ($r > 0.60$, $p < 0.05$) implies tight relation between the flows of passenger cars and light duty vehicles, and the moss element concentrations of Cr, Cu, Fe, and Sb. This is in agreement with the results previously pronounced for the correlation between the flows of light duty vehicles and concentrations of Cu and Fe in the moss samples (Adamo et al, 2011). Zinc has often been reported as one of the tracers for non-exhaust traffic emissions, e.g., tire-wear emissions of Zn are shown to be approximately 1000 and 500 times higher than those of Pb and Cu, respectively (Napier et al, 2008). Nevertheless, in this study, very low correlation coefficients ($r < 0.20$) were obtained between the moss concentrations of Zn and traffic flows. A distinct spatial variability, which is dependent on traffic flow, was not observed. In addition, in our previous studies (Vuković et al, 2013; Vuković et al, 2015a), there was no regularity in the Zn spatial distribution, related to traffic flow at the study sites. Considering the high RAF values obtained for Zn in this study along with the absence of any other pollution source except traffic, the Zn origin could be assumed as traffic-related. However, Zn could not be considered as reliable tracer of traffic flow variability within urban area.

Could Pedestrian Zones Be Considered as an Urban Background?

It was hypothesized that significantly lower moss element content would be obtained at the control sites in comparison with the remaining on-road sampling sites. However, the markedly elevated concentrations of the majority of elements were determined in the moss bags exposed in the central pedestrian zone. Specifically,

markedly high concentration of Cu was found in this pedestrian zone, which is in accordance with the results of our previous studies (Vuković et al, 2015a; Aničić et al, 2009c). Elevated Cu concentrations was also previously pronounced for the same pedestrian zone in the research related to the usage of the tree leaf biomonitors (Aničić et al, 2011) and the bulk deposition collectors (Mijić et al, 2010). Thus, the marked Cu moss enrichment in this study could not be considered as an accidental case. The moss element content indicated that the second pedestrian zone, situated in peri-urban area, was less polluted than the central pedestrian zone. Finally, the third control site was in the biggest urban forest zone, and since the lowest element content was obtained in the moss bags exposed there, it proved to be the cleanest ambient within the city. According to our findings, control sites should be chosen with caution in experimental set-up in urban areas in regards with its position. The sampling sites situated in green urban niches could be recommended as appropriate for the assessment of the urban background levels of air pollutants.

CONCLUSIONS

The *S. girgensohnii* moss bag biomonitoring has outlined distinct spatial decline in the airborne toxic element content along crossroads, two- and one-lane streets. This result points to a need for monitoring and better characterization of micro-scale siting of toxic element distribution. Moss bag technique represents a suitable approach to achieve this goal given by simplicity and cost-effectiveness of its performing. Combined use of moss bag technique and regulatory instrumental measurements could enable dense spatial coverage and consequently, larger database of air pollutant concentrations. In addition, the results marked Sb, Cu, and Cr as reliable traffic tracers regarding the high correlation coefficients ($r > 0.65$) between the moss element concentrations and the counted traffic flows. Since moss bags provide information about long-term pollutant concentrations, the results could be indicative for assessment of the pedestrians, commuters, cyclists and workers exposure to traffic-related Cr, Cu, and Sb emissions.

ACKNOWLEDGEMENT

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REFERENCES

1. Adamo, P., Giordano, S., Sforza, A., Bargagli, R. 2011. Implementation of airborne trace element monitoring with devitalised transplants of *Hypnum cupressiforme* Hedw.: Assessment of temporal trends and element contribution by vehicular traffic in Naples city. Environ. Pollut. 159, 1620-1628.
2. Aničić, M., Tasić, M., Frontasyeva, M.V., Tomašević, M., Rajšić, S., Strelkova, L.P., Popović, A., Steinnes, E. 2009a. Active biomonitoring with wet and dry moss: A case study in an urban area. Environ. Chem. Lett. 7, 55-60.
3. Aničić, M., Tomašević, M., Tasić, M., Rajšić, S., Popović, A., Frontasyeva, M.V., Lierhagen, S., Steinnes, E. 2009b. Monitoring of trace element atmospheric deposition using dry and wet moss bags: Accumulation capacity versus exposure time. J. Hazard. Mater. 171, 182-188.
4. Aničić, M.,. Tasić, M, Frontasyeva, M.V., Tomašević, M., Rajšić, S., Mijić, Z., Popović, A. 2009c. Active moss biomonitoring of trace elements with *Sphagnum girgensohnii* moss bags in relation to atmospheric bulk deposition in Belgrade, Serbia. Environ. Pollut. 157, 673-679.
5. Aničić, M., Spasić, T., Tomašević, M., Rajšić, S., Tasić, M. 2011. Trace elements accumulation and temporal trends in leaves of urban deciduous trees (*Aesculus hippocastanum* & *Tilia* spp.). Ecol. Ind. 11, 824-830.
6. Ares, Á., Aboal, J.R., Carballeira, A., Giordano, S., Adamo, P., Fernández, J.A. 2014. Moss bag biomonitoring: A methodological review. Sci. Total Environ. 432, 143-158.
7. Brauer, M. 2010. How Much, How Long, What, and Where, Air Pollution Exposure Assessment for Epidemiologic Studies of Respiratory Disease. Proc. Am. Thorac. Soc. 7, 111-115.
8. Brown, D.H., Bates, J.W. 1990. Bryophytes and nutrient cycling. J Linn Soc Bot 104, 129-147.
9. Directive 2004/107/EC of the Europen parliament and of the council of 15 December 2004 relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air, Official Journal of the European Union, 23, 1-16, (26/01/2005).
10. Directive 2008/50/EC of the Europen parliament and of the council of 21 May 2008 on ambient air and cleaner air for Europe, Officional Journal of the European Union, 1-44, (11/06/2008).
11. Dołęgowska, S., Migaszewski, Z.M. 2013. Anomalous concentrations of rare earth elements in the moss–soil system from south-central Poland. Environ. Pollut. 178, 33-40.

12. EMEP/EEA air pollutant emission inventory guidebook. Passenger cars, light commercial trucks, heavy-duty vehicles including buses and motor cycles 2013, update Septembar, 2014 http://www.eea.europa.eu/publications/emep-eea-guidebook-2013/
13. European Environment Agency, 2013. The Contribution of the Transport Sector to Total Emissions of the Main Air Pollutants in 2009 (EEA-32). Retrieved March 16, 2013, from. http://www.eea.europa.eu/data-and-maps/figures/thecontribution-of-the-transport-1.
14. Gietl, K.J., Lawrence, R., Thorpe, J.A., Harrison, M.J. 2010. Identification of brake wear particles and derivation of a quantitative tracer for brake dust at a major road. Atmos. Environ. 44, 141-146.
15. Goodman, T.G., Roberts, T.M. 1971. Plants and soils as indicators of metals in the air. Nature 231, 287-292.
16. Mijić, Z., Stojić, A., Perišić, M., Rajšić, S., Tasić, M., Radenković, M., Joksić, J. 2010. Seasonal variability and source apportionment of metals in the atmospheric deposition in Belgrade. Atmos. Environ. 44, 3630-3637.
17. Napier, F., D'Arcy, B., Jefferies, C. 2008. A review of vehicle related metals and polycyclic aromatic hydrocarbons in the UK environment. Desalination 226, 143-150.
18. Rivera, M., Zechmeister, H., Medina-Ramón, M., Basagaña, X., Foraster, M., Bouso, L., Moreno, T., 2011. Monitoring of Heavy Metal Concentrations in Home Outdoor Air Using Moss Bags. Environ. Pollut. 159 (4), 954-62.
19. Steinnes, E., Rühling, A., Lippo, H., Mäkinen, A. 1997. Reference materials for large scale metal deposition surveys. Accred Qual Assur 2, 243-249.
20. Tsai, J.H., Chiang, H.L., Hsu, Y.C., Weng, H.C., Yang, C.Y. 2003. The speciation of volatile organic compounds (VOCs) from motorcycle engine exhaust at different driving modes, Atmos. Environ. 37, 2485-2496.
21. Vuković, G., Aničić Urošević, M., Razumenić, I., Goryainova, Z., Frontasyeva, M.,Tomašević, M., Popović, A. 2013. Active Moss Biomonitoring of Small-Scale Spatial Distribution of Airborne Major and Trace Elements in the Belgrade Urban Area. Environ. Sci. Pollut. Res. 20, 5461-70.
22. Vuković, G., Aničić Urošević, M., Goryainova, Z., Pergal, M., Škrivanj, S., Samson, R., Popović, A. 2015a. Active moss biomonitoring for extensive screening of urban air pollution: Magnetic and chemical analyses. Sci. Total Environ. 521-522, 200-210.
23. Vuković, G., Aničić Urošević, M., Pergal, M., Janković, M., Goryainova, Z., Tomašević, M., Popović, A. 2015b. Residential heating contribution to persistent air pollutants (PAHs, trace and rare earth elements): a moss bag case study. Environ. Sci. Pollut. Res. 23, 18956-18966.
24. WHO, 2013. Review of Evidence on Health Aspects of Air Pollution REVIHAAP Project. Technical Report. World Health Organization, Regional Office for Europe, Copenhagen, Denmark.
25. Zechmeister, H.G., Hohenwallner, D., Riss, A., Hanus-Illnar, A. 2005. Estimation of element deposition derived from road traffic sources by using mosses. Environ. Pollut. 138, 238-249.
26. Zechmeister, H.G., Hagendorfer, H., Hohenwallner, D., Hanus-Illnar, A., Riss, A., 2006. Analyses of platinum group elements in mosses as indicators of road traffic emissions in Austria. Atmos. Environ. 40, 7720-32.

2.9 IMPACT OF WIND SPEED ON THE CONCENTRATION OF $PM_{2.5}$ IN AMBIENT AIR

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ABSTRACT

Twenty-four hour measurements of $PM_{2.5}$ particulate matter have been carried out during the period between the 22nd January and the 25th February 2013 in a suburban area of Belgrade. $PM_{2.5}$ samples were collected on 47 mm filters, with the use of Sven Leckel gravimetric samplers, while a meteorological station recorded meteorological data nearby the sampling instrumentation. The daily average $PM_{2.5}$ concentrations were in the range of 7,05 μg m^{-3} to 76,43 μg m^{-3}. Wind direction in combination with wind speed is an important factor for pollutant transportation, dispersion and accumulation. A correlative analysis was used to investigate the relationship among $PM_{2.5}$ concentrations and meteorological parameters (i.e. wind speed). A negative correlation between wind speed and the concentration of $PM_{2.5}$ was observed based on the measurements: lower particle concentrations were registered at higher wind speeds.

Keywords: $PM_{2.5}$, ambient air, wind speed

INTRODUCTION

Ambient particles are recognized to have strong impact on the atmospheric air quality and are of great concern in health-related problems. Particulate Matter (PM) is defined as material suspended in the air in the form of small solid particles or liquid droplets, usually considered as an atmospheric pollutant with significant impact on human health (Martinelli et al, 2013). Fine particles ($PM_{2.5}$), with an aerodynamic diameter smaller than 2.5 μm, are considered to be more hazardous than those of larger size. $PM_{2,5}$ due to its longer residence time in the atmosphere, and they can penetrate deep into the alveoli of human beings through breathing (Feng et al, 2009). They contribute to a variety of adverse health effects including asthma, lung cancer, cardiopulmonary disease and even mortality (Pope and Dockery, 2006). Fine particles are derived primarily from direct emissions from combustion processes, such as vehicle use of gasoline and diesel, wood burning, coal burning for power generation, and industrial processes, such as smelters, cement plants, paper mills, and steel mills. Airborne particulate matter has a long residence time, it can be transported over long distances depending upon atmospheric circulation. Smaller particles can stay within the atmosphere for several weeks. Thus small particles are likely to travel with the atmospheric current, and affect the surrounding environment (Furuta et al 2005). High $PM_{2.5}$ levels have been shown to reduce visibility (Shendriker and Steinmetz, 2003) which may affect transportation safety. Therefore it is important to monitor the concentration of $PM_{2,5}$ particles in ambient air.

Atmospheric (meteorological) conditions significantly affect local and global air quality. The distribution of emitted polluting particles directly depends on meteorological conditions, both with respect to their diffusion or their transportation from one area to another (vertical and horizontal air circulation), which may reduce atmospheric concentrations. If there is no wind, further transportation of these polluting particles from the source is slow, thereby decreasing the rate of removal. The direction of particulate transportation and the local and global distribution depends on the direction, duration and intensity of the wind blowing. Additionally, rainfall will clean the atmosphere also decreasing their concentration (Đuković and Bojanić, 2000).

The aim of this work is to investigate the impact of wind speed onto the air pollution level with the suspended $PM_{2.5}$ particles.

METHODOLOGY

Twenty-four hour measurements of $PM_{2.5}$ particulate matter have been carried out during the period between the 22nd January to 25th February 2013 in a suburban area of Belgrade. The monitoring site was located in the Institute of Nuclear Sciences "Vinča", on the roof of Laboratory 060, about 5 m above the ground and about 14 km away from the center of Belgrade. The monitoring site was about 200 m away from a not so crowded road

(only for employees). It was also surrounded by domestic houses not closer than one kilometer from the sampling point. Coal and wood is predominantly used for heating in those houses. $PM_{2.5}$ samples were collected on Quartz Whatman QM-A filters diameter 47 mm, with the use of Sven Leckel gravimetric samplers, flow rate (2,3 m^3/h). Along with sampling, monitoring of the meteorological parameters was also carried out by a meteorological station installed at the same measurement site as the sampler. The meterological station monitored the following: temperature, wind speed, wind direction, relative humidity, atmospheric pressure.

$PM_{2,5}$ mass concentrations were determined by gravimetric measurements using an Radwag microbalance with a resolution of 10^{-6} g. The filters were conditioned at a constant relative humidity of 50 ± 5 % and temperature of 20 ± 1 °C for 48 h, before and after sample collection. The gravimetric mass was calculated as the subtraction of the weight of the filter after sampling from that of the prior sampling. The filter mass data obtained were corrected for field blank values and presented as μg m^{-3}.

Correlative analysis was used to analyse the mutual dependence between $PM_{2,5}$ concentration and wind speed.. The aim of the correlative analysis was to investigate whether there was a quantitative correlation between the variations of the observed measured data and if so, to what degree. This is defined on the basis of level of determination coefficient value r^2.

RESULTS AND DISCUSSION

The daily values of $PM_{2.5}$ concentrations were in the range of 7,05 μg/m^3 to 76,43 μg/m^3. The average daily $PM_{2,5}$ concentration was 39,98 μg /m^3. From the total 35 sampling days, $PM_{2.5}$ values were above the U.S. Environmental Pollution Agency (US EPA) daily limit (35 μg/m^3)[6] for 21 days (60% of the measurement period). So far, the European Union has not established the ambient air quality standard for $PM_{2.5}$. The daily limit of $PM_{2,5}$ has not been established by our legislation rules either.

Daily temperatures were in the range of -2 ^oC to 11 ^oC. The average daily temperature was 3 ^oC. Daily relative humidity during the sampling period was between 50 % and 95 %. Wind speed was in the range of 0 to 7,1 m/s. The average wind speed during the sampling period was 2 m/s. Daily periods without wind happened twice and during this period concentrations of suspended $PM_{2,.5}$ particles were 70,49 μg/m^3 and 69,14 μg/m^3.

A correlative analysis was used to investigate the relationship among $PM_{2.5}$ concentrations and meteorological parameters (wind speed). Figure 1 shows negative correlation between $PM_{2.5}$ and wind speed. When the wind speed is low, it can blow away the pollutants within a certain geographical range but, when the wind speed is high enough, it can transport large quantities of pollutants from far away. Determination coefficient value r^2= 0,5983, points out that the wind speed greatly affects the increase of $PM_{2,5}$ concentration on the sampling site. Obtained high mass concentrations are due to the prevalence of low wind speed.

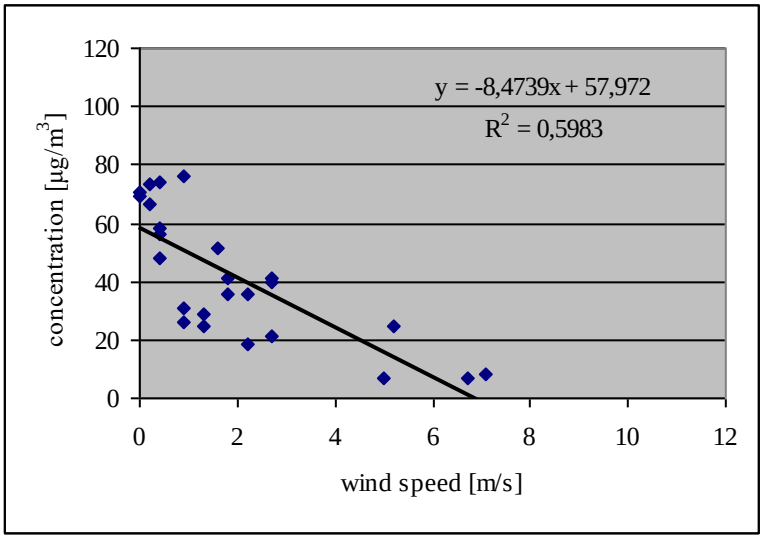

Figure 1. *The relationship between $PM_{2.5}$ and wind speed.*

The dominant wind directions were South (S), South-southwest (SSW), Southeast (SE), North (N) i Northeast (NE). Figure 2 shows that the wind direction with the highest frequency was the South.

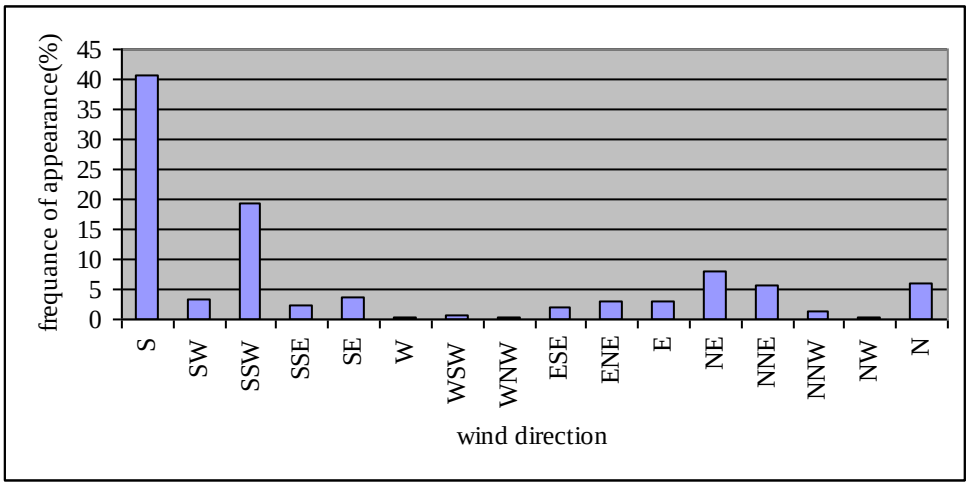

Figure 2. *Frequency of appearance (%) of each wind direction type during the whole experimental campaign.*

The wind direction is an important parameter affecting $PM_{2.5}$. The wind from different directions transported different amount of pollutants. Figure 3 shows the AWP (Average Weighted $PM_{2.5}$ by wind speed) for different wind directions during the sampling period.

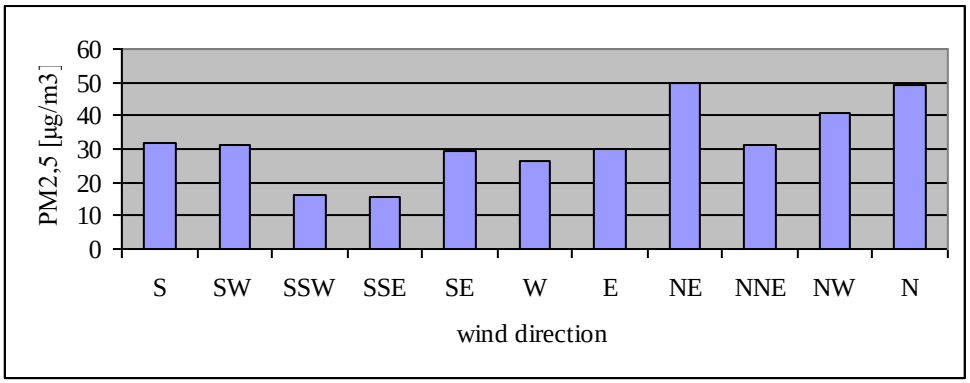

Figure 3. *The relationship between PM2.5 and wind direction*

Northeast, North and Northwest wind transported more pollutants than wind in other directions. The highest concentrations of fine particles were transported to the investigated area by air masses from Northeast direction. The wind direction of the highest frequency of appearance was not necessarily an indicator of the highest $PM_{2,5}$ concentration values.

CONCLUSIONS

These observed facts indicate that the variations of $PM_{2.5}$ mass concentration in suburban areas are influenced by complex meteorological factors and human activities. On the basis of the obtained results, a negative correlation between $PM_{2,5}$ concentration and wind speed was confirmed. Determination coefficient value r^2= 0,5983, points out that the wind speed greatly affects the increase of $PM_{2,5}$ concentration at the sampling site. Lower particle concentrations were registered at higher wind speeds and vice versa. Strong winds “wash out” pollution from the system and weaker winds enable pollution level to rise.

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REFERENCES

1. Shendriker A.D. , Steinmetz W.K., 2003. Integrating nepholometer measurements for air-borne fine particulate matter (PM2.5) mass concentration, Atmospheric Environment, 37, 1383–1392
2. Pope C.A., Dockery D.W., 2006. Health Effects of Fine Particulate Air Pollution:Lines that Connect, J. Air Waste Manage. Assoc., 56(6)709-742.
3. Feng X.D., Dang Z., Huang W.L., Yang C. 2009. Chemical Speciation of Fine Particle Bound Trace Metals, Int. J. Environ. Sci. Technol. 6, 337–346
4. Furuta N., Iijima A., Kambe A., Sakai K. and Sato K., 2005, Concentrations, enrichment and predominant sources of Sb and other trace elements in size classified airborne particulate matter collected in Tokyo from 1995 to 2004., J. Environ. Monit.,7, 1155–1161
5. Martinelli N., Olivieri O. , Girelli D., 2013, Air particulate matter and cardiovascular disease: A narrative review, European Journal of Internal Medicine 24: 295–302.
6. United States Environmental Protection Agency (US EPA), 2012. Particulate Matter, National Ambient Air Quality Standards (NAAQS) – Air and Radiation, Available at: http://www3.epa.gov/ttn/naaqs/criteria.html
7. Đuković J., Bojanić V., 2000. Aerozagađenje, pojam, stanje, izvori, kontrola i tehnološka rješenja, DP Institut zaštite i ekologije, Banja Luka.

2.10 RETENTION MODELLING OF ION CHROMATOGRAPHY FOR CATIONS IN ATMOSPHERIC AEROSOLS

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ABSTRACT

Concentrations of six water-soluble cations (lithium, sodium, ammonium, potassium, magnesium and calcium) in atmospheric aerosol samples, collected in a suburb of Belgrade (Serbia), were determined by ion chromatography (IC). In order to obtain a better separation, interpretive retention modeling was employed to optimize the isocratic ion chromatographic (IC) separation with the methanesulfonic acid (MSA) eluent. The influence of wide variations of the MSA concentration (5-45 mM) on the IC separation was studied. The quadratic model shows a very good prediction power. For the most optimal conditions in the experimental design, the global resolution was optimized. The eluent concentration of 18 mM of MSA was found to be an optimum for cations separation on a Dionex CS12 column with the total analysis time of less than 10 minutes. Time-series analysis strongly suggests that concentrations of cations in aerosol samples are affected by mineral dust from both natural and anthropogenic sources.

INTRODUCTION

Increasing industrial development and urbanization in the past decades has resulted in a world-wide increase of airborne particulate matter which has an important influence on human health (Kumar et al, 2010). The contribution from anthropogenic sources to aerosol loading has grown significantly, especially over urban and industrial areas. In urban regions, water-soluble ions accounted for one-third or more of the aerosol particles mass (Zhang et al, 2011). These ions are a major component of the atmospheric aerosols for which observations on chemical composition would be valuable to understand their chemical and physical characteristics, origins and behaviour. Therefore, it is scientifically important to investigate the characteristics of water-soluble ions for understanding aerosol properties, sources, behaviours and formation mechanisms (Wang et al, 2015). Water-soluble components of atmospheric aerosol include many important compounds, which can change the size, composition, number and lifetime of aerosols due to their hygroscopic nature. These components can contribute the solubility of toxic organic compounds and increase their toxicity. Characterization of water-soluble cations and anions, as major components of atmospheric aerosols, has been studied extensively in recent years. Concentrations and particulate distributions of ions in atmospheric particles depend on local sources, weather and reaction conditions and long-range transportation (Zhao et al, 2011).

Ion chromatography (IC) has become the best and routine method for the determination of water-soluble ions. Good quality separation in chromatography can be accomplished by applying optimization criteria. Optimization of IC separations is usually achieved by changes the eluent compositions after the selection of an appropriate stationary phase. Different models have been developed to predict retention times for the separations under isocratic and gradient conditions in order to find optimal separation conditions more easily. According to the quadratic model (Ko and Ford, 2001):

$$\log k' = A + B\log[E^y] + C(\log[E^y])^2 \qquad (1)$$

where k is the retention factor of a solute, E^y is solvent composition, A, B and C is the model parameters which can be calculated numerically with a set of simultaneous equations.
In this work concentrations of six water-soluble cations (lithium, sodium, ammonium, potassium, magnesium and calcium) in 94 atmospheric aerosol samples, collected in a suburb of Belgrade (Serbia), were determined by IC. In order to obtain a good chromatographic separation, retention modeling was employed to optimize the isocratic ion chromatographic resolution with the methanesulfonic acid (MSA) eluent. The influence of wide variations of the MSA concentration on the IC separation was studied with a quadratic model. Concentration levels and the seasonal variations of the measured species are also studied.

METHODOLOGY

A total of 94 daily samples of atmospheric aerosols were collected between September 2013 and June 2014 at Mirijevo, a suburb of Belgrade, Serbia. Aerosols were collected with the TCR Tecora (Echo Hi-Vol) filter sampler continuously for 24 hours at a flow rate of 225 L/min. The collected samples were stored at a temperature of -18 oC, until the time of analysis. Deionized water was used to dissolve the samples with the aid of a mechanical shaker. After the filtration of samples through 0,22 μm syringe filters, the cations were quantified on a Dionex DX-300 IC system (Dionex, Sunnyvale, CA, USA) equipped with conductometric detector, CSRS-ultra self regenerating suppressor, CS12 (250 x 4 mm) analytical column and CG12 (50 x 4 mm) guard column and methanesulfonic acid (MSA) as eluent.. A Spectra-Physics model AS3500 autosampler was used for the direct programmed injection of samples. The injection sample loop was 100 μL.

All standard solutions of six cations were obtained from AccuStandard (New Haven, USA). Milli-Q system (Millipore Co., Bedford, MA, USA) processed water (18 $M\Omega cm^{-1}$) was used for preparation of working mixture. Before targeted samples analysis, standard solution and blank tests were performed and the correlation coefficients of calibration curves were more than 0.999 for all six cations. The influence of wide variations of the MSA on the IC separation was studied with nine eluent concentrations of 5.0, 10, 15, 20, 25, 30, 35, 40 and 45 mM. The estimation of model parameters were performed using Mathcad 2000 software (MathSoft Inc. USA).

RESULTS AND DISCUSSION

Prior to analyzing aerosol samples, in order to obtain a good chromatographic separation, retention modelling was employed to optimize the isocratic ion chromatographic resolution with the methanesulfonic acid (MSA) as eluent. The influence of wide variations of the MSA on the IC separation was studied with nine eluent concentrations of 5.0, 10, 15, 20, 25, 30, 35, 40 and 45 mM for a mixture of cations getting nine retention data set. The data from these runs are fitted to Eq. (1) for all six cations, using each of the eluent compositions in the data set, to predict retention data. The prediction powers of the applied model were tested and results are shown in Fig. 1. Good agreements between experimentally measured and predicted retention coefficients were obtained.

The essential part of a chromatographic separation study is the selection of an appropriate response function to quantify numerically the chromatogram. According to the normalized resolution product (r) criterion, described by the following equation:

$$r = \prod_{i=1}^{n-1} \{R_{Si,i+1} / [(n-1)^{-1} \sum_{i=1}^{n-1} R_{Si,i+1}]\} \quad (2)$$

where n is the number of peaks and $R_{S\,i,i+1}$ is the resolution between peaks i and i+1, 18 mM MSA was selected as the optimum mobile phase on a Dionex CS12 column as it gave the maximum value of the resolution product and satisfactory retention times.

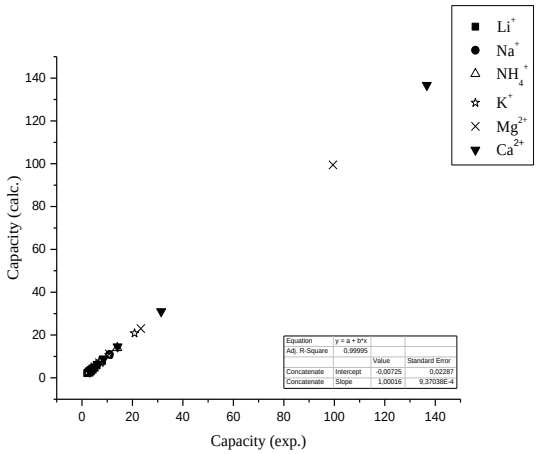

Fig. 1. Experimentally measured and predicted retention coefficients for the optimized quadratic model of six cations

Ninety-four aerosol samples were studied based on the obtained results. Typical IC chromatograms of an aerosol particle extract are shown in Fig. 2. In the cation-exchange mode, five common cations (sodium, ammonium, to quantify numerically the chromatogram. According to the normalized resolution product (r) criterion, described by the following equation:

$$r = \prod_{i=1}^{n-1} \{R_{Si,i+1} / [(n-1)^{-1} \sum_{i=1}^{n-1} R_{Si,i+1}]\} \quad (2)$$

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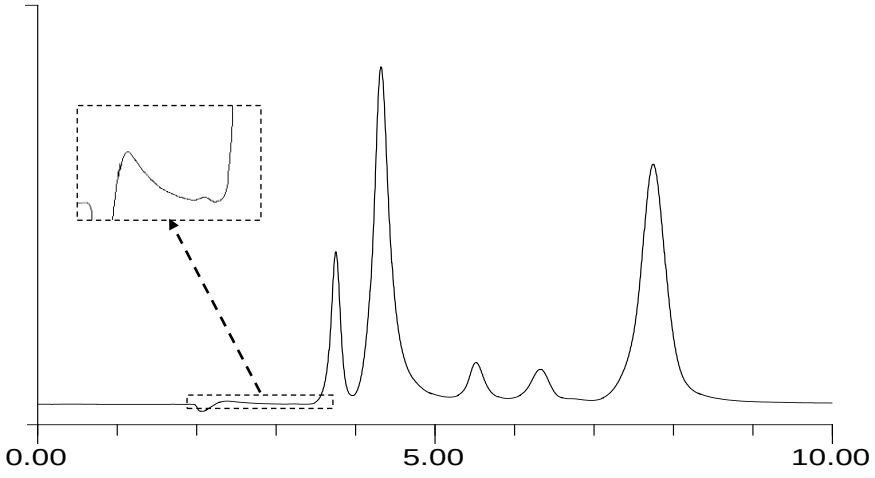
Ninety-four aerosol samples were studied based on the obtained results. Typical IC chromatograms of an aerosol particle extract are shown in Fig. 2. In the cation-exchange mode, five common cations (sodium, ammonium, potassium, magnesium and calcium) were easily separated in less than ten minutes. In some samples, lithium-ion was detected at trace levels, but it was not quantified for the purposes of this study. The arithmetic means, minimum values, maximum values and standard deviations for the obtained concentrations of all analyzed cations in the studied aerosol samples were calculated (as shown in Table 1).

Table 1. *Descriptive statistics for the data for the studied water-soluble substances in atmospheric aerosols (ng/m^3) at one site in outskirt of Belgrade in the period 09.09.2013. - 25.06.2014.*

Variable	Mean	SD*	Min.**	Max.***
Sodium	861.6	609.2	94.42	2305
Ammonium	2851	2914	304.0	14886
Potassium	172.5	77.09	69.15	449.3
Magnesium	149.3	100.4	26.59	650.0
Calcium	664.7	320.4	228.8	1602



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

Figure 2. *Typical cation chromatogram of an aerosol sample extract. Column: Dionex CS12. Eluent: 18 mM methanesulfonic acid (isocratic). Peaks: (1) lithium, (2) sodium, (3) ammonium, (4) potassium, (5) magnesium, (6) calcium*

In the studied aerosol samples, ammonium, sodium and calcium are considered to be the major ions while potassium and magnesium are ions present at a medium level. Lithium ion was detected at trace level. The mean values of analyzed water-soluble cations in atmospheric aerosols obtained were: 861, 2851, 172, 149 and 665 ng/m^3 for sodium, ammonium, potassium, magnesium and calcium, respectively

To examine the trends of the concentration changes over a ten-month period (fall 2013 to summer 2014), the concentrations of analyzed cations for various emission sources were plotted by the moving averages for all samples, Fig.3. The time-trends of these variables were also fitted by quadratic curves. A significant fluctuation is present with all analyzed variables. No monthly periodicity was revealed. There is a chromatographic-like time trend for ammonia, which suggest that anthropogenic effects are present sporadically. Ammonia shows a strong preponderance to change over time, with some peak values in the fall to baseline during the winter, followed by some peaks through the spring in 2014. Sodium, potassium, magnesium and calcium showed opposite trends over the same time-period. Time-series analysis strongly suggests that concentrations of cations in aerosol samples are affected by mineral dust from both natural and anthropogenic sources. The mineral dust influence is more pronounced in winter.

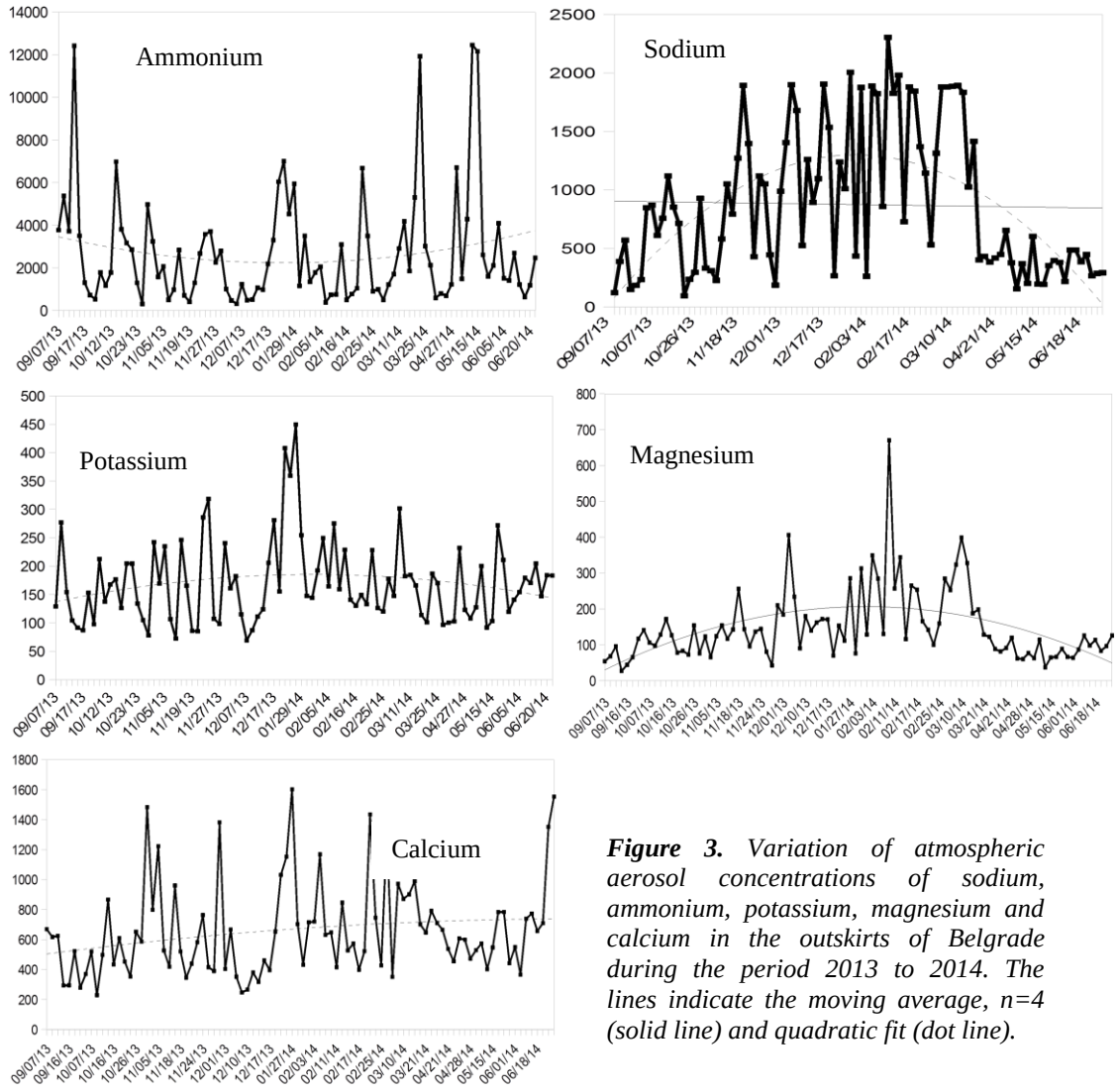


Figure 3. *Variation of atmospheric aerosol concentrations of sodium, ammonium, potassium, magnesium and calcium in the outskirts of Belgrade during the period 2013 to 2014. The lines indicate the moving average, n=4 (solid line) and quadratic fit (dot line).*

CONCLUSIONS

In this work interpretative models were used for retention modelling of six common cations in isocratic ion chromatography. The experimental and the calculated values of retention times were in good agreement. A concentration of18 mM MSA was selected as the optimum mobile phase composition by normalized resolution product criterion. Water-soluble cations, as important source markers in aerosol samples, can be successfully quantified by IC. The mineral dust particles are identified as dominant factor that contribute to pollution levels at the studied site. High levels of ammonium ion in the atmospheric aerosols at the analyzed site indicated high anthropogenic influence. The time-trends shows significant fluctuation for all analyzed variables.

ACKNOWLEDGEMENTS

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REFERENCES

1. Ko, J., Ford, J.C. 2001. Comparison of selected retention models in reversed-phase liquid chromatography. J. Chromatogr. A 913, 3-13.
2. Kumar, A., Mishra, M.K., Divkar, J.K., Rout, S., Narayanan, U., Hegde, A.G. 2010. Impact of particle size on distribution of major ions in acid-and water-soluble components of PM10 atmospheric aerosols in the coastal region of Mumbai. Atmos. Res. 98, 406-415.
3. Wang, H., Zhu, B., Shen, L., Xu, H., An, J., Xue, G. 2015. Water-soluble ions in atmospheric aerosols measured in five sites in the Yangtze River Delta, China: Size-fractionated, seasonal variations and sources. Atmos. Environ 123, 370-379.
4. Zhang, T., Cao, J.J., Tie, X.X., Shen, Z.X., Liu, S.X., Ding, H., Han, Y.M., Wang, G.H., Ho, K.F., Qiang, J., Li, W.T. 2011. Water-soluble ions in atmospheric aerosols measured in Xi'an, China: Seasonal variations and sources. Atmos. Res. 102, 110-119.
5. Zhao, J., Zhang, F., Xu, Y., Chen, J. 2011. Characterization of water-soluble inorganic ions in size–segregated aerosols in coastal city, Xiamen. Atmos. Res. 99, 546-562.

2.11 SOIL POLLUTION IN THE VICINITY OF THERMAL POWER PLANT IN SERBIA

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The paper presents results of the investigation of soil quality in the vicinity of the Kostolac Electric Power Plants and Mines in terms of possible contamination of soil by hazardous and harmful elements (As, Cr, Ni, Pb, Cu, Zn, Cd, Co). The alluvial soil of the Danube and Mlave valleys, where the power plant is located, represents a priority development area with very favourable conditions for life, agriculture, tourism, etc. Exploitation of thermal power plants results in the emission and immission of pollutants into the air, water and soil. A main objective of the study was determination of the state of soil pollution by inorganic pollutants in order to identify areas of vulnerability.

Total and DTPA-soluble concentrations of microelements were determined on ICAP 6300 optical emission spectrometer and on AAC analyzer. Field studies were carried out in two phases: in the vegetation and non-vegetation seasons. Seventy-eight samples of soil were taken at seventy measuring points. The investigated area was divided into 3 impact zones and 1 control zone (beyond the impact zone) based on the distance from the origin of the pollutants (the central point between Kostolac landfills and two power plant blocks). Impact zones were classed as level I in a radius of 2-2.5 km from the pollution centre; II impact zone in a radius of 2,5-5 km from the pollution centre; III impact zone in a radius of 5-10 km from the pollution centre; and the Control zone: beyond the impact of the pollutants.

The content of total and „available“ (DTPA soluble) forms of the studied microelements in soils from both sampled seasons was similar. The exception was the only sample in the level I impact zone, where the concentration of As was two times higher than the MAC (maximum allowed concentration) values and was on a level of the median remediation value.

No changes were observed in the impact zones in the content of some elements (Zn, Pb). This stage of investigation cannot establish a statistically reliable cause of these changes, specifically because of the large variation of values within the same zone, as well as the heterogeneity of soil cover. The Content of pollutants by depth is similar, indicating their geochemical origin. The only sample that showed a distinct inversion in the content of As occurred during flooding in 2014, which is explained by the proximity of the landfill and the increased mobility of As in reducing conditions. Generally, the differences in the content of analyzed elements was due to the heterogeneity of soil types, and depended on the geochemical composition of the substrate. Areas where the elements appear in the values around and above the MAC are vulnerable zones, which are to be monitored at the marked measuring points for the sake of a reliable identification of the causes of changes and/or pollution in soil quality.

2.12 POTENTIAL OF BIOMETHANE PRODUCTION BY USING DOUBLE-CROPPING SYSTEMS

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Production of methane-rich biogas through anaerobic digestion of organic materials has been evaluated as one of the most energy efficient and environmentally benign pathways of renewable energy generation. The special importance of the production and use of biogas is to prevent emission of methane in the air that increases the greenhouse effect (the intensity is 23 times greater than carbon dioxide).

The European Union has set the aim of increasing the share of energy consumption from renewable energies to 20% in 2020. Serbia, as a member of European Energy Community is obliged to follow European energy policy. Biomethane can be used in replacement for fossil fuels in both heat and power generation and as a vehicle fuel, thus contributing to cutting down the emission of greenhouse gases and slowing down the climate change. A growing number of plants for the production of biogas in EU especially in Germany and Austria influenced a significant increase in demand for crops rich in energy. Most biogas plants were built on farms dealing with livestock and crop production, where there are many sources of organic matter for the production of biogas: manure, dairy and processing industry waste, but the most important source is energy plants, so-called biogas crops. Many conventional forage crops together with maize are easy to cultivate and produce a large amount of biomass. The most important parameter in choosing crops for methane production is the net energy yield per hectare, which is defined mainly by biomass yield and convertibility of the biomass to methane. On the other side, continuous production of homogeneous biomass is crucial for a constant supply of digester. In order to meet these targets the double-cropping system has been suggested for the production of biogas crops over the last years. It involves the cultivation of two crops during 1 year with the combination of winter-hardy crops (first crop) and summer crops (second crop). A field experiment was carried out during the 2012-2013 and 2013-2014 growing seasons at the experimental field of the Institute of Field and Vegetable Crops in Novi Sad, Serbia. The main purpose of this study was to evaluate potential of methane production with 7 different double-cropping systems (winter pea, oat, triticale monocultures as well as mixtures of winter pea with both cereals, in two seeding ratios (50:50 and 75:25) and maize and sorghum as succeeding second crops). Double-cropping systems with oat or triticale as first crop and sorghum as second crop achieved highest DM yields of 30 t DM ha−1 on average, followed by double-cropping system of mixtures of winter pea with oat in both seeding ratios (50:50 and 75:25) and sorghum as a summer crop. Methane yield per hectare was positively correlated with DM yield. Triticale and oat monocultures, as well as both mixtures of winter pea-oat provided higher methane yield of 5000 m^3ha^{-1}DM on average than other winter-hardy crops. The highest methane production in the second part of growing seasons was achieved with sorghum (4760 m^3ha^{-1}DM on average).

2.13 MONITORING OF POLLUTANT CONCENTRATIONS EMITTED WITH MOTOR VEHICLE EXHAUSTS OVER A SECTION OF THE NIŠ-BELGRADE MOTORWAY

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ABSTRACT

This paper presents the results of measurements of concentrations of standard pollutants present in ambient air at the measuring location "Nais toll station" on the European route E75 near the City of Niš, Serbia. Pollutant concentration measurements were performed by means of the airpointer® automatic measuring station from 10 July to 31 October 2014. During the monitored period, one-hour pollutant concentrations did not exceed the limits. However, the 24-hour concentration of suspended particulate matter did exceed the allowed limit. This paper analyzes the correlation of instances of maximum concentrations between specific monitored pollutants that were emitted through motor vehicle exhausts.

Keywords: air pollution, air pollutants, vehicle exhausts

INTRODUCTION

Air pollution can be considered an important etiological and favourable factor for the occurrence and development of phenomena and processes that lead to environmental degradation and create conditions for the development of respiratory, cardiovascular, and malignant diseases, as well as other defined and undefined pathological conditions in the exposed population. One of the most important steps in the monitoring of air pollution and implementation of safety measures is to determine the source of the pollution and control pollutant emissions .

Recent studies indicate a growing cause-and-effect relationship between air quality and volume of traffic. It is well known that road traffic is the dominant emitter of pollutants (US EPA, 2012).

In the road traffic of EU countries, passenger cars range from 75% to 90%, light and heavy trucks from 8% to 20%, and buses and motorcycles only from 1% to 2% (EEA Report No 4/2012).

Emission of exhausts in road traffic occurs due to fuel combustion in gasoline and diesel engines. The fuels used are gasoline, diesel, LPG, and natural gas. The most significant pollutants emitted from road vehicles are the following: ozone precursors (CO, NO_x, and $NMVOC_s$); greenhouse gases (CO_2, CH_4, and N_2O); acids (NH_3, NO, NO_2, and SO_2); particulate matter (PM); carcinogenic compounds (PAH_s and POP_s); toxic substances – dioxins and furans; and heavy metals (Djordjevic et al, 2005).

Fuel combustion in gasoline and diesel engines emits high concentrations of partially oxidized hydrocarbons, aldehydes (acrolein and formaldehyde), non-decomposed hydrocarbons (olefins, pentane, and hexane), benzopyrene, organic acids, lead vapour, and halogenides. Highly toxic substances include benzene, formaldehyde, acetaldehyde, 1,3-butadiene, and lead (from leaded gasoline combustion), and these substances are classified as mobile source air toxics (MSATs).

During incomplete fuel combustion, a portion of the hydrocarbons turns into soot, which contains resinous substances. Large amounts of soot and resin are generated from the operation of technically faulty engines due to reduced air/fuel ratio in the engine.

Motor vehicle speed also affects the concentration of pollutants in exhausts.

If light and heavy trucks and buses move at higher speeds, then the emission of nitrogen oxides, carbon dioxide, and hydrocarbons is lower. When passenger cars move at higher speeds, the concentration of exhaust nitrogen oxides is higher, while the concentration of carbon dioxide and hydrocarbons is lower.

In EU countries, out of the total amount of air pollutants from anthropogenic sources, traffic contributes to ca. 62% of carbon monoxide emissions, ca. 42% of nitrogen oxides, 25% of suspended particulate matter, and ca. 28% of non-methane hydrocarbons (EEA, 2012).

So far, no comprehensive research to determine the amounts of gaseous pollutants emitted from traffic has been conducted in Serbia. Only partial studies and studies limited in scope were conducted (SEPA, 2013).

This paper provides the results of ambient air pollutant monitoring in the immediate vicinity of the Nais toll station, which operates under the Public Company "Putevi Srbije (Roads of Serbia)", Sector for Toll Collection. The toll station is located on the European route E75, northwest of the City of Niš. It is located ca. 12 km away from downtown Niš, 43°23'25.43" latitude and 21°48'6.50" longitude.

In the immediate vicinity of the toll station to the northeast, there are small prefabricated toll collection administrative buildings, and to the northwest there is a traffic police substation. To the west of the toll station there are no buildings, only farmland. The European route E75, a European A-class road, extends in the southeast-northwest direction in relation to the Nais toll station, connecting the far north of Europe (Norway) and the south (Island of Crete, Greece), and it is the longest international road passing through Serbia.

The highest volume of vehicle traffic at the toll station has been recorded during the summer, from June to September, during the vacation season. It is also the period when the highest pollutant concentrations in ambient air, emitted from fuel combustion, are to be expected.

METHODOLOGY

We monitored the concentrations of pollutants from fuel combustion in road traffic at a measuring point located 78 m south of the Nais toll station on the E75, using the airpointer® automated measuring station (Figure 1). The automated measuring station is an autonomous platform for independent measurement of a number of air pollutants by means of reference methods approved by the EU. The airpointer® is designed for outdoor use and non-stop operation. Carbon monoxide measurement is performed by means of a non-dispersive IR method, ozone is analyzed by means of UV photometry, sulphur dioxide is analyzed by means of UV fluorescence, nitrogen oxides are analyzed by means of chemiluminescence, and particulate matter is analyzed nephelometrically.

We performed pollutant concentration measurements at the Nais toll station from 10 July to 31 October 2014 (Rašić et al, 2014.).

Figure 1. *Position of the airpointer® automated measuring station*

The pollution rose, which was monitored simultaneously with concentration measurements, suggests that motor vehicles from the motorway are the sole sources of pollutants at this location. The direction from which pollutants enter the analyzed area is shown on the example of a pollution rose plotted on 11 July 2014 (Figure 2).

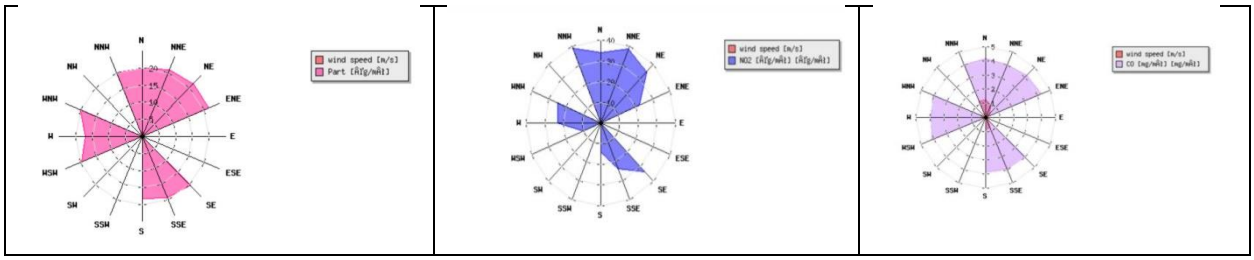

Figure 2. *Pollutant spreading direction on the E75 at the Nais toll station near Niš*

RESULTS AND DISCUSSION

Having analyzed the concentrations of carbon monoxide (CO), nitrogen dioxide (NO_2), ozone (O_3), suspended particulate matter $PM_{2.5}$, and sulphur dioxide (SO_2), the pollutants recorded at the measuring point, we concluded that one-hour limit values were never exceeded during the entire monitored period. However, one-hour $PM_{2.5}$ concentrations in July were relatively high during the day, ranging from 19.698 µg/m^3 to 37.656 µg/m^3, which lead to exceeded 24-hour limits over four days, while the 24-hour concentrations during six days in July were closer to the limit values during rainless days, Regulation on Monitoring Conditions and Air Quality Requirements (Official Gazette of the Republic of Serbia, 2010, 2013).

In August, the values of 24-hour concentrations of carbon monoxide ranged from 2.568 mg/m^3 to 3.475 mg/m^3, which resulted in the mean monthly concentrations of carbon monoxide exceeding the limit value for long-term exposure of 3mg/m^3 (Figure 3). 24-hour values of the measured $PM_{2.5}$ concentrations were above the allowed limit (30µg/m^3) for s total of 28 days, which resulted in $PM_{2.5}$ concentrations exceeding the limit value for long-term exposure of 25µg/m^3 (Figure 6).

In September, 24-hour $PM_{2.5}$ concentrations exceeded the allowed limits for five days. Other monitored substances were below their 24-hour limit levels, with a note that carbon monoxide was very close to the limit for five days. After 20 September the concentration levels of the monitored pollutants suddenly dropped.

The concentrations of the monitored pollutants decreased significantly in October, with none exceeding the allowed limit. Such decrease in concentrations can be attributed to the smaller volume of vehicle traffic.

Results from the entire monitored period indicate that sulphur dioxide concentrations were considerably below the allowed limits, which was expected, so we did not analyse their value range during the monitoring (Papić and Vidović, 2010).

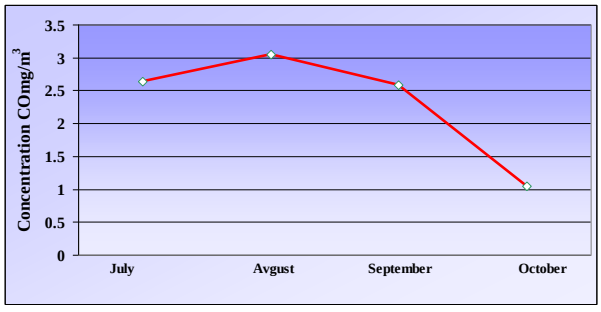

Figure 3. *Line chart of monthly CO concentrations on the E75 at the Nais toll station near Niš from July to October 2014*

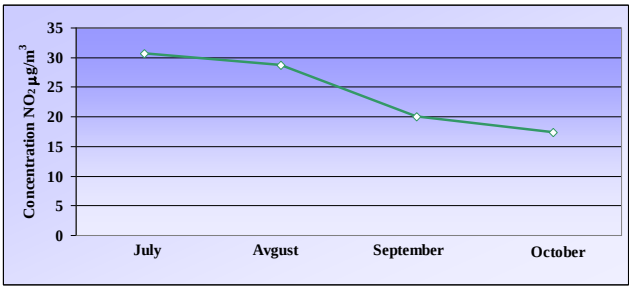

Figure 4. *Line chart of monthly NO_2 concentrations on the E75 at the Nais toll station near Niš from July to October 2014*

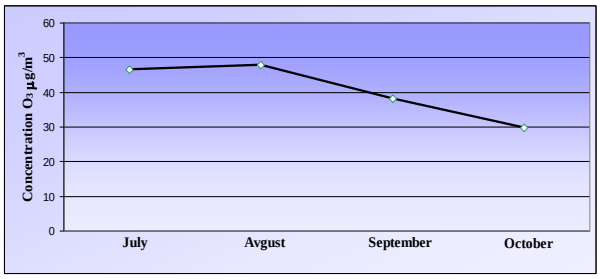

Figure 5*. Line chart of monthly O_3 concentrations on the E75 at the Nais toll station near Niš from July to October 2014*

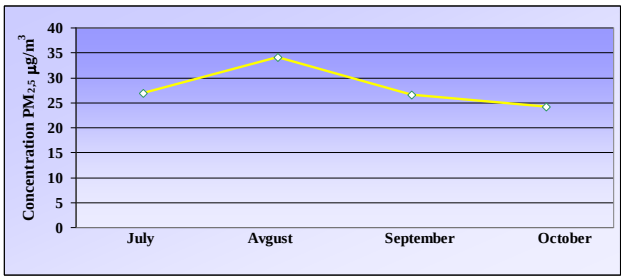

Figure 6. *Line chart of monthly $PM_{2.5}$ concentrations on the E75 at the Nais toll station near Niš from July to October 2014*

We concluded from the analysis of 24-hour pollutant concentration flow between July and October 2014 that the concentrations usually increased in the afternoon and late evening.

The maximum recorder values and the time of their occurrence during the 24-hour monitoring are shown only for July in the column charts (Figure 7).

Analysis of the time of occurrence of maximum concentrations during a day reveals that in most cases there is a correlation between the time of occurrence of maximum $PM_{2.5}$ and O_3 concentrations on the one hand, and between the time of occurrence of maximum NO_2 and CO concentrations.

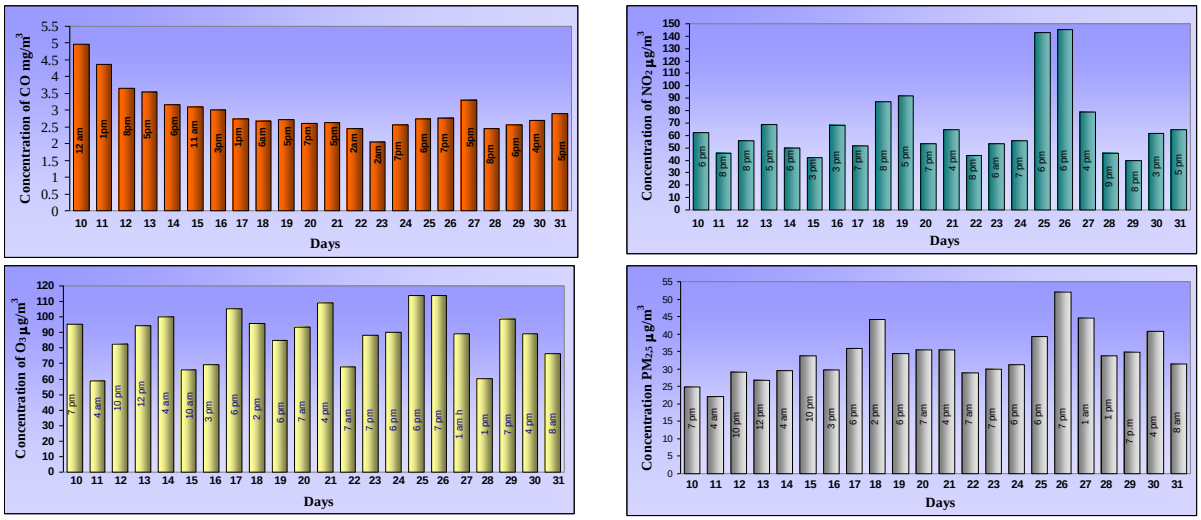

Figure 7. *Maximum daily concentrations of pollutants and their time of occurrence at the Nais toll station near Niš in July 2014*

CONCLUSION

During the monitoring period (July to October 2014), concentrations of pollutants emitted with motor vehicle exhausts in the immediate vicinity of the Nais toll station near the City of Niš were unexpectedly low. One-hour concentrations did not exceed the legal limits, whereas 24-hour concentrations exceeded the limits only during specific monitored days. Low concentrations can be attributed to the meteorological conditions, which were highly unusual for this period of the year. Average air temperatures were lower, and there were also much more rainy days, which might have affected the reduction of ambient air pollutant concentrations. The unexpectedly low concentrations of monitored pollutants below the one-hour limits are probably due to the fact that the monitored period saw large amounts of rainfall. With the increase in precipitation, pollutant concentrations become reduced due to pollutant wash-off below the clouds.

After analysing the 24-hour flow of pollutant concentration from July to October 2014, we observed that the increase in concentrations occurred mostly during the afternoon and late evening and that the volume of vehicle traffic is also one of the factors influencing air pollutant concentrations. We recorded the highest pollutant concentrations in August, when the volume of vehicle traffic was the biggest.

The analysis also led us to conclude that there is a correlation between the time of occurrence of maximum $PM_{2.5}$ and O_3 concentrations on the one hand, and between the time of occurrence of maximum NO_2 and CO concentrations on the other hand. These correlations should be investigated further in terms of the influence of meteorological parameters and the chemism of air pollutants.

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REFERENCES

1. Đorđević A., Živković N., Todorović B., Stanković M., 2005. Uticaj Saobraćaja na kvalitet vazduha urbanih sredina, 12 Simpozijum termičara, Energetika, Efikasnost, Ekologija, 15-21 oktobar, 2005, Soko Banja, Srbija, str. 291-296, ISBN: 86-80587-51-6.
2. European Environment Agency (EEA), 2012., Air quality in Europe — 2012 report, EEA Report No 4/2012

3. Serbian Environmental Protection Agency (SEPA) 2013. Annual Report on the State of Air Quality in Serbia, 2013, Ministry of Agriculture and Environmental Protection of Republic of Serbia
4. Rašić R., Đorđević A., Krstić I., Stevanović V., 2014, *Motor vehicle exhaust emissions in the City of Niš***,** Journal for Scientists and Engineers, Safety Engineering, 3(2).
5. Papić V., Vidović M., 2010. Determining the Quantity of Gaseous Pollutants Emitted from Road Traffic Using the COPERT 4 Model of the European Environment Agency, University of Belgrade, Faculty of Transport and Traffic Engineering, Institute of Faculty of Transport and Traffic Engineering, Belgrade, October 2010.
6. Regulation on Monitoring Conditions and Air Quality Requirements (Official Gazette of the Republic of Serbia, No. 11/2010, 75/2010, and 63/2013).
7. United States Environmental Protection Agency (US EPA), 2012. Air pollutants [Internet]. Washington, DC: United States Environmental Protection Agency; 2012 [cited 2014 Apr 10]. Available from: https://www.epa.gov/sites/production/files/2015-10/documents/ace3_criteria_air_pollutants.pdf

3. PARTICULATE MATTER: COMPOSITION AND MODELLING

3.1 PARTICLE-BOUND PAHS CHARACTERISTICS IN STUDIES PERFORMED IN BELGRADE AND SERBIA

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ABSTRACT

The aim of this paper is to present review of particle-bounded PAH data for period 2008-2015 in urban (Belgrade, Subotica, Novi Sad) and urban/suburban-industrial (Belgrade Metropolitan, Smederevo, Beocin) area of the Republic of Serbia that are collected form published literature and unpublished sources. The PAH concentration obtained at all sampling sites have shown seasonal trends: higher concentration during winter and much lower during summer. The highest average total PAH concentration recorded at suburban industrial location in heating season (H) and it was 97.75 ng/m^3 and the lowest 1.21 ng/m^3 at urban site during non-heating season (NH). At some locations Benzo[a]Pyrene concentration very 1 ng/m^3 during both seasons. BaP toxicity equivalent (BaPeq) value showed that the most negative impact on human health was found during heating season at the suburban/industrial location, 12.96 ng/m^3, (Lazarevac, Belgrade Metropolitean area), followed by typical urban area with impact of individual heating, 11.36 ng/m^3 (city of Subotica) and urban/industrial site at, 10.64 ng/m^3 (city of Smederevo).

INTRODUCTION

Polluted air still remains one of the major factors that determine the quality of life in urban areas, thereby increasing the risk to human health and the environment. In the metropolitans of developing countries the environmental problems are much greater, because of the overwhelming scale and speed of urbanization. In order to develop appropriate plans for air quality management, it is primarily to provide reliable information on the degree of contamination. Reducing air pollution in urban areas is set as one of the key objectives of the strategy of environmental protection in the countries of Eastern and South Eastern Europe (EEA, 2013; EEA, 2014; EEA 2015a). One of the key activities adopted by the WHO and the European Commission (based on WHO criteria) was the optimization of standards related to reduce harmful effects on human health.

Along with rapid increase in the number of vehicles and energy consumption in urban settings, air quality still exists as a big problem, with airborne particle matter (PM) as a major pollutant (EEA, 2013). PM_{10} is composed of inhalable particles with an aerodynamic diameter less than 10 μm. It is a complex heterogeneous mixture whose size and chemical composition can change in time and space due to different chemical species bonded on PM surfaces. Among these chemical compounds, polycyclic aromatic hydrocarbons (PAHs) are of major significance.

PAHs are a group of organic compounds containing only carbon and hydrogen and constituted by two or more aromatic rings fused together. Anthropogenic emissions are the main contributors to PM levels over Europe. They are mainly formed by incomplete combustion processes of organic materials (space heating activities, vehicles emissions, industrial activities, almost any combustion process, but also natural emissions such as volcanoes, biogenic formation etc. (Ravindra et al., 2008; Katsoyiannis et al., 2011; Ratola et al., 2012; Cristale et al., 2012). Some PAHs are present at ambient temperature in air due to their low vapor pressure. The PAHs with low molecular weight are found almost in gas phase, unlike heavier PAHs bonded on PM surfaces.

Their main concern is related to their potential exposure and adverse health effects on humans and some of them have been identified as carcinogenic, mutagenic and teratogenic. The US-EPA (2001) has classified seven PAH (benzo[a]pyrene,benz(a)anthracene,chrysene, benzo(b)fluoranthene,benzo(k)fluoranthene, dibenz(a,h)anthracene and indeno(1,2,3-cd)pyrene) as Group B2, probable human carcinogens. These seven PAH have also been classified by the International Agency for Research on Cancer (IARC, 2013) where benz(a)anthracene and benzo[a]pyrene are considered as Group 2A, probable human carcinogens and the other PAH as possible human carcinogens (Group 2B). In this paper we determined 16 priority US EPA PAHs: Naphtalene (Nap), Acenaphtylene (ACY), Acenaphtene (ACE), Fluorene (FLU), Phenanthrene (PHE), Anthracene (ANT), Fluoranthen (FLT), Pyrene (PYR), Benzo[a]anthracene (BaA), Chrysene (CRY), Benzo[b]fluoranthene (BbF), Benzo(k]fluoranthene (BkF), Benzo[a]pyrene (BaP), Indeno[1.2.3-cd]pyrene (InP), Dibenzo[ah]anthracene (DahA), Benzo[ghi]perylene (BghiP).

According to EEA (2015a) about 20% of the total European population was exposed to BaP annual mean concentrations above the European target value in 2012 and about 88% lives in areas with concentrations above the estimated reference level, that is 0.12 ng/m3 (EEA, 2015a). Considering only urban populations, in 2013, 25% of the EU28 urban population was exposed to BaP concentrations above the target value, and as much as 91% was exposed to BaP concentrations above the estimated reference level. About half of the BaP measurement stations in Europe continue measuring concentrations above the target value threshold (1 ng/m3 annual average, to be met by 2013) in 2013. Exceedances were measured mainly at urban and suburban stations, with 97% of all stations in exceedance located in urban and suburban locations, and 87% of all exceedances measured at suburban and urban background stations. As in previous years, in 2014. exceedances are most predominant in central and eastern Europe (Austria, Bulgaria, Croatia, the Czech Republic, Hungary, Italy, Lithuania, Poland and Slovenia), although there are also exceedances in France, Germany, Spain and the United Kingdom (EEA, 2015).

In study conducted at 15 EMEP stations, sites that show regional background ambient pollutant levels, located at several European countries (Norway, Finland, Estonia, Sweden, Latvia, Germany, UK, Belgium, Chech Republic) (Garrido et al., 2014), the highest total PAH (aerosol +air) mean concentration was found in Kosetice (Czech Republic), with 0.994 ± 1.543 ng m−3, followed by Preila (Lithuania), with 0.701 ng m−3.

EXPERIMENTAL METHOD

The analyzed data was collected from the different studies conducted at sampling sites within the local monitoring network of municipalities of Belgrade, Smederevo, Beočin, Subotica and Novi Sad, Figure 1. .

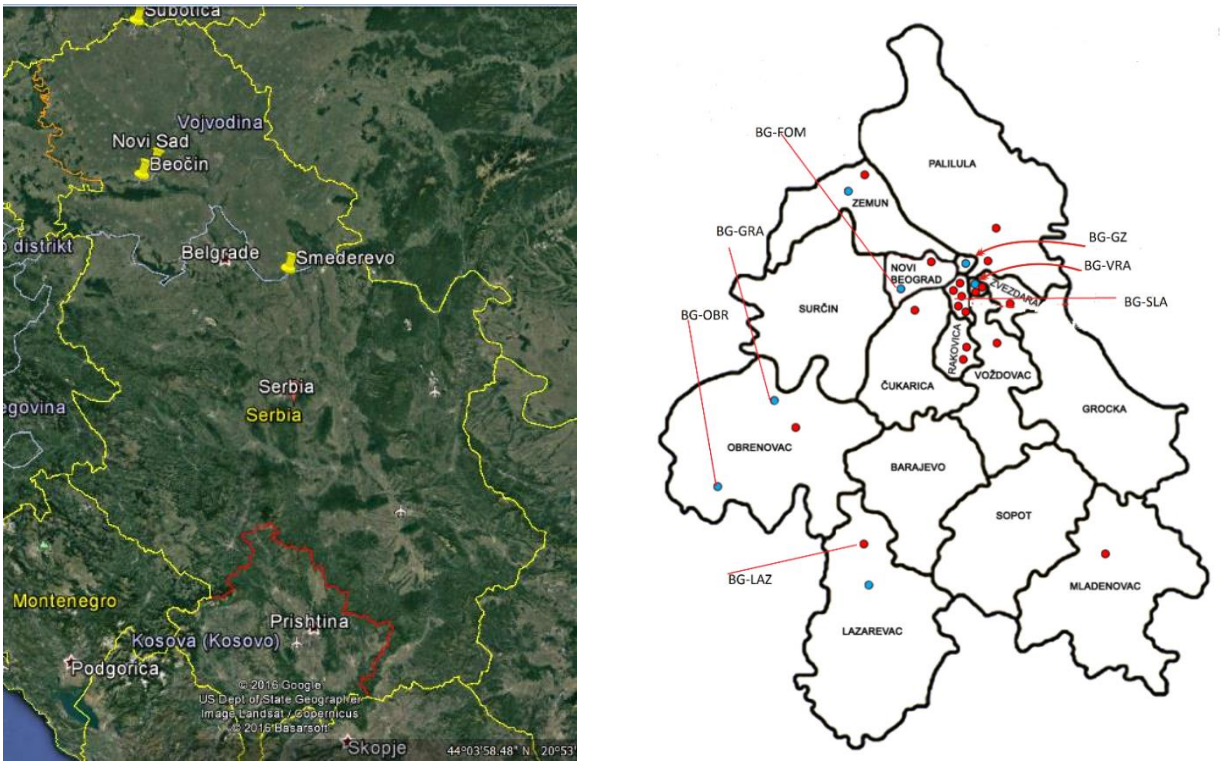

Figure 1. *Measurement sites for PAH-bounded particles in Serbian cities and in Belgrade Metropolitean area reviewed in this study*

All PM_{10} samples were collected by European reference low-volume sampler (Sven/Leckel LVS3 with flow rates 2.3 $m^3\ h^{-1}$). Samples were collected onto 47 mm Whatman filters on a daily basis (24 hours) with one 'field blank' per week (EEC, 1999). Gravimetric measurements were conducted according to EN 12341 for PM_{10} (CEN, 1998). Filters were exposed in opened Petri-slides for 48 hours at 20 ± 1°C temperature and 50 ± 5% relative humidity in a Class 100 clean room with automatic temperature/pressure regulation. Following the gravimetric measurements, loaded filters were stored in a cool room at 4 °C until analysis.

Collected samples were prepared according to ISO standard (ISO 12884:2000, US EPA 1999) using Gas Chromatography with Mass Selective Detector and Capillary column RESTEK (40m x 0,18mm x 0,07µm) in SIM mode. PAHs were prepared as described in paper by Cvetković et al (2015a). Method Quantification Limit (MQL) for all PAHs was 0.02 ng /m^3.

BaP is usually used as an indicator of human exposure to PAHs (Bostrom et al., 2002). In order to estimate the health risks for humans the benzo(a)pyrene-equivalent (BaPeq) was evaluated by multiplying the concentrations of each PAH with their toxic equivalent factors (TEF) (Akyüz at al., 2008). Toxic effect of some PAHs are stronger, even at much lower concentrations, due to its high TEF, which have been reported by many researches (Knafla et al., 2006).

RESULTS AND DISSCUSSION

Measurement sites, coordinate, cite type number of samples and concentrations for total mean and standard deviation of particle bounded PAHs, mean BaP and man BaP toxic equivalent – BaPeq are presented in the Table 1.

In Belgrade local monitoring network for TSP collection and BaP analyzes was established in 2005., while PM_{10} samples has been collected since middle of 2008 (Cvetkovic, 2010).

Cvetkovic et al [2015a] compared PAH concentration at same sampling site in urban area of Belgrade (BG-FOM) during nonheating season in 2009. and 2012. Although there was not identified statistical difference for total particle bounded PAHs and number of priority PAHs, it was identified that ANT, PYR and DahA mean values were significantly higher and BaA and BaP significantly lower in NH 2009. The explanation could be due to influence of the so-called "cardboard city", an informal settlement, locally classified as unhygienic settlement that was removed after campaign 2009. [Cvetković et al., 2015a].

Mean concentrations for sum of PAHs at the same site (BG-FOM) were more than 10 times higher during H (30.10 ng/m^3 and 17.92 ng/m^3) than NH campaign (2.55 ng/m^3 and 1.86 ng/m^3) for PM_{10} and PM_1 respectively. Concentration for PM_{10} was in range for European cities in literature data (Pascal et al., 2013; Kassomenos et al., 2014). Particulate phase PAHs dominated in H session (Teixeira et al., 2012; Callen et al., 2012; Okuda et al., 2010). During the NH relative contribution of BaP, BbF, CRY, BaA and PYR to total PAHs were higher for $PM_{1.0}$ than PM_{10} (4.44%, 8.40%, 10.89%, 7.33%, 13.32% and 3.41%, 7.06%, 9.69%, 4.15%, 12.23%, respectively).

Cvetkovic et al (2015b) analyzed PAH collected at three sampling site in the Metropolitan area of Belgrade. Rural/industrial site, Grabovac (BG-GRA), suburban/industrial, Lazarevac (BG-LAZ) and urban, Slavija (BG-SLA) during 2010-2011 have shown seasonal variation of PAH concentration. The sum PAH concentrations for the H season was the highest at LAZ and the lowest at GRA because of influence of heavy traffic, domestic heating and stationary sources. During the NH, total PAH values were lower for one magnitude order, the highest concentration was at GRA No significant difference ($P<0.05$) between sampling sites was observed for variance or for mean values of Acy, Ace, Flu, BghiP, in NH and Nap and Ant in H campaign. Nap, Phe and BaA in NH and total PAH as well as ACY, FLU, PYR, BaA, CRY, BbF, BkF, BaP InP, DahA and BghiP, in H were significantly different.

There were also particle bounded PAHs collected at three more sampling site within the Local Monitoring Network of Belgrade during 2012-2013 at sites: urban/traffic BG-GZ, urban/traffic/residential BG-VRA and suburban/industrial BG-OBR. The obtained results have shown that concentrations of the total PAH in NH were the highest at BG-GZ due to traffic, as the measurement site is in street canyon with a very large influence of traffic jam. High values for total PAHs during H are due to individual domestic heating (coal and wood combustion). During H the highest total PAHs concentrations was at BG-OBR because of influence of individual domestic heating. The PAHs concentration showed a distinct seasonal pattern and with maximum in H and a minimum in NH. During H concentration were almost twice higher than in NH.

In Smederevo city, urban/industrial sampling site, air quality is beside other under huge impact of steel manufacturing conglomerate (steel plant, hot and cold mill). Sampling period covered heating and non-heating season. The sum of total PAH concentrations during 2012-2014 was the highest in 2012 and the lowest in 2014 in NH. In 2012, almost all values for BaP in H season were above limit value. In 2013 and 2014 only few BaP concentrations were above 1 ng/m^3 when steel complex work with reduced capacity.

Table 1. *Characteristics of measurement sites, campaigns and results for particle bounded PAHs collected in Serbian cities during heating (H) and nonheating (NH) season.*

City	Measurement site-season	Cite type	Coordinate	Sampling		Total PAH (ng/m^3) mean and SD	BaP (ng/m^3)	BaPeq (ng/m^3)
				period	no			
Beočin	Beočin-H	urban/ residential /industry	$45^0$12' 39.4" $19^0$43' 14.0"	29.10-04.11.2008.	50	14.25±7.8	0.79	1.61
Novi Sad	I1-NH	urban/ industry	45°15'18'' 19°50'41''	26.06.-10.07.2008 22.01.2008.-05.02.2009	84	1.77±0.68	0.18	0.28
	I1-H					6.33±6.24	0.51	0.80
	I2- NH	urban/traffic				1.21±0.55	0.18	0.35
	I2- H					6.41±7.10	0.30	0.53
	I3- NH	urban /residential				1.42±0.61	0.16	0.26
	I3- H					7.25±9.84	0.22	0.54
Belgrade	BG-FOM- NH	urban /residential /traffic	44°49'7" 20°28'5"	25.05.-20.06.2009.	53	2.55±1.60	0.09	0.34
	BG-FOM- H			18.02-19.03; 13.11-14.12.2009	62	30.10±31.09	3.55	5.57
	BG-LAZ- NH	suburban/ industry	44°38´42.15´´ 20°26´52.48´´	2010/2011	91	6.13±16.63	0.59	1.47
	BG-LAZ- H				72	97.75±119.28	8.99	12.96
	BG-GRA- NH	rural / industry	44°36´11.74´´ 20°06´09.30´´		79	6.81±7.63	0.67	1.14
	BG-GRA- H				84	48.28±49.79	3.70	6.99
	BG-SLA- NH	urban/ traffic	44°48´03.5´´ 20°27´57.8´´		73	5.49±5.59	0.39	0.74
	BG-SLA- H				75	52.89±53.36	4.72	6.78
	BG-VRA- NH	urban/traffic/ residential	44°47´41.0´´ 20°28´59´´	2012/2013	49	3.45±2.61	0.30	0.55
	BG-VRA- H				42	27.62±31.84	2.71	4.6
	BG-GZ- NH	urban/traffic	44°49´67.8´´ 20°47´03.6´´		64	2.60±1.2	0.21	0.39
	BG-GZ- H				63	27.42±26.69	2.95	4.86
	BG-OBR- NH	suburban/ industry	44°40´8.90´´ 20°11´49.4´´		63	2.49±1.44	0.23	0.44
	BG-OBR- H				64	29.69±27.54	3.48	6.26
Subotica	NH	urban/ residential	46°04'57" 19°40'21"	23.09.2014.-10.05.2015.	14	5.37±5.81	0.67	0.99
	H				21	79.67±168.52	7.12	11.35
Smederevo	NH	urban/ residential/ industry	44º 39,9' 20º 55,5'	2012	22	4.83±2.88	0.49	0.88
	H				39	71.10±82.36	6.29	10.64
	NH			2013	28	9.45±10.98	1.02	1.76
	H				42	45.98±36.26	4.47	7.85
	NH			2014	36	4.20±4.85	0.34	1.08
	H				18	62.20±58.32	6.15	10.39

In study performed in Subotica samples were analyzed on PAH concentration in framework of regular environmental monitoring. The sampling site was established at urban station, within the city hospital. There are many individual heating facilities in the town and it is the main source emission of PAHs in air. The total PAH concentrations was the highest in H. Almost all values for BaP expect one in H season were above 1 ng/m^3 and about 30 % in NH season.

In Novi Sad, campaign was also performed during the NH and H period. The levels of particulate fractions 16 PAHs were determined at three sampling site in Novi Sad (Jovčić et al., 2013): I1 in the industrial zone of the city, located nearby oil refinery, power plate plant and roads with a high frequency of transport vehicles; I2 (about 850 m from the location I1) located in a high traffic zone, with dense traffic especially during rush hours; I3 located in the city center, in a residential area, about 1.5 km far from the oil refinery. The average annual

concentration of particulate fractions PAH for sampled collected at all sites was 4.06 ng/m^3, while during the NH period measured average concentration of 1.47 ng/m^3. The contribution of potentially carcinogenic polycyclic aromatic hydrocarbons in total particulate fraction of PAH ranged from 43.01 to 48.38% during H, while in NH this proportion ranged in interval of 53.87 to 66.76%.

Air quality in Beočin, is under influence of big cement factory. There were analyzed daily samples in H season at four sampling sites, 8 days per site and it was found that 30% samples had BaP higher than 1 ng/m^3.

The PAH concentration at all sampling sites in the analyzed studies have shown seasonal trends. The seasonal variation of PAH concentration is well known and it is due to the influence of meteorological conditions: high temperature, high photochemical degradation during NH but also reduced dissipation of pollutants and increased burning of wood and coal in domestic heating during the H (Lai et al., 2011 Agudelo-Castaned et al., 2014). Total PAH concentration was in range 1.21 (NS-I2-NH) to 97.5 ng/m^3 (at LAZ in H) while BaP concentrations were from 0.09 (BG-FOM-NH) to 8.9 ng/m^3 (also at LAZ in H). These values 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).

According to the obtained results for PAHs and TEF for each individual PAH the total of BaPeq was calculated. The total carcinogenic activities (total BaPeq concentrations) for collected PM_{10} during the H season were found to be between 5.86 and 12.96 ng/m^3, highest at the LAZ site (Figure 2 and Figure 3). During the NH season BaPeq were between 0.67 and 1.14 ng/m^3, lowest at the SLA site and highest at GRA. During both seasons, BaPeq were similar at SLA and GRA and about two times as high at LAZ sampling site (Cvetković et al., 2015b). According to the results obtained for relative contribution of each PAH to the BaPeq levels BaP dominated. The carcinogenicity activity contribution of BaP was in the range of 57.5-69.3% in both season at all sampling sites (Yang et al., 2010; Agudelo-Castaned et. al., 2014, Cvetković et al., 2015b). It was notified that the carcinogenic risks for humans are much higher during H time at all sites but the highest risk is at LAZ (Figure 4).

The obtained results for total carcinogenic activities (total BaPeq concentrations) at Smederevo during the H season were found to be between 7.84 and 10.64 ng/m^3, highest in 2012 (Figure 3, 4). The carcinogenicity activity contribution of BaP was higher during H in the range of 35.39-59.18% in both season at all sampling sites (Table 2). The contribution of DahA was higher than at other sites (in range 15.91-51.58 ng/m^3, highest in NH 2012). In the study performed in Novi Sad the obtained values for BaPeq were much lower than in other studies: 0.26-0.35 ng/m^3 during NH and 0.53-0.80 ng/m^3 during H. The contribution of BaP to total carcinogenic activities was between 40.76-64.47 ng/m^3. BaPeq values at Subotica were 0.99 during NH and 11.36 ng/m^3 in H and contribution of BaP and DahA to total carcinogenic activities were between 62.68 and 66.61 % and 7.2-14.43 %, respectively. BaPeq value at Beocin was 1.61 ng/m^3 in H season and contribution of BaP and DahA to total carcinogenic activities were 49.26 and 14.43 % respectively.

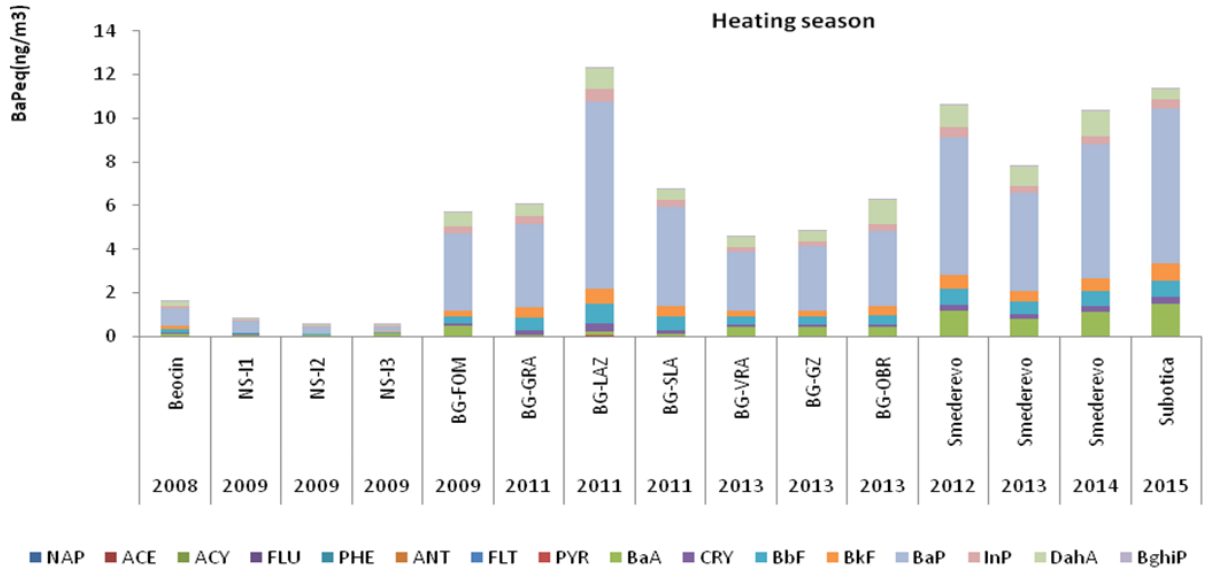

Figure 2. *The carcinogenic activities individual PAHs to total BaPeq concentrations in heating season*

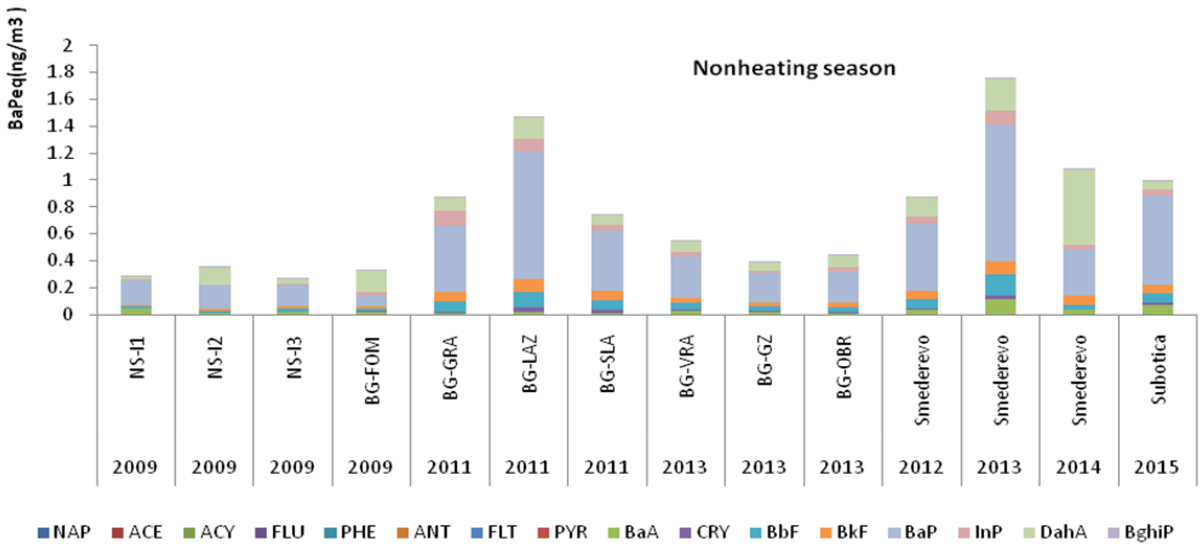

Figure 3. *The carcinogenic activities individual PAHs to total BaPeq concentrations in nonheating season*

The highest obtained BaPeq values were 10.64 ng/m^3 (at Smederevo), 11.36 ng/m^3 (at Subotica) and 12.96 ng/m^3 (at Lazarevac). The lowest BaPeq value was recorded at Novi Sad 0.26 ng/m^3. BaP and DahA dominated the BapEq levels. The contribution of BaP to total carcinogenic activities was almost in range from 52.7 to 69.3% and DahA from 7.2 to 15.91%. Note that the carcinogenic risks for humans was the highest at LAZ site due to strong impact from the Kolubara mining-industrial complex, consisting of coal mine, thermal power plant and other facilities. The source emission of PAH in air at LAZ were traffic from the heavy-duty vehicles, stationary sources and coal combustion as a significant source emission (Cvetković et al., 2015).

Table 2. *Relative contribution of individual PAHs to total carcinogenic activities*

Sampling site	Type of sampling site	BaP		DahA	
		H	NH	H	NH
BG-FOM	urban /residential/traffic	63.70	53.89	12.75	49.08
BG-VRA	urban/traffic/residential	58.77	54.81	10.34	15.17
BG-GZ	urban/traffic	60.67	55.03	9.67	15.37
BG-OBR	suburban/industry	55.64	52.70	15.51	15.50
BG-LAZ	suburban/ industry	69.30	63.37	7.85	10.86
BG-SLA	urban/traffic	66.74	60.89	7.38	8.43
BG-GRA	rural/industry	63.06	57.50	9.14	11.09
SMEDEREVO	urban/residential/industry	59.18	57.75	15.91	51.58
SUBOTICA	urban/residential	62.68	66.61	14.43	7.20
NOVI SAD	urban/residential;urban/traffic; urban/industrial	63.94	64.47	8.36	15.84

CONCLUSION

This paper summarized the results obtained in different studies performed in Belgrade and Serbia during 2008 to 2015. According to the obtained results the highest PAH concentration associated with PM_{10} were found at LAZ, followed by Subotica and Smederevo and the lowest at Novi Sad. The PAH have shown seasonal trends with highest concentration during the heating season. The highest average total PAH concentration recorded at suburban industrial location (LAZ) and it was 97.75 ng/m^3 and the lowest 1.21 ng/m^3 at urban site (Novi Sad) in non-heating season. The BaP was concentration very often above target value during both sampling seasons and ranged from 0.09 ng/m^3 (BG-FOM-NH) to 8.9 ng/m^3(at LAZ in heating season). Health risk assessment (BaPeq value) showed that the most negative impact was found at the suburban industrial location (12.96 ng/m^3), followed by urban (11.36 ng/m^3) and urban industrial site (10.64 ng/m^3). The highest carcinogenic risks for

humans were obtained at LAZ due to traffic related source of diesel and gasoline emissions that contribute with more than 50% in both seasons, followed by stationary emission with more than 35% and biomass burning less than 11% and the lowest at Novi Sad. BaP and DahA dominated the BapE levels. The contribution of BaP to total carcinogenic activities was almost in range from 52.7 to 69.3% and DahA from 7.2 to 15.91%. Results presented in this study provide very important information about level of PAH in ambient air in Serbia in order to estimate the health risks for humans.

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REFERENCES

1. Agudelo-Castaned D. M., Teixeira E.C. 2014. Seasonal changes, identification and source apportionment of PAH in PM1.0, Atmospheric Environment, 96, 186-200
2. Akyüz M., Çabuk H. 2008. Particle-associated polycyclic aromatic hydrocarbons in the atmospheric environment of Zonguldak, Turkey, Science of the Total Environmental, 405, 62-70
3. Akyüz, M., Çabuk, H., 2010. Gaseparticle partitioning and seasonal variation of polycyclic aromatic hydrocarbons in the atmosphere of Zonguldak, Turkey, Science of the Total Environment, 408, 5550-5558.
4. Albuquerque M., Coutinho M., Borego C. 2016,Long-term monitoring and seasonal analysis of polycyclic aromatic hydrocarbons (PAHS) measured over decade in the ambijent air of Porto, Portugal, Science of the Total Environment, 543,439-448
5. Boström, C.E., Gerde, P., Hanberg, A., Jernström, B., Johansson, C., Kyrklund, T.,Rannug, A., Törnqvist, M., Victorin, K., Westerholm, R., 2002. Cancer risk assessment, indicators and guidelines for polycyclic aromatic hydrocarbons in the ambient air. Environmental Health Perspectives, 110, 451-488
6. Callen M.S., Lopez, J.M., Iturmendi, A., Mastral, A.M., 2012. Nature and sources of particle associated polycyclic aromatic hydrocarbons (PAH) in the atmospheric environment of an urban area. Environmental Pollution, 30, 1-9
7. CEN, 1998. Air Quality. Determination of PM10 Fraction of Suspended Particulate Matter. Reference Method and Field Test Particulate to Demonstrate Reference Equivalence of Measurement Methods Brussels, EN 12341
8. Cristale, F.S. Silva, G.J. Zocolo, M.R.R. Marchi, 2012. Influence of sugarcane burning on indoor/outdoor PAH air pollution in Brazil, Environ. Pollut., 169 210–216
9. Cvetković A., Jovašević-Stojanović M., Adjanski-Spasić Lj., Matić-Besarabic S., Marković D.A. 2010. Seasonal variation of benzo(a)pyrene in suspended-particle in Belgrade City, Serbia, Chemical Industry & Chemical Engineering Quarterly 16(3) 259-268
10. Cvetković A., Jovašević-Stojanović M., Marković D., Ristovski Z., 2015a. Concentration and source identification of polycyclic aromatic hydrocarbons in the metropolitan area of Belgrade, Serbia, Atmospheric Environment, Volume 112, 335-343
11. Cvetković A., Jovašević-Stojanović M, Matić-Besarabić S., Marković D.A., Bartoňová A., 2015b. Comparison of sources of urban ambient particle bound PAHs between non-heating seasons 2009 and 2012 in Belgrade, Serbia, CICEQ, 21 (1-2), 211-220
12. EEA 2012, Air quality in Europe-2012, EEA Report No 4/2012, doi:10.2800/55823
13. EEA 2013, Air quality in Europe-2013, EEA Report No 9/2013, doi:10.2800/92843
14. EEA 2014, Air quality in Europe-2014, EEA Report No 5/2014, doi:10.2800/22775
15. EEA 2015. Air quality in Europe-2015, EEA Report No 5/2015, doi:10.2800/62459
16. EEA 2015a, Air Quality e-Reporting Database (http://www.eea.europa.eu/data-and-maps/data/aqereporting) accessed 4 November 2015
17. EEC, 1999. European Council Directive 1999/30/EC, Official Journal L 163, 41-59
18. Garrido A., Jim P., Jimenez-Guerrero P., Ratola N., 2014. Levels, trends and health concerns of atmospheric PAHs in Europe, Atmospheric Environment, 99, 474-484
19. IARC, 2013. International Agency for Research on Cancer, 2013. Agents Classified by the IARC Monographs. http://monographs.iarc.fr/ENG/Cassification/index.php (assessed October 2016)
20. ISO 12884:2000, Ambient air — Determination of total (gas and particle phase) polycyclic aromatic hydrocarbons — Collection on sorbent-backed filters with gas chromatographic/mass spectrometric analysis
21. Jovičić N., Radonić J., Sekulić Turk M., Vojinović Miloradov M., Popov S., 2013. Identification of emission sources of particle-bound polycyclic aromatic hydrocarbons in the vicinity of the industrial zone of the city of Novi Sad, Chem ind. 67 (2) 337-348

22. Kassomenos P.A., Vardoulakis S., Chaloulakou A., Paschalidou A.K., Grivas G., Borge R., Lumbreras J., 2014. Study of PM_{10} and $PM_{2.5}$ levels in three European cities: Analysis of intra and inter urban variations, Atmospheric Environment, 87, 153-163
23. Katsoyiannis, A.J. Sweetman, K.C. Jones, 2011. PAH molecular diagnostic ratios applied to atmospheric sources: a critical evaluation using two decades of source inventory and air concentration data from the UK, Environ. Sci. Technol., 45 (20) 8897–8906
24. Knafla, A., Phillipps, K.A., Brecher, R.W., Petrovic S., Richardson M., 2006. Development of a dermal cancer slope factor for benzo(a)pyrene. Regulatory Toxicology and Pharmacology, 45, 159-168
25. Lai C., Lee C.L., Zeng K.Y., Huang H.C., 2011. Seasonal variation of atmospheric polycyclic aromatic hydrocarbons along the Kaohsiung coast, Journal of Environmental Management 92, 2029-2037
26. Mantis, J., Chaloulakou, A., Samara, C., 2005. PM10-bound polycyclic aromatic hydrocarbons (PAHs) in the Greater Area of Athens, Greece, Chemosphere, 59, 593-604
27. Okuda T., Kazuki Okamoto A., Shigeru Tanaka A., Zhenxing Shen B, Yuemei Han B, Zongquan Huo 2010. Measurement and source identification of polycyclic aromatic hydrocarbons (PAHs) in the aerosol in Xi'an, China, by using automated column chromatography and applying positive matrix factorization (PMF) Science of the Total Environment 408, 1909–1914
28. Pascal M., Corso M., Chanel O., Declercq C., Badaloni C., Cesaroni G., Henschel S., Meister K., Haluza D., Martin-Olmedo P., Medina S., 2013. Assessing the public health impacts of urban air pollution in 25 European cities: Results of the Aphekom project, Science of The Total Environment, 449, 390-400
29. Pribylova p., Kares r., Boruvkova j., Cupr P., Prokes R., Kohoutek J., Holoubek I., Klanova J., 2012. Levels of persistent organic pollutants and polycyclic aromatic hydrocarbons in ambient air of Central and Eastern Europe, Atmospheric Pollution Research, 3, 494–505
30. Ratola N., Alves A., Lacorte S., Barceló D., 2012. Distribution and sources of PAHs using three pine species along the Ebro River,Environ. Monit. Assess., 184 (2) 985–999
31. Teixeira, E.C., Mattiuzi, C.D.P., Feltes, S., Wiegand, F., Santana, E.R.R., 2012. Estimated atmospheric emissions from biodiesel and characterization of pollutants in the metropolitan area of Porto Alegre-RS. An. Acad. Bras. Ciencias 84 (3), 245-261.
32. US EPA U.S. Environmental Protection Agency, 1999. Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Air Using Gas Chromatography/ Mass Spectrometry (GC/MS). Compendium Method TO-13A, second ed.. In: Compendium of Methods for the Determination of Toxic Organic Compounds inAmbient Air Center for Environmental Research Information. Office of Research and Development. U.S. Environmental Protection Agency, Cincinnati, OH.
33. Yang Y., Guo P., Zhang O., Li D., Zhao L., Mu D., 2010. Seasonal variation, sources and gas/particle partitioning of polycyclic aromatic hydrocarbons in Guangzhou, China , Science of the Total Environment, 408, 2492–2500

3.2 PLANETARY BOUNDARY LAYER AND ELEVATED AEROSOL LAYER HEIGHT RETRIEVAL FROM LIDAR SIGNAL IN BELGRADE

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ABSTRACT

The planetary boundary layer (PBL) is the interfacial layer between the Earth's surface and the atmosphere where exchanges of heat, moisture, momentum and pollution take place. An inversion layer forms between the PBL and the free troposphere, trapping pollutants emitted from the surface and inducing high concentrations within the PBL. In this study, we estimate the heights of PBL and elevated aerosol layers in the free troposphere from lidar measurements in Belgrade. The measurements were made on July 6, 2014. During this period, synoptic conditions were favorable for a Saharan dust intrusion episode and the presence of Saharan dust was confirmed by DREAM model forecasts and satellite data. We analyzed the PBL evolution and the elevated dust layer height, based on lidar measurements. Additionally, we compared the PBL heights retrieved from lidar signal to those estimated from radiosounding from a nearby weather station.

INTRODUCTION

The planetary boundary layer (PBL) is the part of the troposphere which is directly influenced by the Earth's surface and it plays an important role in atmospheric processes and dispersion of air pollutants. The PBL quickly responds to surface forcing, producing turbulent eddies of different temporal and spatial scales. The PBL height, ranging from as low as a few hundred meters to a few kilometers, is variable in space and time, showing diurnal and seasonal variabilities. In general, a convective boundary layer (CBL) develops with the sunrise by the sun-induced heating of the surface, reaching a steady state in the afternoon. With the sunset, due to surface cooling, a surface inversion is formed. The CBL remains as a residual layer until the development of a new mixing layer on the following day. Turbulence within the PBL is responsible for mixing and dispersion of pollutants, while air pollution concentrations in the PBL are generally higher than those in the free troposphere (Stull, 1988). Understanding of PBL structure, evolution and underlying dynamics is essential in weather prediction, climate and air quality studies.

In order to quantify the PBL height, a variety of methods can be used depending on available measurements (Emeis et al, 2008). Differences between PBL and free troposphere can be observed using standard radiosounnding measurements which provide vertical profiles of thermodynamic quantities and wind. Lidar observations using atmospheric aerosol as a tracer can be used to determine heights of both PBL and elevated aerosol layers if present in the atmosphere.

METHODOLOGY

Detection of PBL and Elevated Aerosol Layer Heights from Lidar Measurements

Aerosol lidar is an active remote sensing instrument which measures vertical profiles of the backscattered light from atmospheric constituents. Regular measurements using a Raman lidar have been performed since February 2014 at Institute of Physics Belgrade (44.86 N, 20.39 E, 89 m asl). The instrument operates as a Nd:YAG laser emitting 5 ns pulses with a 20 Hz repetition rate at wavelengths of 1064, 532 and 355 nm. The receiving system operates at two wavelengths, detecting elastic backscatter signal at 355 nm and inelastic Raman signal at 387 nm in analog and photon-counting mode. In this study, only the elastic backscatter analog signal at 355 nm was analyzed. The lidar signal, obtained with high vertical (7.5 m) and temporal (1 minute) resolutions can be used for detection and characterization of aerosols and PBL. This type of continuous measurements can provide insights into shorter-term PBL behavior and finer resolution of aerosol layer structure.

There are several methods for estimating PBL height based on lidar measurements (Sicard et al, 2006, Baars et al, 2008). The gradient method was used in this study to determine the position of the strongest gradient of the aerosol vertical distribution, associated with the PBL height (Flamant et al, 1997). The first step in analyzing the

signal was background correction of the raw signal. Then the vertical profiles of the range corrected signal (RCS) were smoothed by applying the Savitzky-Golay filter. The position of a strong negative peak which can be identified as the absolute minimum of the RCS's derivative, determines the PBL top height. Other local minima in the signal derivative, with absolute values above a specified threshold and with transition intervals including a minimum of five points, are associated with elevated aerosol layer top heights (Flamant et al, 1997).

Detection of PBL Height Using the Richardson Number Method

The Richardson number method is commonly used for PBL height estimation from radiosounding measurements (Stull, 1988). Weather data, provided by the use of radio sounding two times each day, at 00 and 12 UTC, were obtained from a weather station (Belgrade Košutnjak, WMO number 13275), located 10 km away from the lidar measurement site at 203 m altitude. Since meteorological data are available at discrete heights, a bulk Richardson number is used to calculate PBL height from temperature and wind observations. The Richardson number is defined as (Stull, 1988):

$$R_{ib} = \frac{g[z - z_0][\theta(z) - \theta(z_0)]}{\theta(z)[u(z)^2 + v(z)^2]}$$

where g is acceleration due to gravity, z_0 is the altitude of the weather station, $\theta(z)$ is the potential temperature and $u(z)$ and $v(z)$ are zonal and meridional components of wind. The layers in which it is above the critical value of 0.21 (Vogelezang and Holtslag, 1996; Menut et al, 1999) are considered to be above the PBL.

Satellite Measurements and Models

To identify the type of aerosols present in the observed layers, satellite measurements, numerical model of atmospheric dust cycle and a backtrajectory model were used.

CALIPSO (Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observations) satellite carries CALIOP (Cloud-Aerosol LIdar with Orthogonal Polarization) lidar for aerosol and cloud studies. CALIPSO Aerosol Subtype product (Omar et al, 2009) was used to estimate the type of aerosols in the layers present and their vertical extent near the measurement site.

Dust Regional Atmospheric Model (DREAM) embedded into the NCEP/NMME non-hydrostatic atmospheric model is capable of simulating and predicting atmospheric cycle of mineral dust aerosol (Nickovic et al, 2001). The model was used to provide the Saharan dust forecast for the period of measurements, producing dust load over Europe and time evolution of dust concentrations in Belgrade. Model domain covers Saharan and Middle East dust sources, as well as a large part of the European continent with horizontal resolution of 1/5° (~ 30 km) and 28 vertical levels.

Airmass backtrajectory analysis was performed using Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (http://ready.arl.noaa.gov/HYSPLIT.php, Draxler et al, 2015) with Global Data Assimilation System (GDAS) meteorological data. The HYSPLIT model was used to determine the origin of airmasses present over the measurement site.

RESULTS AND DISCUSSION

Lidar measurements in Belgrade were made during a Saharan dust intrusion period over July 4-6, 2014, as forecasted by the DREAM model (Figure 1). Synoptic conditions enabled the dust plume to reach Belgrade from south-west with maximum concentrations on July 6. On the same day CALIPSO satellite ground track distance from measurement station was about 70 km minutes before 12 UTC. The presence of a polluted dust layer intruding into the PBL below 1 km and reaching approximately 2.5 km height was confirmed by CALIPSO aerosol subtyping algorithm (Figure 1).

The time series of RCS vertical profiles at 355 nm, measured using Belgrade lidar on July 6, 2014, are presented in Figure 2. These data, taken in two measurement sessions: during the daylight (from 10:15 UTC until 15:25 UTC) and after the sunset (from 19:45 until 22:50 UTC), were analyzed for the PBL evolution and presence of elevated aerosol layers. At the beginning of the measurement period, the CBL was still not fully developed. An increase in PBL height with some fluctuations, attributed to convection, can be observed until 12:30 UTC. The PBL height was then relatively stable at about 1700 m until 13:30 UTC, when it started decreasing, reaching 700 m at about 23 UTC. It should be noted that clouds were forming above 6 km height around 14 UTC. One-hour averaged values of PBL height around noon and during the last hour of the measurements were calculated for

comparison with results from radiosounding. The obtained values from lidar measurements (1270 m around noon and 709 m in the evening) were lower than those from radiosounding (1600 m and 810 m).

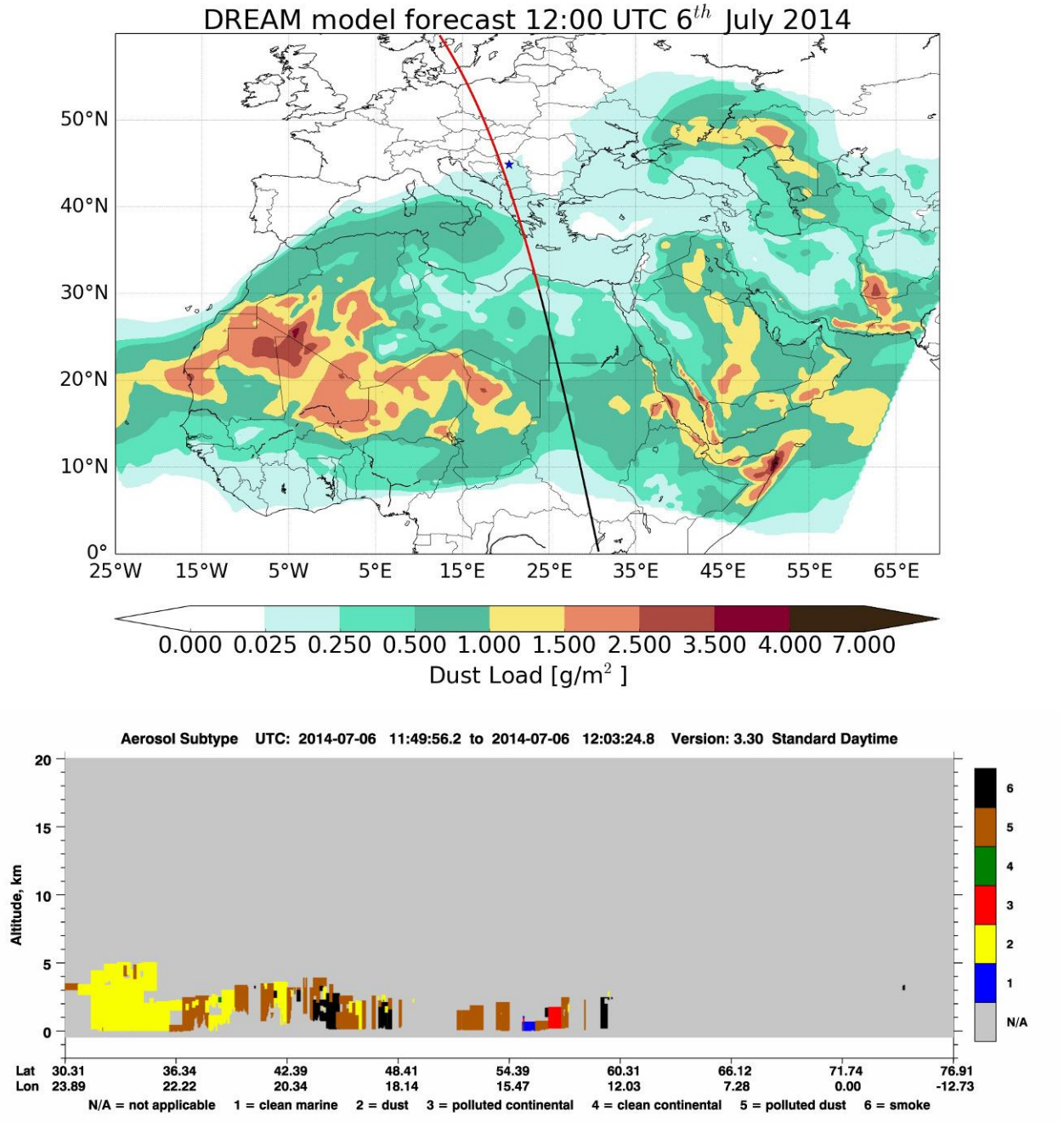

Figure 1. *(top) DREAM-simulated dust load (in g/m^2) over Europe and Northern Africa with CALIPSO overpass ground track (red and black line) close to Belgrade (blue star). (bottom) CALIPSO aerosol subtypes along the red section of the ground track.*

The difference of results obtained from radiosounding and lidar can be due to local effects at two measurement sites and differences in the methods used. Different surface properties and elevations of measurement sites influence the heat and momentum fluxes contributing to the PBL development. Lidar is operated on a fixed location during the whole period of measurement, providing information on vertical column of air directly above the instrument. Radiosounding profiles are affected by the horizontal drift of the instrument caused by wind and depend on whether the ascent is made in a thermal or between thermals (Stull 1988). A further study involving

more cases of measurements will be conducted in the future, to provide more information on the agreement of the two methods in different meteorological conditions, seasons and times of day.

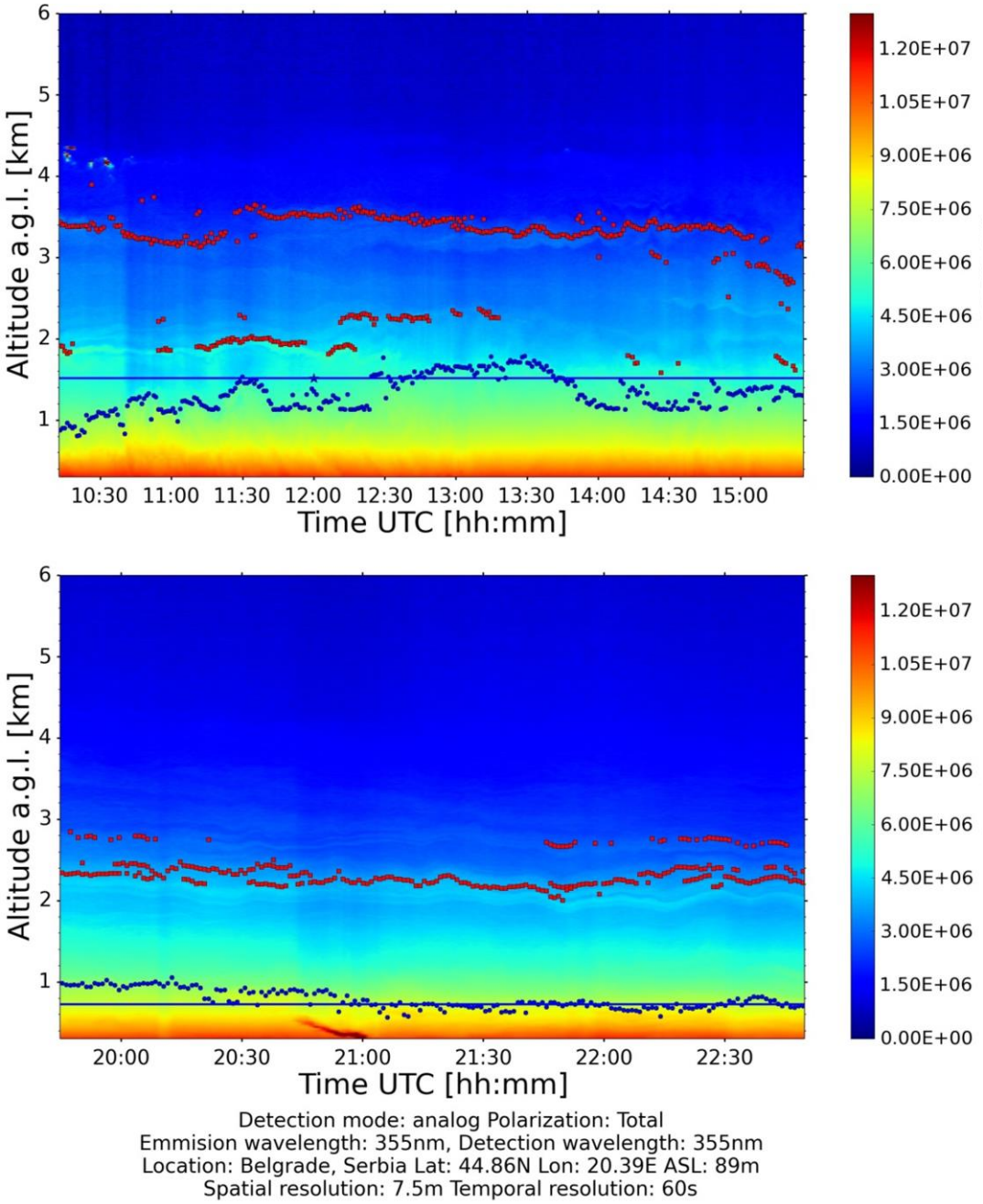

Figure 2. *Temporal evolution of PBL (blue) and elevated aerosol layers (red). Colormaps represent the lidar RCS at 355nm on July 6 2014. Horizontal blue lines represent PBL height retrieved from radiosounding at 12 UTC (top) and 00 UTC (bottom).*

An elevated aerosol layer, with top height decreasing from 3.5 km at the beginning of the lidar measurements to below 3 km towards evening, was evident in Figure 1. Backtrajectories at 12 UTC and 21 UTC show air mass arriving from within the dust plume in the south-west and reaching Belgrade at 2000 m height (Figure 3). Both DREAM forecast and CALIPSO measurements at 12 UTC suggest the presence of dust at these altitudes, as well as its intrusion into the PBL. To confirm this with our lidar measurements, further investigation is needed, that would involve analysis of changes in aerosol optical properties in the PBL. The DREAM model simulation also

shows a gradual decrease of the layer height of about 500 m in the evening (Figure 4), confirmed by the lidar measurements.

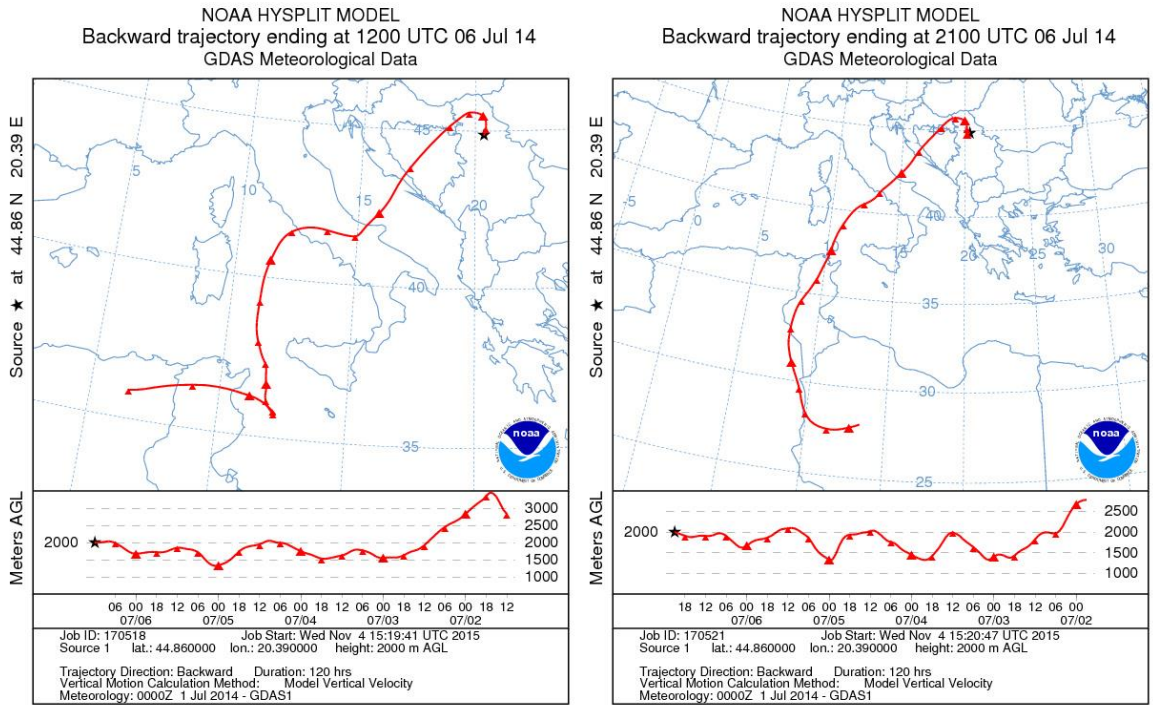

Figure 3. *HYSPLIT backtrajectories ending at 12 UTC (left) and 21 UTC (right) on July 6, 2014 at 2000 m a.g.l (Belgrade, 44.86N, 20.39E).*

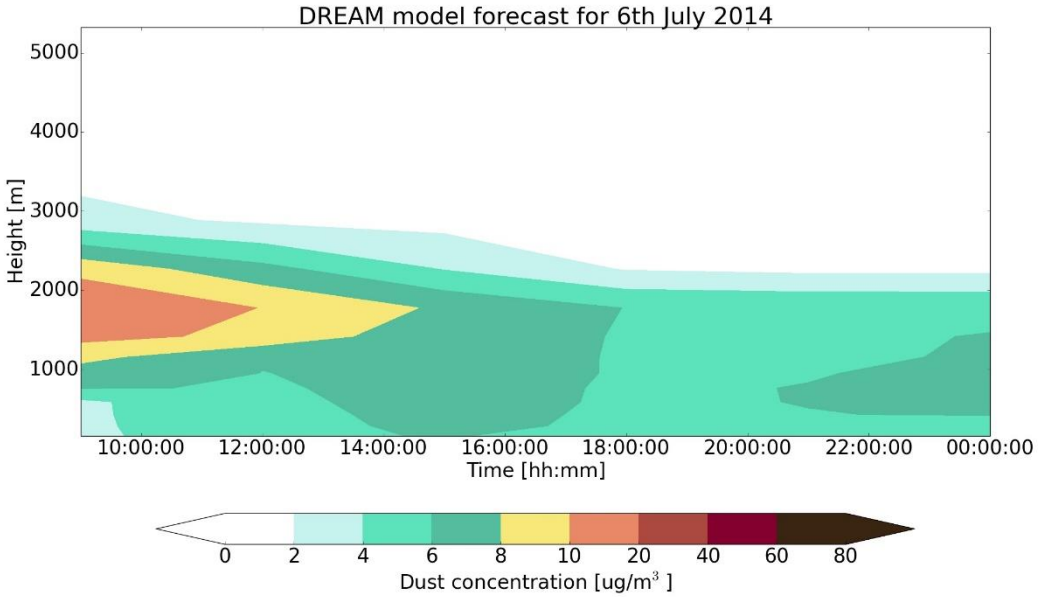

Figure 4*. Time evolution of vertical dust concentrations (in μg/m^3) over Belgrade on July 6, 2014, simulated by DREAM model.*

CONCLUSIONS

Ground-based aerosol lidar measurements were made during a dust intrusion episode in Belgrade. The gradient method was used for identification of PBL and elevated aerosol heights. This method provided PBL height information in higher temporal and spatial resolution than radiosounding measurements. By this means, the diurnal cycle of the PBL was observed. In the morning, with surface heating, the PBL started increasing until reaching a stable height of about 1700 m around 13 UTC. After an hour, the PBL height started decreasing gradually to about 700 m at 23 UTC. The gradient method showed lower PBL heights than those estimated from radiosounding from a weather station 10 km away at 12 UTC and 00 UTC.

The DREAM model and CALIPSO satellite data showed a dust layer reaching 3.5 km height and intruding into the PBL. Based on lidar observations, this layer was present during the whole period of measurements, but decreasing in height by about 500 m in the afternoon. The origin of airmasses coming from Northern Africa was confirmed by backtrajectory analysis with HYSPLIT. Influence of dust intrusion on PBL evolution will be further investigated in the future.

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REFERENCES

1. Baars, H., Ansmann, A., Engelmann, R., Althausen, D. 2008. Continuous monitoring of the boundary-layer top with lidar, Atmos. Chem. Phys., 8, 7281–7296, doi: 10.5194/acp-8-7281-2008.
2. Draxler, R.R., Rolph, G.D. 2015. HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website (http://ready.arl.noaa.gov/HYSPLIT.php). NOAA Air Resources Laboratory, Silver Spring, MD.
3. Flamant, C., Pelon, J., Flamant, P. H., Durand, P. 1997. 'Lidar determination of the entrainement zone thickness at the top of the unstable marine atmospheric boundary-layer', Boundary-Layer Meteorol. 83, 247–284.
4. Emeis, S., Schafer, K., Munkel, C. 2008. Surface-based remote sensing of the mixing-layer height – a review, Meteorologische Zeitschrift, Vol. 17, No. 5, 621-630.
5. Menut, L., Flamant, C., Pelon, J., Flamant, P. H. 1999. Evidence of interaction between synoptic and local scales in the surface layer over the Paris area, Boundary Layer Meteorol., 93, 269–286, doi:10.1023/A:1002013631786.
6. Nickovic S., Papadopoulos, A., Kakaliagou O., Kallos G. 2001. Model for prediction of desert dust cycle in the atmosphere. J. Geophys. Res., 106, 18113-18129.
7. Omar, A. H., Winker, D. M., Kittaka, V., Vaughan, M. A., Liu, Z., Hu, Y., Trepte, C. R., Rogers, R. R., Ferrare, R. A., Lee, K., Kuehn, R. E., Hostetler, C. A. 2009. The CALIPSO Automated Aerosol Classification and Lidar Ratio Selection Algorithm, Journal of Atmospheric and Oceanitc Technlogy, 26, 1994-2014, doi: 10.1175/2009JTECHA1231.1.
8. Sicard, M., Pérez, C., Rocadenbosch**, F.,** Baldasano, J. M., García-Vizcaino, D. 2006. Mixed-Layer Depth Determination in the Barcelona Coastal Area From Regular Lidar Measurements: Methods, Results and Limitations,Boundary-Layer Meteorology Volume 119, Issue 1 , pp 135-157, doi:10.1007/s10546-005-9005-9.
9. Stull, R. B. 1988. An Introduction to Boundary Layer Meteorology, Kluwer Acad., Dordrecht, The Netherlands.
10. Vogelezang, D. H. P., Holtslag, A. A. M. 1996. Evolution and model impacts of alternative boundary layer formulations, Boundary Layer Meteorol., 81, 245–269, doi:10.1007/BF02430331.

3.3 LAND USE REGRESSION FOR PARTICULATE MATTER MAPPING: DATA COLLECTION TECHNIQUES, CHOICE OF PREDICTOR VARIABLES AND POSSIBILITIES FOR VALIDATION AND IMPROVEMENT OF MAPS

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ABSTRACT

In this paper, techniques needed for successful application of land use regression modeling (LUR) of particulate matter (PM) are discussed and summarized. Some of the techniques are applied to create $PM_{2.5}$ map for the city of Belgrade, using a multicity European LUR model (Wang et al, 2014).

Data collection techniques are described along with issues that are often encountered in practice, such as temporal and spatial variability (Dos Santos-Juusela et al, 2013; Liu et al, 2015; Weichenthal et al, 2015). Temporal limits of the typical LUR models are also presented. Since quality of data collection largely depends on placement of measuring points, strategies for optimal placement of fixed monitoring devices (Wang et al, 2013), choice of routes when mobile devices are used (Weichenthal et al, 2015; Mueller et al, 2016) and choice of total number of sampling points are discussed.

Important LUR concepts such as types of predictor variables and procedures for choosing an optimal set of predictor variables are described in detail. Since traffic related predictors are often the most important predictor variables for PM mass concentration and researchers often do not have detailed traffic counts and sophisticated model at their disposal, simplified models may be needed. One such model is developed and presented for the city of Belgrade. Possibilities for improvement and validation of the obtained pollution maps, such as data assimilation (Lahoz, 2014), are presented.

INTRODUCTION

LUR modeling is a statistical modeling technique, that has in recent years become widely used method for air pollution modeling (Liu et al, 2015; Johnson et al, 2010; Mueller et al, 2015; Rivera et al, 2012; Zhang et al, 2015). The technique was pioneered by Briggs (Briggs et al, 1997) for purposes of mapping based on data available in local GIS databases. It should be noted that while LUR is statistical technique, it may include physical modeling, e.g. in the calculation of predictor variables. Predictor variables can include concentration fields obtained via physical model (Marjovi et al, 2015), or meteorological data (Liu et al, 2015), effectively blurring, to some extent, the line between statistical and physical modeling.

In this paper focus is directed to particulate matter (PM). It is also assumed that mass concentration, divided into fractions according to aerodynamic diameter of a particle, is used as a measure of level of PM pollution. It should be noted that PM has a very diverse and complex chemical composition (Smith et al, 2013) and that even the sites with similar mass concentration of PM may have different chemical composition, which can result in diverse health outcomes (Harrison et al, 2000). However, mass concentration is still a very relevant indicator of air pollution and current regulations and guidelines focus on regulating PM mass concentration, aiming for its steady decrease in the future (Smith et al, 2013).

Development of a LUR model for PM mass concentration requires the following steps:

- Measurement of PM concentration in a large number of points, distributed in the area of interest. In each of the measuring points the value of the predictor variables is known either through measurements, or derived from some underlying model. A more correct term at this step would be possible predictor variables or candidate predictor variables, because not all of them might end up being used in the final model. Predictor variables may include traffic counts, distance to the road network, amount of green and natural surfaces in the vicinity of a point, value of background concentration relevant for studied area etc.
- Measurements of mass concentration are correlated with the predictor variables, resulting in a multilinear regression formula which establishes a quantitative relation (multilinear) between predictor variables and mass concentration of PM. In this step, the size of initial set of predictor variables is reduced, typically based on the amount to which each predictor variable explains the variability of the measured data.
- A map of PM mass concentration is produced, based on the multilinear regression formula derived in the second step and using only values of predictor variables at each point of interest, without the need for additional measurements

In a way, the LUR technique is an interpolation technique which instead of using higher order polynomials of spatial variables for interpolation uses a linear polynomial of predictor variables for interpolation. This approach thus may even allow spatial extrapolation of a model to other areas of interest not used for development of model, as long as ranges of predictor variables used for mapping are consistent with ranges of predictor variables used for development of LUR model. Such extensions of a LUR model are reasonable to make if considered areas have similar sources of air pollution and similar topology.

Further sections of this paper elaborate on each of the steps of LUR modeling. In the second section data collection techniques used for mapping of PM, such as types of measuring points, optimal number of measuring points and strategies for placement of measuring equipment are described. In the third section, the types of predictor variables and algorithms used for choosing an optimal set of predictor variables are described. In this section modeling efforts needed to obtain traffic counts, in absence of higher quality model is briefly discussed. In the fourth section the process of map creation and some techniques for measuring quality of maps and improvement of maps are described. Some of the discussed aspects of LUR modeling are illustrated using a $PM_{2.5}$ map for the city of Belgrade.

DATA COLLECTION TECHNIQUES FOR MAPPING OF PARTICULATE MATTER

In order to be able to conduct meaningful health studies it is desirable to have high spatial resolution maps. Obtaining high resolution maps usually requires additional efforts in data collection. In the absence of high resolution data exposure can still be estimated, but with higher uncertainty. As an example of difficulties encountered by researchers regarding limited spatial resolution consider a recent study on influence of PM mass concentration on low-birth weight babies (Harris et al, 2014) conducted in New York. Since there was no high quality exposure data for all participants, authors had to use either home address of a mother and nearest measuring point for calculating exposure or average value *for the entire county*. In a lack of better estimate, background concentrations are sometimes used for exposure estimates, e.g. for study of correlation between exposure and background levels (McCreddin et al, 2015).

Researchers usually have available some, but often not sufficient, amount of PM mass concentration data for purposes of high resolution mapping. What is typically available is data from state and local monitoring networks for air pollution. While data from fixed monitoring networks is of high quality, due to high cost instruments, their maintenance and calibration, typically there is a very limited number of stations available. Due to this, they lack spatial coverage. It should be noted that mapping procedures typically involve fixed data points, and that measuring points obtained in other manners, e.g. measurements from moving instruments, need to be preprocessed in order to be used. For example, if data points are obtained via an instrument that is located in a vehicle taking various routes along city, such measuring points can be reduced to fixed points by averaging both spatially and temporally, and using for example the midpoint of a route portion as the location of a data point. Spatial resolution and variability are not the only concern in the process of data collection. Temporal resolution and temporal variability also need to be considered during data collection. Issues stemming from temporal variability can, and are typically remedied using data from fixed stations (Weichenthal et al, 2015; Saukh et al, 2015).

In order to improve spatial coverage researchers must utilize additional resources, e.g. by deploying temporary networks or carrying out data collecting campaigns and not only rely on data collected from traditional monitoring networks. The term network is used in broad sense here, since it may describe either a fixed network of low cost sensors (Rada, 2012), or a network of personal sensors (which are of course not fixed in space), or several vehicles carrying high quality equipment along city routes (Weichenthal et al, 2015), or even a fleet of low cost sensors mounted on public transport vehicles (Mueller, 2016). Data points from such instruments are usually available every few minutes and each data point is geolocated.

The output of deployed sensors can be improved by frequent calibration or even on-the-fly calibration (Saukh et al, 2015) which uses measurement from nearby fixed stations. If a large number of sensors is deployed, it is possible to perform quick calibration updates to the whole fleet of sensors. Each time a sensor passes by a fixed station it can be calibrated (one-hop calibration), or each time a sensor passes near more recently calibrated sensor it is calibrated (two-hop calibration) (Saukh et al, 2015). While such “rendezvous” calibration was applied to gas sensors, instruments measuring PM could potentially benefit from a similar scheme. In addition, instruments measuring PM would benefit from frequent maintenance, such as replacement of internal filters,

check of internal laser and similar. Proximity to a fixed monitoring station can be used if not for calibration then for improvement of estimates of long term averages in presence of high temporal variability in measurements. During longer campaigns, there are usually several readings located in the same place but during different days or time of day. Such measurements usually have high temporal variability, which may lead to wrong estimates of the long term average value, if only simple averaging is performed. Since relations between measured value and long term average are much better known for fixed stations, measurements having high temporal variability can be appropriately scaled and then used for long term average estimates. Since only the ratio between currently measured value and long term average is of interest it is not strictly necessary to use PM measurements. Other quantities can be used to obtain this ratio, such as temperature since it is known that temperature is an important predictor of day-to-day fluctuations e.g. in ambient ultrafine particle concentration (Weichenthal et al, 2015).

When the set of input data is diverse, and has been collected using different approaches it is necessary to have a method of assembling, or fusing, the data together. Such methods are under development (Lahoz, 2014; Schneider, 2015) and can bring additional quality and value to each member of input set. Spatial resolution of maps obtained using additional data from personal monitors is sometimes referred to as personal level resolution (Zambelli, 2015). Data fusion techniques are illustrated in the fourth section of this paper.

Placement of nodes in temporary network in urban area has a high impact on the quality of maps. However, a larger number of nodes doesn't necessarily translate to a higher quality map, see for example (Ryan, 2007) where the authors, somewhat surprisingly, observed a negative trend in explained variation with increased number of measuring points, further illustrating need for careful placement of sensors. When a temporary network of sensors is deployed, it typically includes 20 to 100 sensors (Li et al, 2014). (Wang et al, 2014) used 20 urban sites and 20 monitoring sites per area resulting in total around 400 measuring points for creation of LUR model. The approach used by Wang is somewhat non-orthodox because LUR is typically developed and used for a single site. Some guiding principles for placement of fixed sensors are the following (Wang et al, 2013): Firstly, air pollution maps are usually created for purposes of estimating exposure, e.g. exposure of participants of the health study. In that case, sensors can be placed, or point measurements taken, near the place of residence of participants of the health study (Rivera et al, 2012). The advantage of point measurements is that they can be taken using higher quality equipment. Since estimation of exposure is the main goal, points which correspond to high levels of pollutant, such as road junctions, but are not a significant factor in exposure, due to steep gradients away from junction, or participants only spend brief amounts of time in the vicinity of junction, can be omitted. However, these kind of points should not be automatically discarded as outliers if they are relevant for estimation of exposure. If studying the air pollution near a road junction is of interest, then it is not sufficient to take only one measuring point, since this kind of measurement would not capture steep gradients of air pollution in such location.

In addition to avoiding accidental measurement of outliers, care should be taken to include various urban regions and to place sufficient number of sensors in each region. For examples, sensors should be equally placed in areas of high traffic counts, medium and low traffic counts. Sites having low air pollution which are to be used as background sites should be carefully selected, and should not be influenced by local traffic and other local sources of air pollution (e. g. domestic heating, district heating facilities, industry etc.). Some LUR models may use the background level of air pollution as a predictor variable, and in that case it is needed to track the background level in several regions of urban area of interest.

If previous iterations of maps are available, more precise boundaries of urban regions can be derived, by using clustering techniques, such as kernel K-means method (Hu et al, 2013). These techniques enable one to partition an urban area of interest into clusters, based on an air pollution map and number of desired clusters.

TYPE AND CHOICE OF PREDICTOR VARIABLES

It is possible to classify predictor variables in several ways. The most important way of classification of predictor variables is according to the physical process the predictor variable can be associated with. Physical processes associated to air pollution can be classified as emission, dilution and deposition processes of particular air pollutants (Ghassoun et al, 2016). Predictor variables associated with emission could be the 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), shortest distance to the sea, since sea is a significant source of aerosols, etc. The process of dilution is related to amount of air volume in certain area, and is especially important near high traffic areas, where buildings can create narrow street canyons where air pollutant is diluted in smaller volume of

air. Buildings can also provide an effective barrier to propagation of PM. Predictor variables associated with the process of deposition typically take into account areas where emission is not a dominant physical process, such as green and natural areas, recreational areas (e.g. the total area of parks in a buffer, total area of water surface in buffer etc.). The main purpose of physical classification of predictor variables in the context of LUR modelling is the choice of the sign of the coefficient associated with the predictor variable in regression equation. The sign of the predictor variable can either be specified in advance, or either sign can be allowed in the algorithm, and then only models with clear physical meaning of predictor variable sign can be accepted (Zhang et al, 2015). In addition, physical classification motivates an informed choice of an initial set of predictor variables, since only variables with clear physical interpretation are included and use of adjusted R-squared value as the only guidance is avoided.

Predictor variables can also be classified according to the way in which they are calculated. Calculations are done using GIS software and available layers. Most common GIS operations are buffer intersection and nearest distance to layer feature. For example, if layer contains multiple polygons describing boundaries of green and natural areas, buffer type predictor variable in certain point A is formed by intersecting a circle of a specified size (the centre of circle is in point A) with all polygons in layer, and then calculating area of polygons within the buffer. Similarly, the length of intersected features from layer is a typically used (for example the length of roads in buffer).

The most common types of buffers are 2D circular buffers but it is also possible to use 3D buffers (cylindrical buffers). If 3D data about geometry of buildings is available such buffers can be used to calculate additional predictor variables, e.g. volumetric density as ratio of built environment and air (this predictor is related to the dilution process). It should be noted, however, that if such high quality 3D input data is available, other types of modeling (diffusion models) may be a better option than LUR modelling. Some authors, even use irregularly shaped buffers (wind rose shape) to model pollutant dispersion from potential sources (Zhang et al, 2015).

It should be noted that some urban areas need location specific predictor variables. For example, in Barcelona it is reasonable to use predictor variable distance to sea shore (Wang et al, 2014). However, one should not be tempted to directly transfer predictors to another location, for example to use distance to Sava and Danube rivers as predictor for Belgrade, even though riversides are around 153 km long in zone of Master plan of Belgrade. While similar from GIS perspective, the distance to sea shore can be classified as emission variable, while distance to Sava and Danube rivers, is more close to process of deposition and dilution, thus predictors would have different sign in two LUR models.

During the development of LUR model, values of predictor variables are only needed in points where measurements are taken, while during map creation values of predictor variables are needed at each point of map. In an urban area of 10 km by 10 km in size, with a 100 m spatial resolution, each predictor variables need to be calculated at 10^4 points. The number of points in which predictors need to be calculated and feature count of layers directly increase computational cost, which can quickly overrun available resources. In such cases it is necessary to either decrease the map resolution, or use simplified layers with smaller feature counts.

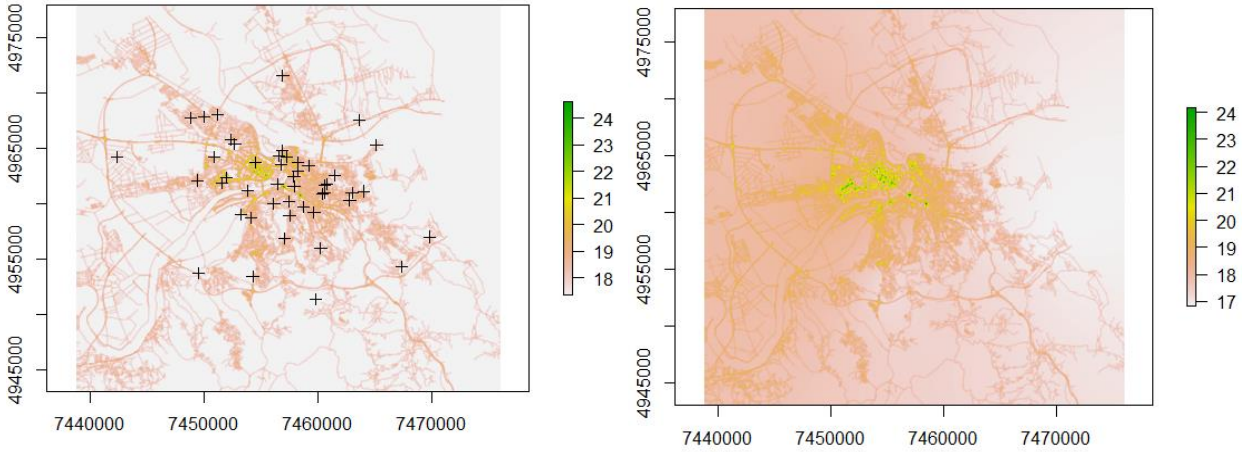
The initial set of predictor variables is formed based on available GIS data and consideration of physical processes characteristic for the considered urban region. The final set of predictors is formed by performing statistical analysis in an iterative process. The first step in statistical analysis is to evaluate a univariate regression for all potential predictor variables. Certain predictors may be explicitly forced to be in the final set, for example value of background concentration. For each of the remaining predictors adjusted R-squared is calculated. Predictors with the highest value of adjusted R-squared is added to the final set of predictors but only if the increase of adjusted R-squared is not less than a certain percentage (e.g. 1% (Wang et al, 2014)). Such constraints are added in order to avoid adding predictors which can only be mathematical artefacts of statistical analysis, thus causing “overfitting” of the model. It should be noted that other methods of selecting the LUR model, besides using adjusted R-squared, also exist but are less widely used. For example, it is possible to generate large number of LUR models based on a fixed size subset of all predictors, and then go through the process of selection using the sign of predictor variables as guidance, high variance inflation factor (Johnson et al, 2010), Akaike information criterion (Zhang et al, 2015), Mallow’s Cp (Johnson et al, 2010) and the estimated mean square error of prediction.

It should be noted that some predictor variables need not be typical GIS variables (derived from geometry of GIS layers) but may be more complex, being the result of additional modelling efforts. Example of such variable is traffic count. City authorities usually have complex models of traffic at their disposal, which are kept up to date

via costly traffic count campaigns. Since up to date traffic model was not at authors disposal when PM map for Belgrade was developed, simple traffic model based on public transport data was developed. The guiding principle during development of this simple model was to make lower bound estimates, such that air pollution would not be overestimated based on traffic counts derived from model. Counts of public transport vehicles were derived by overlapping transport schedules and routes. In a second step, these counts were scaled using linear regression model establishing a relation between bus counts and total traffic. This model was developed based on data from automatic counters which exist on roads in wider area of Belgrade and Serbia. It was noticed that regression line is much steeper when only counters in Belgrade are used, and could result in overestimation of total traffic. Therefore, regression line was derived using all available automatic counters, resulting in a more conservative estimation. Furthermore, since data from counters includes all types of buses (local lines, regional lines etc.) final estimation for Belgrade is more conservative since it only includes public transport.

MAP CREATION AND POSSIBILITIES FOR IMPROVEMENT OF MAPS

Once regression formula is obtained, the map creation process is straightforward. Based on the required spatial resolution of the map, each of the predictor variables is sampled on a regular grid and for each point on grid values of predictors are combined (summed) according to regression formula. Fig. 1a shows the obtained basemap for $PM_{2.5}$, and the approximate locations of low cost sensors which will be placed throughout the area of Belgrade covered by the Master Plan. When the network of sensors becomes active it will provide data about pollutants in near real time, at least once every hour, which will enable production of fused maps. An example of a fused map is shown on fig. 1b, where the observations were simulated using ensemble of Gaussian distributions with mean set to value of basemap in a point of observation and relative standard deviation of 5%.



(a) (b)

Figure 1. *a) Base map for $PM_{2.5}$ [ug/m^3] and position of 47 stations b) Fused map [ug/m^3] (observations were simulated using Gaussian distribution with mean value obtained from basemap and relative standard deviation of 5%)*

It can be observed that while fused simulated observations were very close to the values given by the base map, fused map has different spatial patterns. Note that due to small deviation of simulated measurements from the base map values, range is similar in both maps shown in Fig. 1. Process of data fusion strongly depends on the quality of input data, and it can provide added value only if data input is of high quality.

While the fundamental algorithms behind data fusion process are well understood (Kitanidis, 1997; Isaaks and Srivastava, 1989) they are usually presented having in mind readers with strong background in statistics. Here, all steps of data fusion process are summarized using language more suited to wider audience. The first input to the data fusion algorithm is a base map. The base map is an estimate of the average spatial patterns of a pollutant, intended for further improvement by observations. For example, such a map can be obtained via LUR modelling as described above. The second input to the data fusion algorithm is a relatively small set of additional

measurements which are used to enhance the base map. The first step of the algorithm is to log transform the observations and the values of base map. This is done for purposes of normalizing skewed data, i.e. to achieve distribution closer to Gaussian distribution. This step also ensures that the back transformed data will be positive which is necessary condition for mass concentration.

The next step is to establish a linear regression between the log-transformed observations and log-transformed values of the base map. This linear regression is then used to scale the base map, leading to a regressed map. Note that the initial range of the base map is not relevant once the scaling is performed. The process of regression will reveal the differences between the observations and regression line – residuals. Residuals represent the difference between the observations and the regressed (i.e. scaled) map, which can be either positive or negative. Since the values of residuals are only known at the observation points, it is necessary to interpolate them in order to include them in the final fused map. The type of interpolation which is typically performed in this step is ordinary kriging but other interpolation methods are possible. The kriging procedure takes into account the proximity of the data points when performing interpolation (by using the spatial autocorrelation), and it satisfies B.L.U.E properties (short from Best Linear Unbiased Estimator). The goal of the interpolation is to find best estimate of quantity, in our case residual, using linear estimators. It is desirable to have unbiased estimate, i.e. to have average error of estimation equal to zero. The term Best denotes minimum mean square error of the estimation. Highly optimized libraries implementing kriging algorithm are available in R software environment (R Development Core Team, 2013). Finally, the interpolated residual map is added to the regressed map, and the sum is back-transformed from log space (Denby, 2008).

Once the final fused map is created it should be, as any model, validated. Usually, there is not enough independent observation points to validate the model since points used for development of the fused map cannot be used in its validation. In such cases, leave-one-out cross-correlation is performed, in which one observation points is left out, the fused map is developed based on remaining points, the error calculated for left out point, and then the total error summed for all observation points. Benefit of such a leave-one-out analysis is that, in a way, all measuring points are used for both model development and model validation.

CONCLUSION

In this paper, current practices regarding PM statistical modeling are presented. Each step of land use regression technique was described in details, starting from data collection, the choice of predictor variables, development of regression formula and mapping. A simple traffic model, used as input for PM2.5 predictor variables, was described. Finally, a data fusion process was described and illustrated on the example of map of PM2.5 for Master Plan of Belgrade. Further research will be directed to improvement of steps of the modelling process, such as development of higher quality predictor layers and the collection of a larger number of in situ measurements suitable for high quality mapping.

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REFERENCES

1. Briggs, D. J., Collins, S., Elliott, P., Fischer, P., Kingham, S., Lebret, E. et al, 1997. Mapping urban air pollution using GIS: a regression-based approach, International Journal of Geographical Information Science 11, 699-718.
2. Denby, B., Schaap, M., Segers, A., Builtjes, P. and Horálek, J. 2008. Comparison of two data assimilation methods for assessing PM 10 exceedances on the European scale, Atmospheric Environment 42, 7122-7134.
3. Dos Santos-Juusela, V., Petäjä, T., Kousa, A., and Hämeri, K. 2013. Spatial–temporal variations of particle number concentrations between a busy street and the urban background, Atmospheric Environment 79, 324-333.
4. Ghassoun, Y. and Löwner, M.-O. 2016. Comparison of 2D & 3D parameter-based models in urban fine dust distribution modelling, Advances in 3D Geoinformation. Springer International Publishing, Switzerland.
5. Harris, G., Thompson, W. D., Fitzgerald, E. and Wartenberg, D. 2014. The association of PM 2.5 with full term low birth weight at different spatial scales, Environmental research 134, 427-434.
6. Harrison, R. M. and Yin, J. 2000. Particulate matter in the atmosphere: which particle properties are important for its effects on health?, Science of the total environment 249, 85-101.
7. Hu, M., Jia, L., Wang, J. and Pan, Y. 2013. Spatial and temporal characteristics of particulate matter in Beijing, China using the Empirical Mode Decomposition method, Science of the Total Environment 458, 70-80.
8. Isaaks, E. H. and Srivastava, R. M. 1989. An introduction to applied geostatistics. Oxford University Press.

9. Johnson, M., Isakov, V., Touma, J., Mukerjee, S. and Özkaynak, H. 2010. Evaluation of land-use regression models used to predict air quality concentrations in an urban area, Atmospheric Environment, 44, 3660-3668.
10. Kitanidis, P. 1997. Introduction to geostatistics: applications in hydrogeology. Cambridge University Press.
11. Lahoz, W. A. and Schneider, P. 2014. Data assimilation: making sense of Earth Observation, Frontiers in Environmental Science 2, 16.1-16.28.
12. Li, J. J., Jutzeler, A., and Faltings, B. 2014. Estimating Urban Ultrafine Particle Distributions with Gaussian Process Models, In S. Winter and C. Rizos (Eds.): Research@ Locate'14, 145-153.
13. Liu, W., Li, X., Chen, Z., Zeng, G., León, T., Liang, J., et al. 2015. Land use regression models coupled with meteorology to model spatial and temporal variability of NO2 and PM10 in Changsha, China, Atmospheric Environment 116, 272-280.
14. Marjovi, A., Arfire, A. and Martinoli, A. 2015. High Resolution Air Pollution Maps in Urban Environments Using Mobile Sensor Networks, in The 11th International Conference on Distributed Computing in Sensor Systems (DCOSS 2015).
15. McCreddin, A., Alam, M. and McNabola, A. 2015. Modelling personal exposure to particulate air pollution: An assessment of time-integrated activity modelling, Monte Carlo simulation & artificial neural network approaches, International journal of hygiene and environmental health 218, 107-116.
16. Mueller, M., Hasenfratz, D., Saukh, O., Fierz, M. and Hueglin, C. 2016. Statistical modelling of particle number concentration in Zurich at high spatio-temporal resolution utilizing data from a mobile sensor network, Atmospheric Environment 126, 171-181.
17. Mueller, M., Wagner, M., Barmpadimos, I., and Hueglin, C. 2015. Two-week NO2 maps for the City of Zurich, Switzerland, derived by statistical modelling utilizing data from a routine passive diffusion sampler network, Atmospheric Environment 106, 1-10.
18. R Development Core Team, 2013. R: A language and environment for statistical computing. Vienna, Austria: R Foundation for Statistical Computing; http://www.r-project.org, (access Decembar 2015.)
19. Rada, E. C., Ragazzi, M., Brini, M., Marmo, L., Zambelli, P., Chelodi, M. et al. 2012. Perspectives of low-cost sensors adoption for air quality monitoring, UPB Scientific Bulletin Series D 74, 241-250.
20. Rivera, M., Basagaña, X., Aguilera, I., Agis, D., Bouso, L., Foraster, M. et al. 2012. Spatial distribution of ultrafine particles in urban settings: A land use regression model, Atmospheric Environment 54, 657-666.
21. Ryan, P. H. and LeMasters, G. K. 2007. A review of land-use regression models for characterizing intraurban air pollution exposure," Inhalation toxicology 19, 127-133.
22. Saukh, O., Hasenfratz, D. and Thiele, L. 2015. Reducing multi-hop calibration errors in large-scale mobile sensor networks," in Proceedings of the 14th International Conference on Information Processing in Sensor Networks, 274-285.
23. Schneider, P., Castell, N., Vogt, M., Lahoz, W., Bartoňová, A. 2015. Making sense of crowdsourced observations: Data fusion techniques for real-time mapping of urban air quality, in EGU General Assembly Conference Abstracts 17, 3503.
24. Smith, L., Fuentes, M., Reich, B. and Eder, B. 2013, Prediction of Speciated Particulate Matter and Bias Assessment of Numerical Output Data, IJESER 4(2), 8-17 .
25. Wang, M., Beelen, R., Basagana, X., Becker, T., Cesaroni, G., de Hoogh, K. et al. 2013. Evaluation of land use regression models for NO2 and particulate matter in 20 European study areas: the ESCAPE project, Environmental science & technology 47, 4357-4364.
26. Wang, M., Beelen, R., Bellander, T., Birk, M., Cesaroni, G. , Cirach, M., et al. 2014. Performance of multi-city land use regression models for nitrogen dioxide and fine particles, Environmental health perspectives 122, 843-849.
27. Weichenthal, S., Van Ryswyk, K., Goldstein, A., Shekarrizfard, M., and Hatzopoulou, M. 2015. Characterizing the spatial distribution of ambient ultrafine particles in Toronto, Canada: A land use regression model, Environmental Pollution 208, 241-248.
28. Zambelli, P. 2015. A spatial decision support system to assess personal exposure to air pollution integrating sensor measurements, PhD thesis, University of Trento
29. Zhang, J. J., Sun, L., Barrett, O., Bertazzon, S., Underwood, F. E., and Johnson, M. 2015. Development of land-use regression models for metals associated with airborne particulate matter in a North American city, Atmospheric Environment 106, 165-177.

3.4 COMPARISON OF MULTIVARIATE LINEAR REGRESSION AND ARTIFICIAL NEURAL NETWORKS FOR CALIBRATION OF LOW COST REALTIME OPTICAL PARTICLE COUNTER

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ABSTRACT

This paper presents a comparison between calibration techniques using multivariate linear regression and artificial neural networks. Calibration was performed for a Dylos 1700 device for detecting respirable particle matter (RPM) number concentration. During implementation of the calibration procedures it has been taken into consideration how different meteorological parameters have affect on RPM concentration. The multivariate linear regression method was first analyzed followed by the calibration procedure that used feed-forward neural network with one hidden layer. The hidden layer was taken up by 10 neurons with a sigmoid transfer function. Linear transfer function was used for the output layer. The neural network training was carried out with three different methods: 1) Levenberg-Marquardt algorithm (LM); 2) Resilient backpropagation algorithm (RP) and 3) Conjugate Gradient Powell-Beale algorithm (CG). For network training 70% of the total number of measurements were used for validation while 15% of the total number of measurements were used for testing.

INTRODUCTION

A large number of epidemiological studies have demonstrated that respirable particles may have adverse affect on human health causing high percentage of respiratory mortality and morbidity (Oberdörstera et al, 1995; Pope et al, 2006; Pope et al 1995; Laden et al, 2000). Respirable particles in the air change their physical and chemical properties which affects the distribution of their concentration with steep changes in the spatial and temporal scale. Therefore, in recent years small portable systems implementing low-cost sensors for detection of particle concentrations are increasingly being used to support standard measuring stations (Kularatna et al, 2008; Al-Ali et al, 2010; Katulski et al, 2009). They may be used to provide high spatial and temporal resolution of measurements. Based on experience from studies that have used cheap sensors for air pollution monitoring, it is necessary to perform an evaluation of their characteristics through a calibration procedure (Jovašević-Stojanović et al, 2015).

In this paper a comparison between calibration techniques using multivariate linear regression and ANN (Gemperline et al, 1991) is presented. First, a multivariate linear regression model with meteorological variables as input parameters was established. The best regression line in this model was achieved using the least squares method. This method works by minimizing the sum of squares of vertical deviations for each point relative to the regression line. For ANN three training algorithms were used: 1) Levenberg-Marquardt algorithm (LM); 2) Resilient backpropagation algorithm (RP) and 3) Conjugate Gradient Powell-Beale algorithm (CG). Based on numerous studies it was found that the LM algorithm has a top speed of execution, while on the other hand takes up a significant memory resources of computer during execution. LM training algorithm was used for improving the speed of the training to the second order, without calculating the Hessian matrix. RP algorithm eliminates the negative effects of partial derivative. Sign of the partial derivative is used to determine the direction of weight coefficients, while the amount of the partial derivative does not take affect on the coefficients weight. CG method adjusts the coefficients weight according to the steepest decreasing direction in which the performance function has the fastest decline (Beale et al, 1972; Karul et al, 2000; Riedmuller et al, 1993).

A calibration was performed for a Dylos 1700 device that detects RPM number concentrations (Dylos Corporation, http://www.dylosproducts.com/). The Dylos 1700 is a laser light scattering device designed to detect the concentration of two fractions of particles in range between 0.5-2.5 μm (PMS fraction) and > 2.5 μm (PML fraction). This device was integrated in a platform that was also monitoring selected gasous pollutants and meteorological parameters, EKO700 device. This device was develop for the CITI-SENSE pilot campaign.

In the 2nd section we will present a methodology of multivariate linear regression method and ANN. In the 3rd section results of the calibration procedure with relevant statistical test will be presented. In the 4th section we will make conclusion remarks according to the obtained results in previous section.

METHODOLOGY

Multivariate linear regression

Multivariate linear regression is the most common technique for modeling dependencies between two or more input variables and the response by fitting a linear equation over the corresponding referent signal. Each value of the independent variable x is associated with the corresponding value of y. For p input variables x_1, x_2,… x_p within multivariate linear regression, regression curve in the following form it can be defined:

$$\mu_y = B_0 + B_1 \cdot x1 + \ ... + \ B_p \cdot x_p, \tag{1}$$

This line describes how the mean of response changes with the input variables x_1, x_2,… x_p. The measured values of y vary around their mean μ_y and it is assumed to have the same standard deviation σ.

Since the measured values vary around μ_y, multivariate linear regression must include a member related to this variation. In other words, the model can be described as

$$OUTPUT=fit+residual,$$

where *fit* corresponds to a linear combination of input variables $B_0+B_1 \cdot x_1+ \ ... + \ B_p \cdot x_p$ and *residual* represents deviations of the measured values y from mean μ_y that are normally distributed with mean equal to 0 and variance σ.

Artificial neural networks

The first publications about artificial neural networks as an example of artificial intelligence have emerged in the forties. In the framework of this papers a very simple model of a neuron as well as the biological neuron that processes the signals across the synaptic and somatic operations is described. This very simple model of neurons we called the perceptron. Synaptic operation is represented by multiplying each input signal x_i with the weight coefficient w_i. Next the weighted input signals are added and their sum is compared with a threshold sensitivity of neurons. If the sum of weight signals is greater than the sensitivity threshold of neurons, nonlinear activation function ψ generates neurons output y.

The present model of neurons does not contain dynamic members and its output depends only on the current values of the input signals and the weight coefficients. Therefore, this neuron is called static neuron, and since it is a generalization of perceptron, often it is just called the perceptron. A large number of neural network is constructed with perceptrons that are organized in three or more layers. These networks are usually called multilayer perceptron networks (MLP networks).

Perceptron can be mathematically described by the following equations:

$$v(t) = \sum_{i=1}^{n} w_i(t) - w_{n+1}, \tag{2}$$

$$y(t) = \psi(v), \tag{3}$$

where is:

$x_N(t) = [x_1(t), \dots, x_n(t)]$ - vector of input signals or excitation vector,
$w_S(t) = [w_1(t), \dots, w_n(t)]$ - synaptic weight coefficients vector,
w_{n+1} - threshold,
$v(t)$ - output of confluence operation,
$\psi(v)$ - non-linear activation function,
$y(t)$ - neurons output.

Expression (2) describes the synaptic operation and the first two somatic operations (gathering weight of the input signals and comparing their sum with a threshold sensitivity). These three operations are grouped together making the confluence operation, and the expression (3) describes the non-linear activation function. Therefore, from the mathematical point of view, artificial neuron can be divided into confluence operation and non-linear

activation function. Nonlinear activation function $\psi(v)$, mapping the output of the confluence operation $v(t)$ [- ∞, ∞] into the output neuron $y(t)$. The amounts of neurons output signals is usually limited to a range [0, 1] for unipolar signals and, to [-1, 1] for bipolar signals. Although we have a large number of different functions that allow the neural network to approximate an arbitrary continuous function, some functions are accepted as standard activation function: *logsig* and *tansig* functions. Activation reinforcement typically is selected with a unit amount. It is important to note that in the framework of neural networks linear activation function (*purelin*) can be also applied, since it can often take advantage at the output network layer.

RESULTS AND DISCUSSION

Based on experience from several studies it was found that many variables can affect the operation of low-cost optical sensors for respirable particles monitoring (Jovašević-Stojanović et al, 2015). These variables may be curent meteorological conditions in a particular location at which the measurements are conducted. Due to this one must provide sensor calibration and has to take into consideration the impact of additional parameters on the quality of the regression that is conducted in order to establish a model that would give the calibrated value of the initial measurement results (Spinelle et al, 2015; Hasenfratz et al, 2012).

In this paper the influence of the meteorological parameters and their combinations on a Dylos 1700 device calibration was examined. We have separately analysed data for the Dylos 1700 PMS and Dylos 1700 PML fractions. Meteorological data used as predictor variables during analysis were temperature, humidity and pressure. In addition, the values of RPM concentration obtained in a given period of time from Dylos 1700 devices have also been used as predictor variables. Referent values for $PM_{2.5}$ and PM_{10} from an automatic monitoring station (ATM) were used as target data. The ATM belongs to the state network operated by the Serbian Agency for Environmental Protection (SEPA). The measurements were conducted in the municipalitiy of New Belgrade. The referent station in New Belgrade is an urban traffic-residental type of ATM with a height of 85 m above the sea level

Multivariate linear regression analysis (MLR)

Table 1 shows the results of statistical tests for 4 MLR models for Dylos 1700 PMS and Dylos 1700 PML particle concentrations. In addition, in Table 3 in the first row, the best models for Dylos 1700 PMS and Dylos 1700 PML are presented. It was found that MLRpms-1 (NB) and MLRpml-1 (NB) models best describes changes in the observed signals. For MLRpms-1 (NB) model, parameters of statistical tests had the following values: R^2=0.922, RMSE=5.878, and AARE=3.982, while the statistical values for MLRpml-1 (NB) are R^2=0.862, RMSE=10.360 and AARE=7.216. From the previous results it is evident that the R^2 parameter that determines the degree of correlation between the output and target data has a higher value for the PMS group in comparison to the PML fraction. Also, based on the values of statistical tests for different models it can be concluded that the use of the maximum number of input parameters (T, RH, p) in the model gives the best results. However, differences in the results are not high and with thorough examination of Table 1 it may be noted that humidity and pressure has the greatest impact in the linear regression for Dylos 1700 PMS and PML fraction respectively. If one is to apply regression methods for simplicity, a model that contains only one specific input parameter can also be used.

Table 1. *Performance statistics for MLR models.*

Model	Parameters	R^2	RMSE	AARE
MLRpms-1(NB)	*PMS, T, rH, p*	0.922	5.878	3.982
MLRpms-2(NB)	*PMS, T*	0.921	5.923	4.040
MLRpms-3(NB)	*PMS, rH*	0.922	5.899	4.040
MLRpms-4(NB)	*PMS, p*	0.911	6.272	4.237
MLRpml-1 (NB)	*PML, T, rH, p*	0.862	10.360	7.216
MLRpml-2 (NB)	*PML, T*	0.857	10.528	7.248
MLRpml-3 (NB)	*PML, rH*	0.857	10.524	7.232
MLRpml-4 (NB)	*PML, p*	0.861	10.406	7.287

Analysis using artificial neural networks

Table 2 indicates the performance statistics for 24 developed ANN models for PMS and PML fractions of Dylos1700 devices. Table 3 presents the results of the statistical tests for the best ANN models. Finaly, Table 4 presents the average statistics for all established models for the ATM at the New Belgrade cite.

Architecture of used ANN is the same for all models. Therefore, calculations were implemented with the neural network with one hidden layer in which 10 neurons were built. At the input of the neural network, a sigmoidal transfer function was used, while the output layer used a linear transfer function, which is perfect for the process of function fitting for the sake of simplicity.

Table 2. *Performance statistics for ANN models.*

Model	Parameters	R^2	RMSE	AARE
LMpms-1(NB)	*PMS*, *T*, *rH*, *p*	0.969	3.778	2.478
RPpms-1(NB)	*PMS*, *T*, *rH*, *p*	0.958	4.384	2.962
CGpms-1 (NB)	*PMS*, *T*, *rH*, *p*	0.957	4.432	3.003
LMpms-2(NB)	*PMS*, *T*	0.957	4.400	2.869
RPpms-2(NB)	*PMS*, *T*	0.951	4.695	3.156
CGpms-2(NB)	*PMS*, *T*	0.951	4.687	3.129
LMpms-3(NB)	*PMS*, *rH*	0.955	4.521	3.042
RPpms-3 (NB)	*PMS*, *rH*	0.949	4.810	3.294
CGpms-3 (NB)	*PMS*, *rH*	0.945	4.980	3.455
LMpms-4(NB)	*PMS*, *p*	0.951	4.701	3.217
RPpms-4 (NB)	*PMS*, *p*	0.945	4.979	3.422
CGpms-4 (NB)	*PMS*, *p*	0.935	5.406	3.883
LMpml-1 (NB)	*PML*, *T*, *rH*, *p*	0.949	6.473	3.969
RPpml-1 (NB)	*PML*, *T*, *rH*, *p*	0.910	8.493	5.348
CGpml-1 (NB)	*PML*, *T*, *rH*, *p*	0.929	7.568	4.948
LMpml-2 (NB)	*PML*, *T*	0.890	9.330	6.475
RPpml-2 (NB)	*PML*, *T*	0.883	9.605	6.697
CGpml-2 (NB)	*PML*, *T*	0.848	10.818	7.423
LMpml-3 (NB)	*PML*, *rH*	0.897	9.020	6.120
RPpml-3 (NB)	*PML*, *rH*	0.876	9.858	6.986
CGpml-3 (NB)	*PML*, *rH*	0.888	9.399	6.370
LMpml-4 (NB)	*PML*, *p*	0.925	7.775	4.919
RPpml-4 (NB)	*PML*, *p*	0.904	8.721	5.913
CGpml-4 (NB)	*PML*, *p*	0.898	8.984	6.046

From Table 3 it can be seen that for the PMS and PML fractions, LMpms-1 (NB) and LMpml-1 (NB) are the best ANN LM models with the following test results: R^2=0.969, RMSE=3.778, AARE=2.478 and R^2=0.949, RMSE=6.473, AARE=3.969, respectively.

The best ANN RP models were RPpms-1 (NB) and RPpml-1 (NB) models with the statistical results of R^2=0.958, RMSE=4.384, AARE=2.962 and R^2=0.910, RMSE=8.493 and AARE=5.348.

Finally, the best ANN CG models for small and large particles were CGpms-1 (NB) and CGpml-1 (NB) models. These models were described with the results of statistical tests R^2=0.957, RMSE=4.432 and AARE=3.003, and R^2=0.929, RMSE=7.568 and AARE=4.948.

Table 3. *Performance statistics for the best model for each type of method.*

Model	Parameters	R^2	RMSE	AARE
MLRpms1-(NB)	*PMS, T, rH, p*	0.922	5.878	3.982
LMpms-1(NB)	*PMS, T, rH, p*	0.969	3.778	2.478
RPpms-1 (NB)	*PMS, T, rH, p*	0.958	4.384	2.962
CGpms-1 (NB)	*PMS, T, rH, p*	0.957	4.432	3.003
MLRpml-(NB)	*PML, T, rH, p*	0.862	10.360	7.216
LMpml-1 (NB)	*PML, T, rH, p*	0.949	6.473	3.969
RPpml-1 (NB)	*PML, T, rH, p*	0.910	8.493	5.348
CGpml-1 (NB)	*PML, T, rH, p*	0.929	7.568	4.948

When comparing the best ANN models (Table 3) for PMS and PML particles [LMpms-1 (NB) and LMpml-1 (NB)] with the best CG models [CGpms-1 (NB) and CGpml-1 (NB)], it was found that the LM models have R^2 that was 1.255% (PMS) and 2.108% (PML) more accurate, RMSE that was 14.738% (PMS) and 14.469% (PML) more accurate and AARE that was 17.497% (PMS) and 19.784% (PML) more accurate.

On the other hand, when comparing the best ANN models for PMS and PML particles [LMpms-1 (NB) and LMpml-1 (NB)] with the best RP models [RPpms-1 (NB) and RPpml-1 (NB)], it was found that the LM models had R^2 that was 1.155% (PMS) and 4.277% (PML) more accurate, RMSE, that was 13.813% (PMS) 23.790% (PML) more accurate and AARE that was 16.350% (PMS) and 25.780% (PML) more accurate.

Finally, when comparing the results for LM and MLR models it was found that the R^2 for LM models was 5.012% (PMS) and 10.038% (PML) more accurate, RMSE was 35.720% (PMS) and 37.520% (PML) more accurate, while AARE was 37.768% (PMS) and 44.997 % (PML) more accurate.

Therefore, it can be concluded that in general the highest accuracy was achieved by LM ANN models in comparison to RP and CG ANN and MLR models. In addition all ANN models are better than MLR .

Table 4. *Average performance statistics for each type of method.*

Model	R^2	RMSE	AARE
MLRpms (NB)	0.919	5.993	4.074
LMpms (NB)	0.958	4.350	2.902
RPpms (NB)	0.951	4.717	3.209
CGpms (NB)	0.947	4.876	3.368
MLRpml (NB)	0.859	10.454	7.246
LMpml (NB)	0.915	8.149	5.371
RPpml (NB)	0.893	9.169	6.236
CGpml (NB)	0.891	9.192	6.197

Based on the results available from Table 4. it can be seen that when we calculated the mean values of statistical results for all models, LMpms (NB) and LMpml (NB) shown the best results of statistical tests with values: R^2=0.958, RMSE=4.350, AARE=2.902 and R^2=0.915, RMSE=8.149 and AARE=5.371.

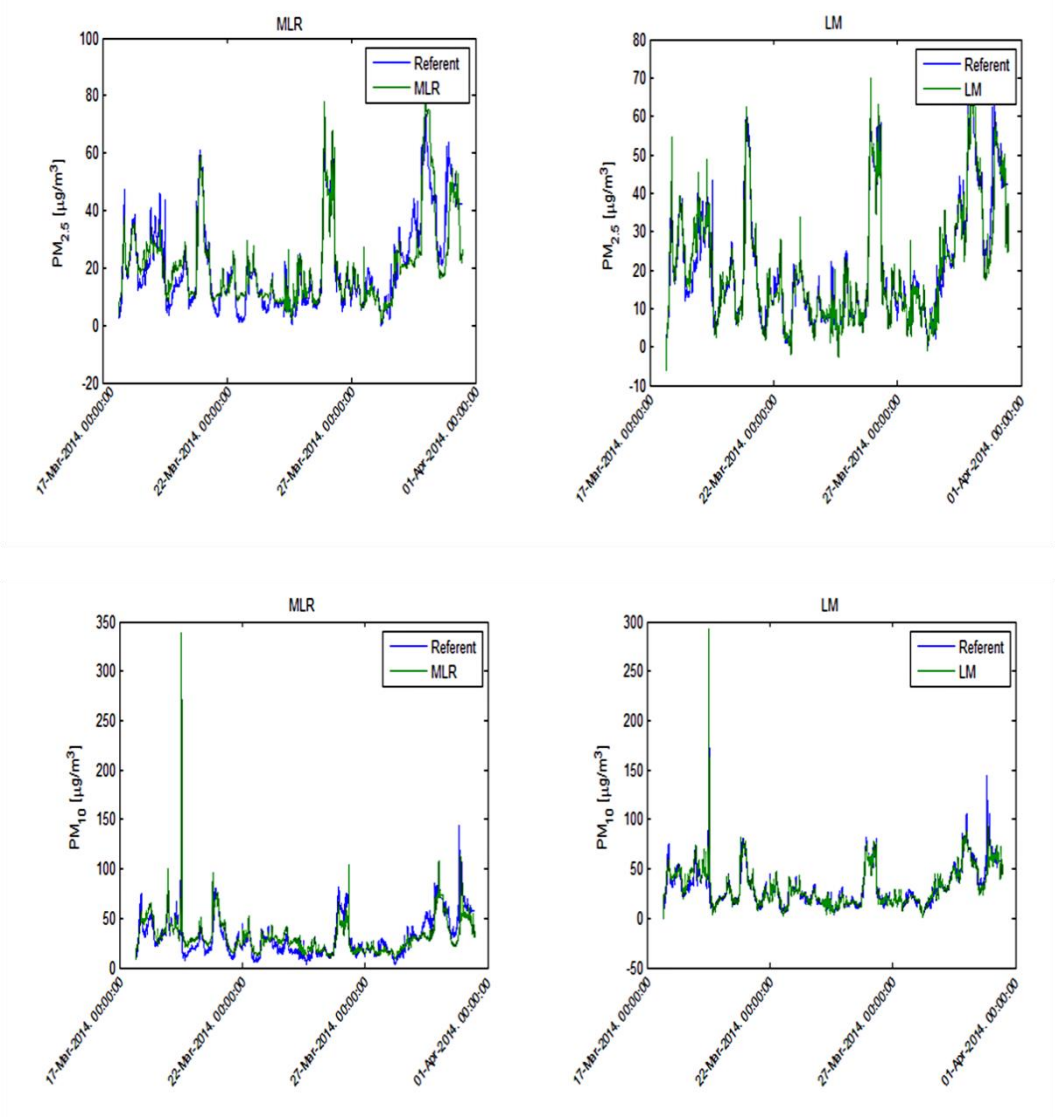

Figure 1. *Comparative analysis of mesaurements for PMS and PML fraction from AMSDylos 1700*

Finally, in Figure 1 we presented measurements from the reference stations and established MLR and LM models with all parameters. From these graphs it can easily be recognised that the results obtained using neural networks (diagrams for $PM_{2.5}$ and PM_{10} from right hand side) is much closer to the reference measurements in comparison to the MLR model.

CONCLUSION

The aim of this study was examination and comparison of the different signal processing techniques that could be 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. ANN models have been developed with three different training algorithms: LM, RP and CG. Based on the results of statistical tests for the established models it was found that the neural networks have shown the ability of automatic modeling of nonlinearities in contrast to the linear regression where usage of explicit models with appropriate transformations was necessary. LM neural networks have shown the best results compared to RP, CG neural networks and multivariate linear regression method.

ACKNOWLEDGEMENTS

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REFERENCES

1. Al-Ali, A. R., Zualkernan, I., and Aloul, F., 2010, A Mobile GPRS-Sensors Array for Air Pollution Monitoring, IEEE Sensors Journal, 10, 1666-1670.
2. Beale, E., 1972, A derivation of conjugate gradients: Numerical methods for nonlinear optimization, Academic, San Diego.
3. Dylos Corporation, DC1700 Air Quality Monitor, http://www.dylosproducts.com/.
4. Gemperline, P.J., Long, J.R., Gregoriou, V.G., 1991, Nonlinear Multivariate Calibration Using Principal Components Regression and Artificial Neural Networks, Analytical Chemistry, 63, 2313-2323.
5. Hasenfratz, D., Saukh, O., Thiele, L., 2012, On-the-fly calibration of low-cost gas sensors, EWSN'12 Proceedings of the 9th European conference on Wireless Sensor, 228-244.
6. Jovašević-Stojanović, M., Bartoňová, A., Topalović, D., Lazović, I., Pokrić, B., Ristovski, Z., 2015, On the use of small and cheaper sensors and devices for indicative citizen-based monitoring of respirable particulate matter, Environmental Pollution, 206, 696-704.
7. Karul, C., Soypak, S., Cilesiz, A. F., Akbay, N., and Germen, E., 2000, Case studies on the use of neural networks in eutrophication modeling, Ecol. Modell., 134, 145-152.
8. Katulski, R. J., Namieśnik, J., Stefański, J., Sadowski, J., Wardencki, W., Szymańska, K., 2009, Mobile monitoring system for gaseous air pollution, Metrology and Measurement Systems, 16, 667-682.
9. Kularatna, N., Sudantha, B., 2008, An Environmental Air Pollution Monitoring System Based on the IEEE 1451 Standard for Low Cost Requirements, IEEE Sensors Journal, 8, 415-422.
10. Laden, F., Neas, L. M., Dockery, D. W., and Schwartz, J., 2000, Association of fine particulate matter from different sources with daily mortality in six U.S. cities., Environ Health Perspect., 108(10): 941–947.
11. Oberdörstera, G., Celeina, R. M, Ferina, J. and Weissa, B., 1995, Association of Particulate Air Pollution and Acute Mortality: Involvement of Ultrafine Particles?, Inhalation Toxicology, 7, 111-124.
12. Pope, C.A., Dockery, D.W., 2006. Health effects of fine particulate air pollution: lines that connect. J. Air Waste Manag. Assoc. 56, 709-742.
13. Pope, C. A., Bates, D. V., and Raizenne, M. E., 1995, Health effects of particulate air pollution: time for reassessment?, Environ Health Perspect., 103(5), 472-480.
14. Riedmuller, M. and Braun, H. 1993, A direct adaptive method for faster backpropagation learning: The RPROP algorithm, Proc. of the IEEE Int. Conf. on Neural Networks, IEEE, New York, 1, 586-591.
15. Spinelle, L., Gerboles, M., Villani, M. G., Aleixandre, M., Bonavitacola, F., 2015, Field calibration of a cluster of low-cost available sensors for air quality monitoring. Part A: Ozone and nitrogen dioxide, Sensors and Actuators B: Chemical, 215, 249-257.

3.5 TRANSPORT CONTRIBUTION TO $PM_{2.5}$ MASS CONCENTRATIONS IN BELGRADE SUB-URBAN AREA

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ABSTRACT

In the present study, hourly $PM_{2.5}$ mass concentrations obtained from the monitoring station in the Belgrade sub-urban area were analyzed for the 2013. The contribution of local and remote pollution sources on measured concentrations were considered. The contribution of transported $PM_{2.5}$ pollution to the observed concentrations was determined by the use of trajectory sector analysis (TSA). A certain proximity sources were identified by means of conditional bivariate probability function (CBPF), while potential source contribution function (PSCF) and concentration weighted trajectory (CWT) hybrid receptor models were used for the identification of potential non-local source regions. Trajectory cluster analysis (TCA) was applied to assess representative pathways of air masses affecting the sampling site. The results suggest significant influence of transport processes in examined area, and potential remote $PM_{2.5}$ sources in neighboring countries and countries of North and East Europe.

INTRODUCTION

Particulate matter (PM) is emitted from a variety of sources including the industrial activities, heat and power generation plants, traffic exhaust and agricultural processes (Heal et al, 2012). Because of adverse effects on human health and environment, fine particles $PM_{2.5}$ (with aerodynamic diameter < 2.5 μm) have become one of the main concerns in highly populated urban areas (WHO, 2013). Air Quality Directive (EU, 2008), establishing the 25 μg m^{-3} as annual limit value for $PM_{2.5}$ to be met in 2015, will become progressively more restrictive in 2020. Although environmental policies have led to significant improving of air quality, in some European cities particle levels still exceed prescribed limit value (Guerreiro et al, 2014). Besides local sources, low wind speed and stable meteorological conditions are important factors leading to air pollution episodes (Engler et al, 2012). The most worrying situations occurred in urban and sub-urban areas during the cold season, where high air pollution may cause serious risks for human health (Pant et al, 2015).

Significant input of $PM_{2.5}$ is provided through the transport processes affecting the air quality all over the Europe (Makra et al, 2011). For deciding any effective abatement measure, knowing the relationship between the local atmospheric circulation and the regional and long-range transport processes in contributing to $PM_{2.5}$ levels, has become very important.

METHODOLOGY

In this study, hourly $PM_{2.5}$ mass concentrations and meteorological parameters (wind speed and direction, temperature, relative humidity and atmospheric pressure) during 2013 were obtained from the Institute of Public Health Belgrade automatic monitoring station Ovča (44°53' N, 20°31' E) located in the Belgrade sub-urban area. The sampling site was chosen because the area is characterized by rather flat landscape with an average altitude of about 70 m, entirely exposed for the influence of different air masses. In order to identify local potential emission sources, conditional bivariate probability function (CBPF) analysis was performed with the statistical software R, using the Openair package (Carslaw and Ropkins, 2012). Considering intervals of concentration, it provides more information on emission strength and location in examined area.

To differentiate the shares of transported and background $PM_{2.5}$ pollution to the observed mass concentrations, a pronounce local contribution was excluded from the time series by the use of frequency differentiated non-linear digital filtering algorithm implemented in the function baseline.RollingBall (wm=8, ws=6) of the Baseline package (Kneen and Annegarn, 1996) of the statistical software R, thus providing a baseline. Subsequently, trajectory sector analysis (TSA) was applied to the derived baseline in order to obtain the monthly mean background levels and time series of transported $PM_{2.5}$ pollution according to Stojić and coauthors (2015a). The whole area with the center at the receptor site was divided into 16 22.5°-sectors and the contribution of the least polluted sector was taken as a background level.

Trajectory cluster analysis (TCA) was applied to the transported $PM_{2.5}$ time series to reveal the major pathways of air masses affecting the sampling site. Furthermore, the estimation of the origin of non-local emission sources and their impacts to the observed concentrations were performed by the use of potential source contribution function (PSCF) and concentration weighted trajectory (CWT) models (Hsu, 2003) according to Stojić and coauthors (2015b). Three days air mass back-trajectories used for the transport analyses were computed every hour UTC for the height of 200 m above the measuring point at the ground level by the use Openair and Opentraj (2015) packages of the statistical software R.

RESULTS AND DISCUSSION

Based on 97% available data, mean annual $PM_{2.5}$ mass concentrations was 39.3 μg m^{-3}, which is significantly higher than the prescribed limit value. The highest concentrations were observed through the colder part of year, with the highest monthly mean of 80.4 μg m^{-3} in December. Summer and spring were characterized with sporadic, short term peaks in the time series, but with the lowest average concentrations (monthly mean in July was 18.2 μg m^{-3}). In order to locate potential emission sources near the sampling site, CBPF analysis was carried out in the four percentile intervals of $PM_{2.5}$ mass concentration (Figure 1). The most probable source of emission in the lowest concentrations range (0-25th percentile) was located in the SW direction which reflects the Belgrade urban area. In the range from 25-50th percentile locations of the most probable source was in the SE direction, which may be related to steel factory located in the suburban area of Smederevo, about 40 km from the measurement site. These sources showed their maximum influence in concentration regions under the 50th percentile and at higher wind speed, which may be related to the distance from the measuring site (Uria-Tellaetxe and Carslaw, 2014). The sources in SE and W direction were dominant between 50th and 75th percentile of concentrations. First one may be associated with industrial complex near Pančevo while second reflects the positions of large agriculture and food production complexes located about 10 kilometers far from the sampling site. The highest concentrations (75-100th percentile) were measured during the calm weather conditions, indicating the main contribution of proximate sources.

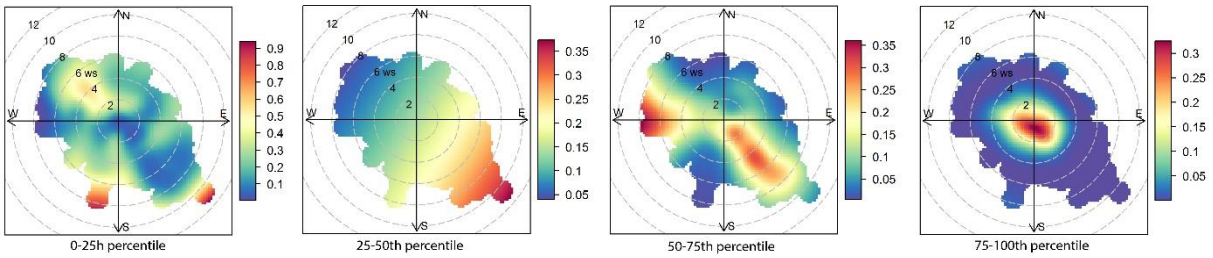

Figure 1. *CBPF plots of $PM_{2.5}$ mass concentrations within four percentile intervals*

Time series of measured and transported concentrations, and average monthly contribution variability of local production, background and transport to the observed mass concentrations during 2013 were presented in Figure 2. The contributions of transport and background were the largest during the winter. During the colder part of year, intensive fossil fuel usage in individual heating units and traffic activity increase significantly contribute to the background concentration in this area. The influence of strong local sources was high in winter, but their maximum contributions were observed in May, Jun and August (60-70%). Droughty summer season characterize intensive agriculture activates and diesel fuel usage in rural environment of the sampling site, which might be the reason for occasional concentration level increase.

TCA derived six representative clusters, with the percent of trajectories belonging to a particular cluster and contribution to transported concentrations presented in Figure 3 (left).The most frequent transport pathways were N and NE, clusters C5 and C6 respectively, but the highest contribution to the observed concentrations was associated with the air masses coming from the SW direction, cluster C3. Monthly average contribution of six representative clusters are presented in Figure 4. The contribution of the remote pollution sources has proved to be highest during winter and spring, with the dominant influences of NW and W directions, with the exception in February, when the largest impact was from E/SE region (cluster C1).

The results of PSCF analysis, presented at the same figure, show potential distant sources of $PM_{2.5}$ located along the direction of the cluster C3, in neighboring countries (Bosnia and Hercegovina and Croatia). CWT analysis (Figure 3, right) shows the additional sources of fine particulates in the countries of North and East Europe,

Lithuania and Ukraine. Results of TSA are also shown in Figure 3 (right). Combining the frequency of arriving air masses with transported concentrations, the contribution of long-range transport to the measured concentrations was estimated. The maximum impact of the long-range transport was from W, SW and E sectors about 10 μg m^{-3}.

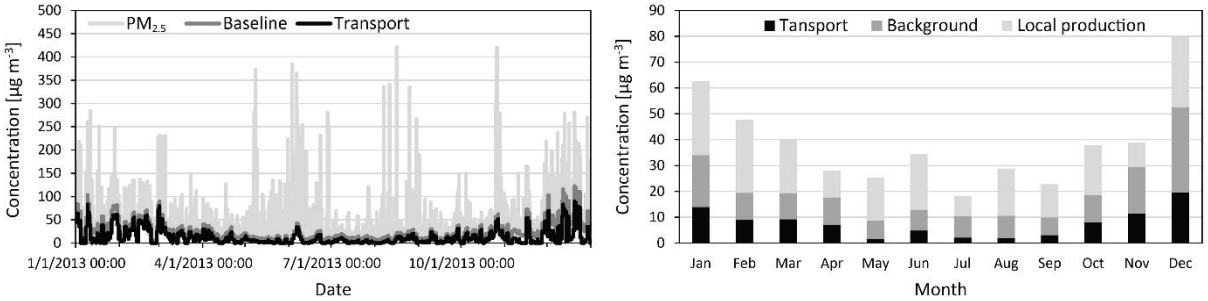

Figure 2. *$PM_{2.5}$ mass concentrations, derived baseline level and transport time series (left), and monthly average transport, background and local production shares in the observed concentrations (right)*

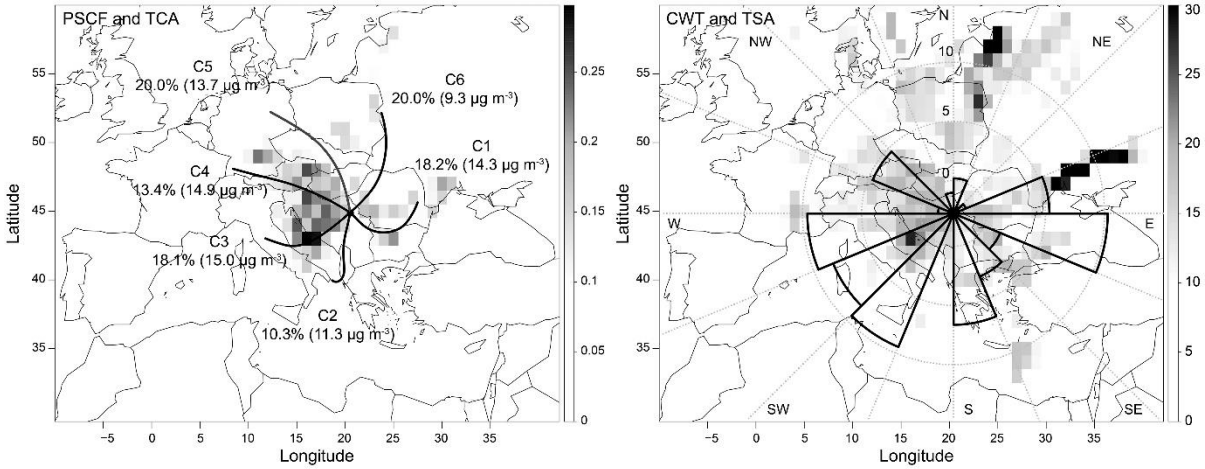

Figure 3. *$PM_{2.5}$ PSCF map and six representative clusters (left), and CWT [μg m^{-3}] map with contribution of transport from different regions (right)*

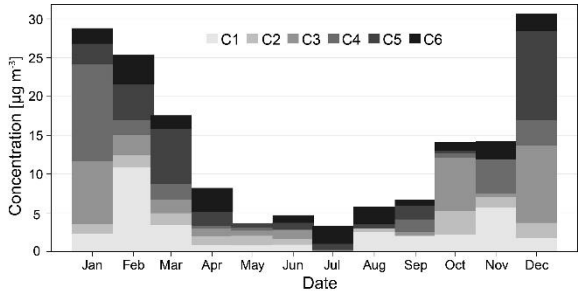

Figure 4*. Time series of cluster contributions to transported $PM_{2.5}$ mass concentrations*

CONCLUSIONS

Annual mean $PM_{2.5}$ concentrations exceed prescribed limit value during the 2013 in the Belgrade sub-urban area, at the sampling site Ovča. Hybrid receptor models were applied in order to distinguish impacts of local production and long-range transport on measured concentrations. CBPF analysis, carried out in the four percentile intervals, allowed the identification of different nearby sources. According to the results of PSCF and CWT analyses, the main remote sources of emission are located in bordering countries, East and North Europe. Summer characterizes the influence of dominant local sources, while transport contribution and background

concentrations were higher during the winter. TSA estimated the transport contribution up to 10 μg m^{-3}, which suggest its significant impact on air quality in this area. In order to reach prescribed limit values for $PM_{2.5}$ in Belgrade sub-urban area, potential environmental regulation measures may not be effective if restricted to mitigating the emission from local sources only.

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REFERENCES

1. Carslaw, D.C. and Ropkins, K., 2012. Openair—an R package for air quality data analysis. Environ. Modell. Softw. 27, 52-61.
2. Engler, C., Birmili, W., Spindler, G. and Wiedensohler, A., 2012. Analysis of exceedances in the daily PM_{10} mass concentration (50 μg m^{-3}) at a roadside station in Leipzig, Germany. Atmos. Chem. Phys. 12, 10107-10123.
3. EU, 2008. Council Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe. Official Journal of European Communications. L152/1, 11/6/2008.
4. Guerreiro, B., Cristina, B., Foltescu, V., de Leeuw, F., 2014. Air quality status and trends in Europe. Atmos. Environ. 98, 376-384.
5. Heal, R.M., Kumarb, P. and Harrison R.M, 2012. Particles, air quality, policy and health. Chem. Soc. Rev. 41, 6606–6630.
6. Hsu, Y.-K., Holsen, T.M. and Hopke, P.K., 2003. Comparison of hybrid receptor models to locate PCB sources in Chicago. Atmos. Environ. 37, 545-562.
7. Kneen, M.A. and Annegarn, H.J., 1996. Algorithm for fitting XRF, SEM and PIXE X-ray spectra backgrounds. Nucl. Inst. Meth. B 109, 209-213.
8. Makra, L., Matyasovszky, I., Guba, Z., Karatzas, K. and Anttila, P., 2011. Monitoring the long-range transport effects on urban PM_{10} levels using 3D clusters of backward trajectories. Atmos. Environ. 45, 2630-2641.
9. Opentraj, 2015. https://cran.r-project.org/web/packages/opentraj/opentraj.pdf, accessed June 2015.
10. Pant, P., Shukla, A., Kohl, S.D., Chow, J.C., Watson, J.G. and Harrison, R.M. 2015. Characterization of ambient $PM_{2.5}$ at a pollution hotspot in New Delhi, India and inference of sources. Atmos. Environ. 109, 178-189.
11. R Core Team, 2012. R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. http://www.R-project.org
12. Stojić, A., Stojić, S. S., Mijić, Z., Šoštarić, A., Rajšić, S. , 2015b. Spatio-temporal distribution of VOC emissions in urban area based on receptor modeling. Atmos. Environ. 106, 71-79.
13. Stojić, A., Stojić, S. S., Šoštarić, A., Ilić, L., Mijić, Z. and Rajšić, S., 2015a. Characterization of VOC sources in an urban area based on PTR-MS measurements and receptor modelling. Environ. Sci. Pollut. R. 22(19) 13137-13152.
14. Uria-Tellaetxe, I. and Carslaw, C. D., 2014. Conditional bivariate probability function for source identification. Environ. Mod. Softw. 59, 1-9.
15. WHO, 2013. Review of Evidence on Health Aspects of Air Pollution e REVIHAAP Project. Technical Report. World Health Organization, Regional Office for Europe, Copenhagen, Denmark.

3.6 INFLUENTIAL PARAMETERS ON PARTICLE DISPERSION IN URBAN ENVIRONMENTS

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ABSTRACT

A series of experimental campaigns was carried out from May to September 2015 in order to assess parameters affecting particle distribution and number concentrations in park and urban areas. The number concentrations were measured by a portable laser particle counters capable of measuring in six size channels from 0.3 to 10 μm. Traffic jam hours, street geometry and wind speed and direction are among the parameters considered to influence the dispersion of freshly emitted particles by the vehicles. The number concentrations of all size fractions measured at the different areas show a decreasing tendency in the course of the day (during the mixing layer development), as the strongest effect is seen in the fine particle size fraction. The increase in the traffic intensity resulted in an increase in the fine particle concentrations. A decrease in the particle number concentrations (by a factor of 2) is seen in case of light wind (2-3 m/s).

INTRODUCTION

Airborne particles, especially those smaller than 10μm in diameter, are recognized to have adverse effects on human health. Exposure to fine particles (smaller than 2.5 μm) is linked to respiratory and cardio-vascular health problems (Kampa and Castanas 2008).

The increased industrialization and number of motor vehicles in the cities contribute significantly to the amount of fine particles emitted into the atmosphere. Concerns arise on the pedestrian safety and indoor and outdoor air quality. Therefore, it is essential that the particle exposure of people living in cities during their daily activities be evaluated. The necessity to know how the urban population exposure depends on the emissions, flow, dispersion and street geometry in urban street canyons has given rise to many field experiments and numerical simulations (Zajic et al, 2011; Buonanno et al, 2011). Overall daily particle exposure is found to be mainly influenced by transportation modes and urban microenvironments (Buonanno et al, 2011).

The present study is aimed at assessing the parameters that affect particle distribution and number concentration in park and urban areas in the city of Sofia, Bulgaria. Traffic jam hours, street geometry, mixing layer (ML) development, and wind speed and direction are among the parameters considered to influence the dispersion of freshly emitted particles by the vehicles. Investigations on the ML development, aerosol optical characteristics, and temporal and spatial distribution of the aerosol in mountain valley have been carried out in Sofia by remote sensing devices (Kolev et al, 2011, Evgenieva et al, 2011, Savov et al, 2002).

INSTRUMENTS AND METHODS

Three portable laser particle counters (LPCs) were used to measure particle number concentrations: (1) Two PC200 (TROTEC®) capable of measuring in six particle size channels: 0.3, 0.5, 1, 2.5, 5 and 10 μm; and (2) One HHPC-6 (Met One®) –this instrument also samples and classifies aerosol particles into six particle size ranges (geometric particle diameter 0.3-0.5 μm, 0.5-0.7 μm, 0.7-1 μm, 1-2 μm, 2-5 μm and >5 μm).

For all of the instruments the sampling flow rate is 2.83 litres per minute and can be programmed to sample in cycles of varying duration. The ouput data are given in terms of number of particles per litre of air samples.

During the initial campaign in May 2015 only one of the PC200 was available (hereafter named "LPC1"). For the following campaigns in June and September 2015 additional LPCs were made available, namely, the second PC200 (named "LPC2" in the text) and the HHPC-6 (named "LPC3"). These three instruments were arranged to sample concomitantly side-by-side for a variety of situations with respect to concentration levels and meteorological conditions so as to yield data sequences enabling instrument inter-comparisons. Despite the somewhat differing designs of LPC1 (LPC2) and LPC3, their measurements could be compared, within a synchronization time difference smaller than 30 seconds, in the particle-size classes 0.3 - 0.5 μm, 0.5 - 1.0 μm, and > 5 μm. LPC1 had been chosen to be the reference device and the LPC2 and LPC3 data were converted to emulate LPC1 data.

For the measurements to be presented in this paper, the devices were programmed to sample in sequences of 3-10 cycles as the measuring time was set so as to sample exactly one liter of air for each cycle. The obtained data were averaged over each sequence and are shown on the graphs together with the standard deviation of the mean.

RESULTS AND DISCUSSION

A few experimental campaigns were carried out from May to September 2015. The results obtained over three days during the different campaigns will be reported here, namely, 08.05.2015, 30.05.2015, and 22.09.2015. These days were chosen in order to show the influence of the different parameters on the particle dispersion and concentrations.

On Fig. 1 a map of the experimental sites is shown. Two measurement schemes were realized: (a) a 30-minute-walking route along a park (positions 1 and 2 on Fig. 1a), on both sides of a boulevard located right next to the park (positions 3 and 4), and a residential area (positions 5 and 6), and (b) three-point stationary measurements in the park area (position 1 on Fig. 1b), in close proximity to the boulevard (position 2), and in the residential area (position 3). Measurements on 08.05.2015 and 30.05.2015 were carried out according to the first measurement scheme when only one LPC was available while those on 22.09.2015 were done according to the second measurement scheme.

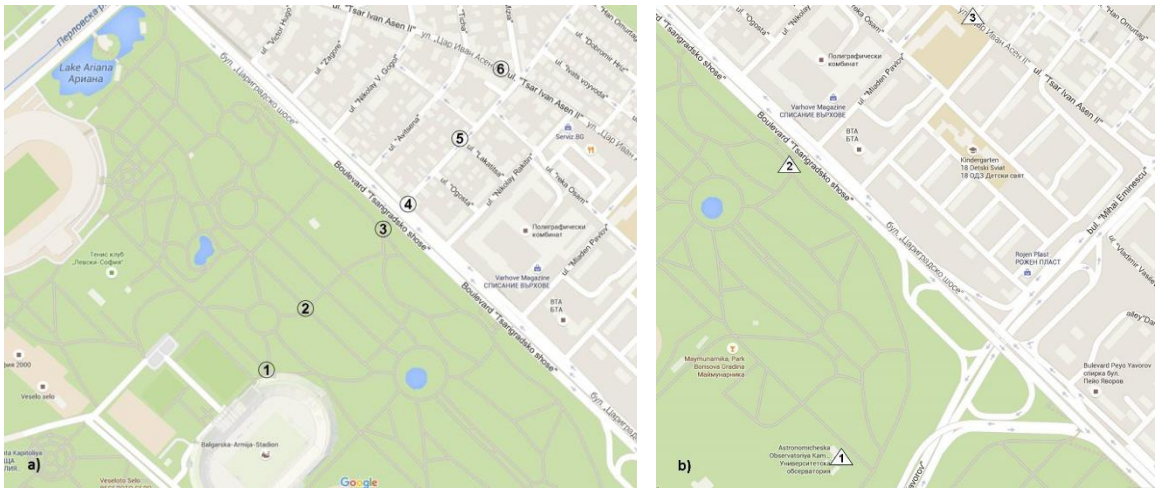

Figure 1. *Map of the experimental sites with the two measurement schemes: a) 30-minute walking route and b) three-point stationary measurements. Source: Google Maps*

The weather on 08.05.2015 and 30.05.2015 was clear and sunny, while on 22.09.2015 it was cloudy with occasional showers in the afternoon and evening hours. Measurements were carried out in the period between 06:30 and 13:30 GMT+2. Meteorological parameters, traffic rate and the ML height in the period of measurements for the above mentioned days are summarized in Table 1.

Table 1. *Meteorological parameters, traffic rate and mixing layer height for the three experimental days in the period of measurements*

Date	Wind Speed m/s	Wind Direction	Relative Humidity %	Traffic rate Vehicles/10min	MLH m
08.05.2015	**2 - 3**	**N, NW**	**75 - 45**	**730**	**1250**
30.05.2015	**1 - 2**	**Variable**	**76 - 35**	**570**	**1000**
22.09.2015	**3 - 4**	**E, ESE**	**83 - 53**	**530**	**1500**

The daily variations in the particle number concentration in size-ranges > 0.3, > 1, > 2.5 and > 10 μm as well as in the ML height (obtained by ceilometer operating 24/7 in the park area) on 08.05.2015 are presented in Fig. 2. The highest values of the fine particle number concentrations were obtained in the morning hours corresponding to the increase in traffic intensity (morning traffic jam hours). A decreasing tendency is seen in the course of the day, especially in the fine aerosol fraction. During the daily ML development, freshly emitted particles are distributed in altitude leading to a decrease in the fine particle number concentration at ground level. The fine

particle concentrations are found to also decrease by a factor of 2 in case of light wind (2 - 3 m/s). The bigger particles (5 - 10 µm) exhibit a stochastic behavior and do not show clear correlation with any of the considered

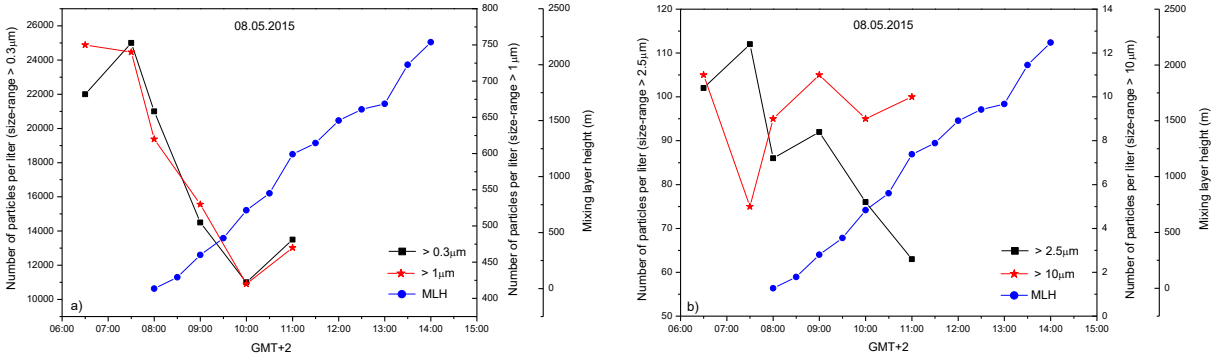

Figure 2. *Daily variations of the mixing layer height and particle number concentrations in size-ranges: a) > 0.3 and > 1 µm, and b) > 2.5 and > 10 µm obtained on 08.05.2015 in the park area*

influential parameters.

In Fig. 3 the particle number concentrations in size classes 0.3 - 0.5 µm (Fig. 3a) and 2.5 – 5 µm (Fig. 3b) obtained on 30.05.2015 at the six positions, according to the measurements scheme (a), are presented. As in the previous day, the highest values were obtained in the morning hours and particle number concentrations decreased during the ML development. Concerning the different positions, the highest values were obtained near to the boulevard, followed by those in the residential area and in the park. This distribution from the main source is found to be dependent on the wind direction and is observed in case of wind with western, north-western or variable direction. The north-western wind direction is parallel to the boulevard.

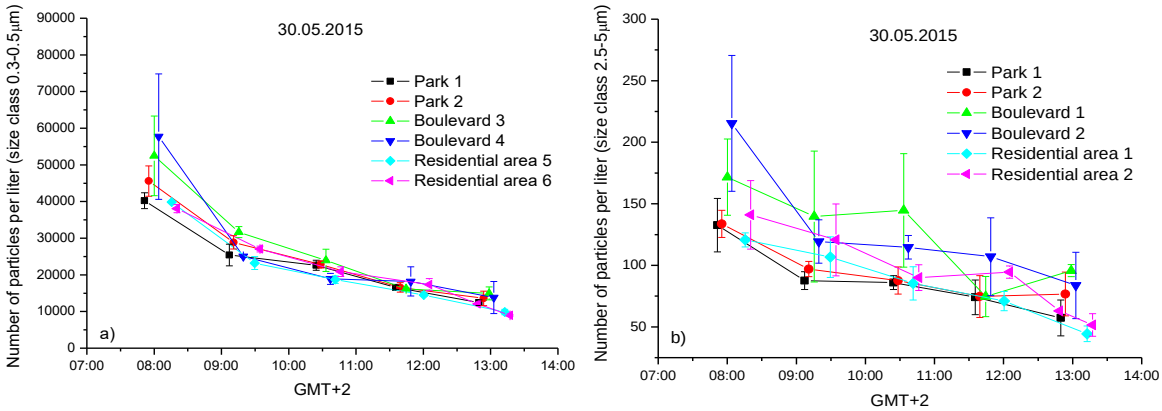

Figure 3. *Daily variations of the particle number concentrations in size classes: a) 0.3 - 0.5 µm and b) 2.5 – 5 µm obtained on 30.05.2015 in the six positions (measurement scheme (a))*

The ranges of variation in the particle number concentrations in the different size - ranges are summarized in Table 2.

Fig. 4 shows the daily variations in particle number concentrations in the size classes 0.3 - 0.5 µm (Fig. 4a), 0.5 - 1 µm (Fig. 4b) and > 5 µm (Fig. 4c) obtained on 22.09.2015 according to measurement scheme (b). The highest number concentrations in the morning hours and the decreasing tendency during the day are also seen in the data obtained on this day. In contrast with the data obtained on 30.05.2015, the highest values were obtained on the boulevard followed by those in the park and in the residential area. This distribution is hypothesized to be caused by the eastern wind that is almost perpendicular to the boulevard and blows the particles from the residential area and the boulevard towards the park. During this day, higher fine particle number concentrations were obtained in comparison with the other experimental days. This could be due to the higher humidity causing an aerosol growth and making aerosols detectable by the LPCs.

Table 2. *Range of variation of the particle number concentrations in the different size-ranges during the three experimental days*

Experimental site	Particle size-range µm	08.05.2015 N/L	30.05.2015 N/L	22.09.2015 N/L
Park	**> 0.3**	**25.10^3 - 11.10^3**	**55.10^3 - 20.10^3**	**90.10^3 - 48.10^3**
	> 2.5	**115 - 60**	**180 - 90**	**250 - 170**
	> 10	**10 - 5**	**12 - 8**	**12 – 10**
Boulevard	**> 0.3**	**28.10^3 - 17.10^3**	**75.10^3 - 25.10^3**	**90.10^3 - 50.10^3**
	> 2.5	**200 - 100**	**230 - 90**	**290 - 190**
	> 10	**23 - 13**	**27 - 8**	**15 - 11**
Residential area	**> 0.3**	**28.10^3 - 16.10^3**	**52.10^3 - 18.10^3**	**75.10^3 - 38.10^3**
	> 2.5	**170 - 100**	**200 - 90**	**130 - 120**
	> 10	**20 - 9**	**16 - 5**	**20 - 18**

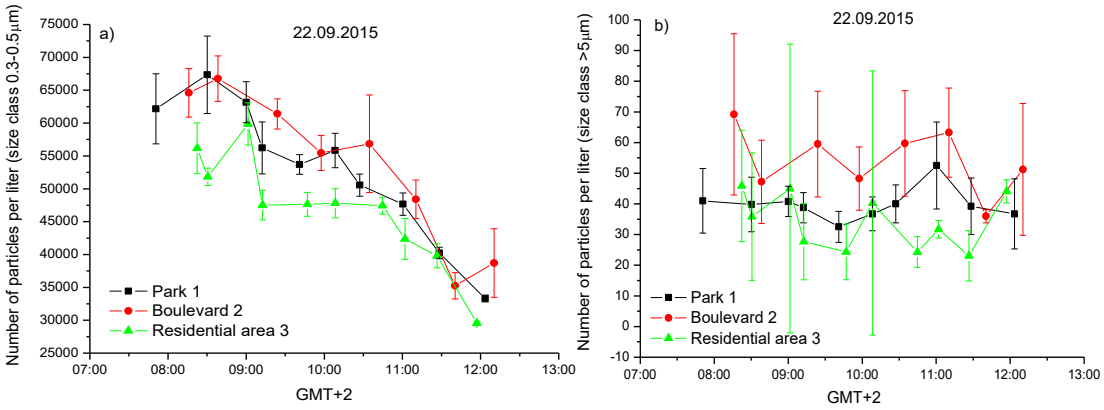

Figure 4. *Daily variations of particle number concentrations in size classes: a) 0.3 - 0.5 µm, and b) > 5 µm obtained on 22.09.2015 in the three positions (measurement scheme (b))*

CONCLUSIONS

The parameters influencing the particle distribution in three areas (a park, a boulevard and a residential area) in the downtown of the city of Sofia were investigated by three portable laser particle counters during a series of experimental campaigns carried out from May 2015 to September 2015. The following parameters were found to influence the particle distribution in the different areas: (1) *traffic intensity* – the increase in the traffic rate leads to an increase in the fine particle number concentrations; (2) *mixing layer development* – the increase in the ML height causes a spreading of the aerosols with altitude and a decrease in the ground level particle number concentrations; (3) *high relative humidity* - leads to growth of small aerosol particles into sizes detectable by the LPCs and thus higher particle number concentrations in observable size classes; (4) *wind speed* – in case of light wind with speed of about 2-3m/s, the fine particle number concentration decreased by a factor of 2; (5) *wind direction* – in case of western and north-western wind, the particle concentrations were the highest on the boulevard, followed by those in the residential area and in the park, while in case of eastern wind, the lowest particle number concentration were in the residential area.

ACNOWLEDGEMENTS

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REFERENCES

1. Buonanno, G., Fuoco, F.C., Stabile, L. 2011. Influential parameters on particle exposure of pedestrians in urban microenvironments. Atmos. Environ. 45, 1434-1443.
2. Evgenieva Ts., Wiman, B.L.B, Kolev, N., Savov, P., Donev, E., Ivanov, D., Danchovski, V., Kaprielov, B., Grigorieva, V., Iliev, I., Kolev I. 2011. Three-point observation in the troposphere over Sofia- Plana Mountain. Bulgaria. I. J. of Remote Sens. 32 (24), 9343-9363.

3. Kampa, M., Castanas, E. 2008. Human health and air pollution. Environ. Pollution 151, 362-367.
4. Kolev, N., Savov, P., Donev, E., Ivanov, D., Evgenieva, Ts., Grigorieva, V., Kolev, I. 2011. Boundary layer development and meteorological parameters impact on the ground level ozone concentration over an urban area in a mountain valley (Sofia, Bulgaria). I. J. of Remote Sens. 32 (24), 8915-8933.
5. Savov, P., Skakalova, T., Kolev, I., Ludwig, F. 2002. Lidar investigation of the temporal and spatial distribution of atmospheric aerosols in mountain valleys, J. of Appl. Meteorol. 41, 528-541.
6. Zajic, D., Fernando, H.J.S., Calhoun, R., Princevac, M., Brown, M.J., Pardyjak, E.R. 2011. Flow and turbulence in an urban canyon. J. of Appl. Meteor. and Climatol. 50, 203-223.

3.7 VARIATION OF ATMOSPHERIC AEROSOLS IN RELATION TO STREET MAINTENANCE ACTIVITIES IN URBAN STREET CANYON

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ABSTRACT

The atmospheric aerosols originate from a variety of sources and processes, some of them initiate others. From previous studies (Amato, 2011; EEA, 2014b) following factors characterise PM concentration. While exhaust emissions are governed by source type and activity, non-exhaust emissions occur and depend on resuspension, road, brake and tyre wear, precipitation, geographical location, traffic speed dependency and other factors.

This paper gives information about PM_{10} variation during street maintenance activities, therefore it will serve as basis for further studies about effectiveness of these activities, to reduce dust pollution. The present study was carried out during the time period of 2012-2014 in Riga, the capital city of Latvia, where street maintenance activities are used in various frequencies, usually depending on meteorological forecasts and stability during last 3 days.

According to study results, overall daily average PM_{10} concentrations mostly are similar, but hourly analysis show strong increase of peak concentrations during street sanding days.

Keywords: particulate matter (PM); dust binding; street cleaning; traction sanding.

INTRODUCTION

Nowadays most of the people live in cities, where air pollution is a significant problem. Right now the focus is on three key pollutants that pose the greatest risk to the achievement of good air quality, one of which is particulate matter (PM) (EEA,2014b).

It is well known, that the main source of air pollution in agglomerations is connected to traffic. Although mainly focus is directed towards exhaust emissions, there are significant amount of studies (Keuken et al, 2010;, Querol, 2004) showing other crucial transport-induced processes, such as, resuspension and abrasion, that increase atmospheric pollution. PM, resulting from movement of the vehicle, main sources are mainly road surface, tyre and brake system wear elements, as well as dust and other particles already settled on the road, such as sand, salt, etc.

As stated in Directive 2008/50/EC [2008], within European Union PM_{10} concentration's daily limit value is 50 $\mu g/m^3$ and it should not be exceeded more than 35 times during a calendar year. Annual limit value is set to 40 $\mu g/m^3$. Almost all European countries, including Latvia, regularly exceed these limits and unfortunately in recent years the situation is not improving.

The choice of this type of research is related to the problems of PM concentration levels in Riga and the difficulties to develop and implement air quality improvement program in Riga. As seen in Fig. 1. during the period from 2008 until 2014, four years PM_{10} concentration exceeds the EU limit (40 $\mu g/m^3$), as well as there is increase in allowed daily limit exceedances. The highest concentrations of PM particles are observed during spring months - March, April, May - which is related to sanding activities during winter.

The aim of this study is to assess variation of PM concentration levels in relation to used street maintenance activities in Riga, capital city of Latvia.

METHODOLOGY

The present study was carried out during the time period of 2012 - 2014 in Riga, the capital city of Latvia (Fig. 2.). Research part was based on PM_{10} measurement hourly data collected from a traffic pollution station that is located in urbanised area on one of the main streets - Kr. Valdemara street - in the city centre (approximate distance from intersection - 25m and 0,5m away from sidewalk, with transport intensity of about 39 000 cars per day). Street width is about 15 m and it is surrounded with 20 – 30 m high buildings on both sides.

Measurements represent PM_{10} concentration ($\mu g/m^3$), they were obtained from HORIBA FH62 (R3) device. Its operation is based on the beta-radiation method, infiltration air flow - 0,8 m^3/h. Meteorological data (wind speed and direction, precipitation, air temperature) from Latvian Environment, Geology and Meteorology Centre was

also used. Data regarding street maintenance activities was provided from Traffic Department of the Riga City Council. During winter, main streets are mostly being treated with wet salt - concentrations 10 – 40 g/m^2 and salt-sand mixture. To detect changes in PM_{10} concentration during street sanding, first, similar days (by month, day of the week, traffic flow and meteorological data) were found - one during which street treatment took place and one without any street maintenance activities. After that these days were compared statistically, resulting in 11 "couples" that represent PM_{10} concentration changes during street sanding. During spring and summer main street maintenance activities include street sweeping using vacuum and wetting devices. Meteorological conditions and performed street cleaning activities were correlated to detect any effects on the PM_{10} concentration using Pearson's correlation in IBM SPSS Statistics program (Ver.22).

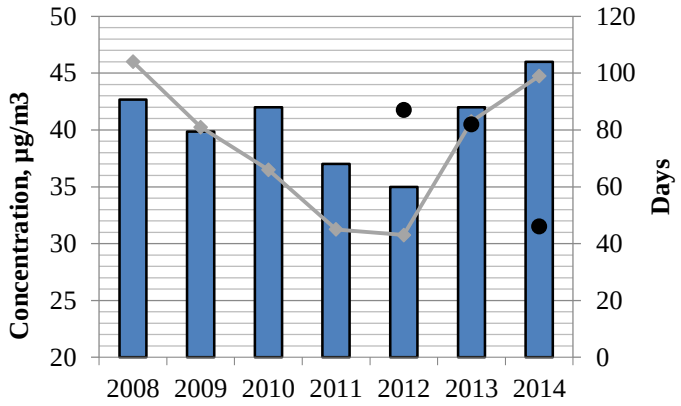

Figure 1. *PM_{10} annual mean concentrations, number of days when EU limit (50 µg/m^3) has been exceeded (line) and number of street sanding days in winter (dots) on Kr. Valdemara street (typical street canyon) in Riga*

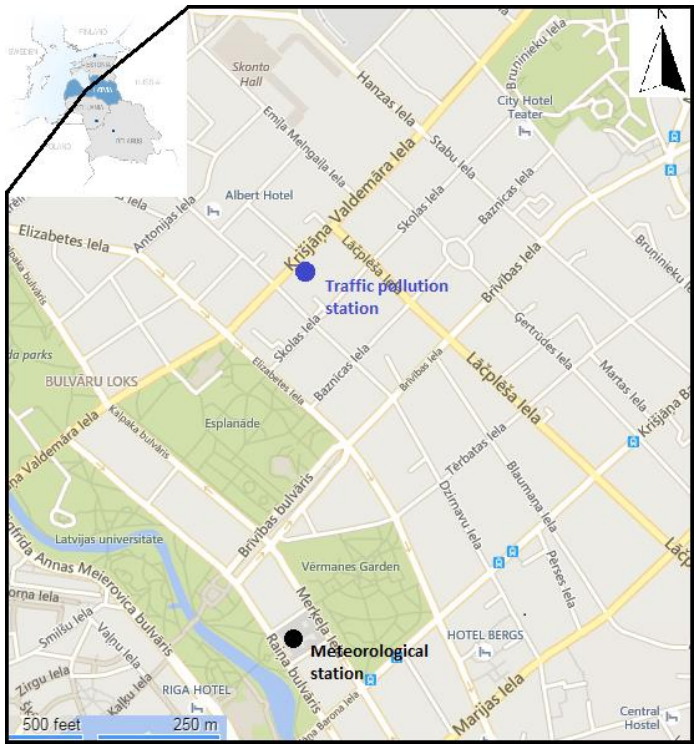

Figure 2. *Location of monitoring sites in Riga, Latvia (map layer from www.bing.com/maps)*

RESULTS

According to results, overall daily average PM_{10} concentrations mostly are very similar, but hourly analysis show strong increase of peak concentrations during or right after street sanding activities.

Fig. 3. shows comparison of two similar days. On January 22, 2013 the average daily value of PM_{10} is 53,80 $\mu g/m^3$, which also exceeds allowed daily limit value. PM_{10} concentration in the same day was about 56% higher (daily average) and about 80% higher (during sanding - 6:00 AM to 10:00 AM) compared to January 18, 2013, when there were no street sanding activities.

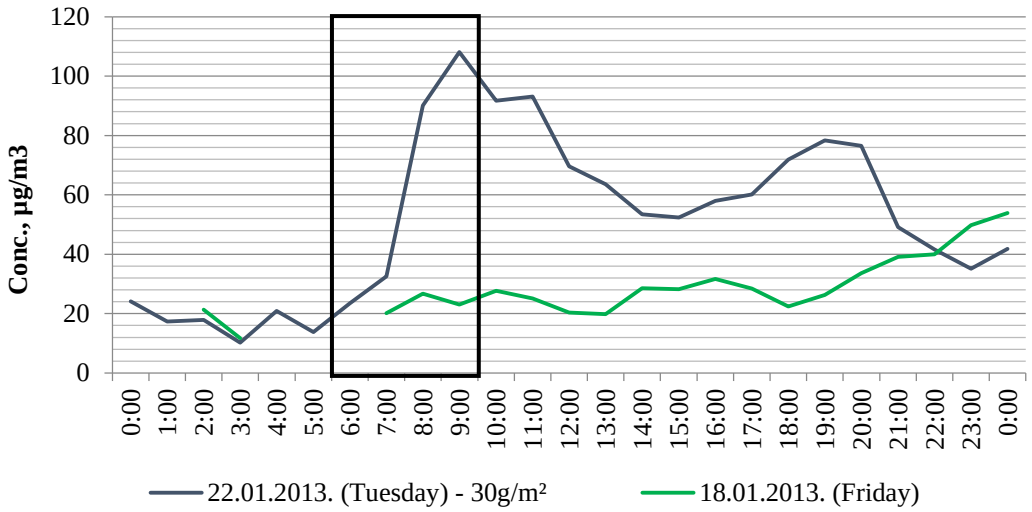

Figure 3. *PM_{10} concentrations ($\mu g/m^3$) on Kr. Valdemara street with (blue)/without (green) sanding*

In the second case PM_{10} concentration reaches its peak after street sanding which takes place from 5:00 AM to 9:00 AM on December 4, 2012 (Fig. 4.). The EU limited average daily PM value was also exceeded (it was 52,39 $\mu g/m^3$), and compared to the day before when sanding was not carried out, PM_{10} concentration in atmosphere was about 29% higher.

In all cases, highest daily concentrations were measured during traffic peak hours when traffic intensity is higher and so is particle resuspension or right at the moment when sanding was carried out which results in salt - sand particle scattering in street level.

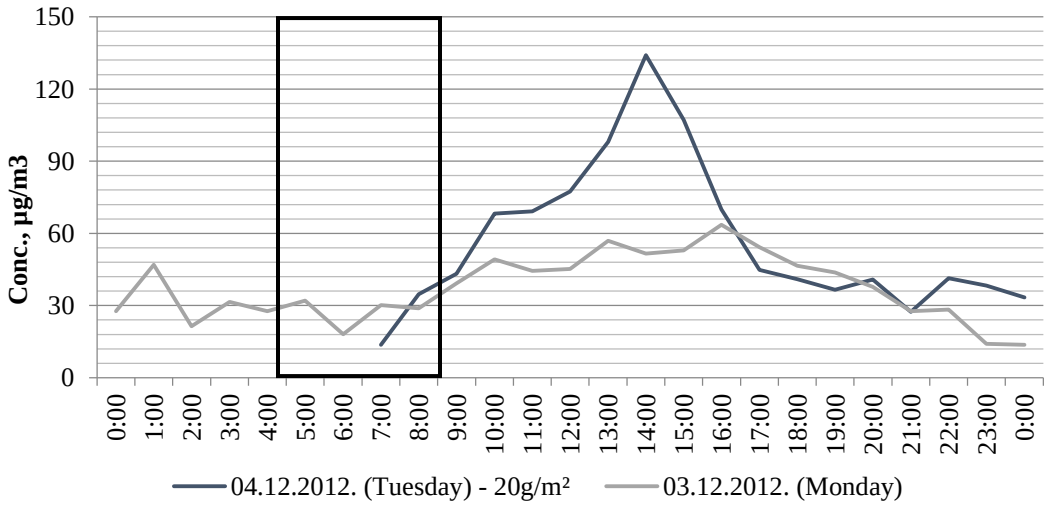

Figure 4. *PM_{10} concentrations ($\mu g/m^3$) on Kr. Valdemara street with (blue)/without (green) sanding*

There were few cases, where PM_{10} concentration was higher on the day when no traction control maintenance activities were carried out. Such cases were inspected further and usually it was because of meteorological differences. As in Fig. 5. on March 10, 2013, there was precipitation during and after sanding activities, as a result particles might have "bonded", that way decreasing PM_{10} resuspension and therefore it also reduced their concentration in atmosphere. In contrary, there were no precipitation or street maintenance activities from March 14, so, on March 17, so PM_{10} concentration probably is higher, due to particle resuspension.

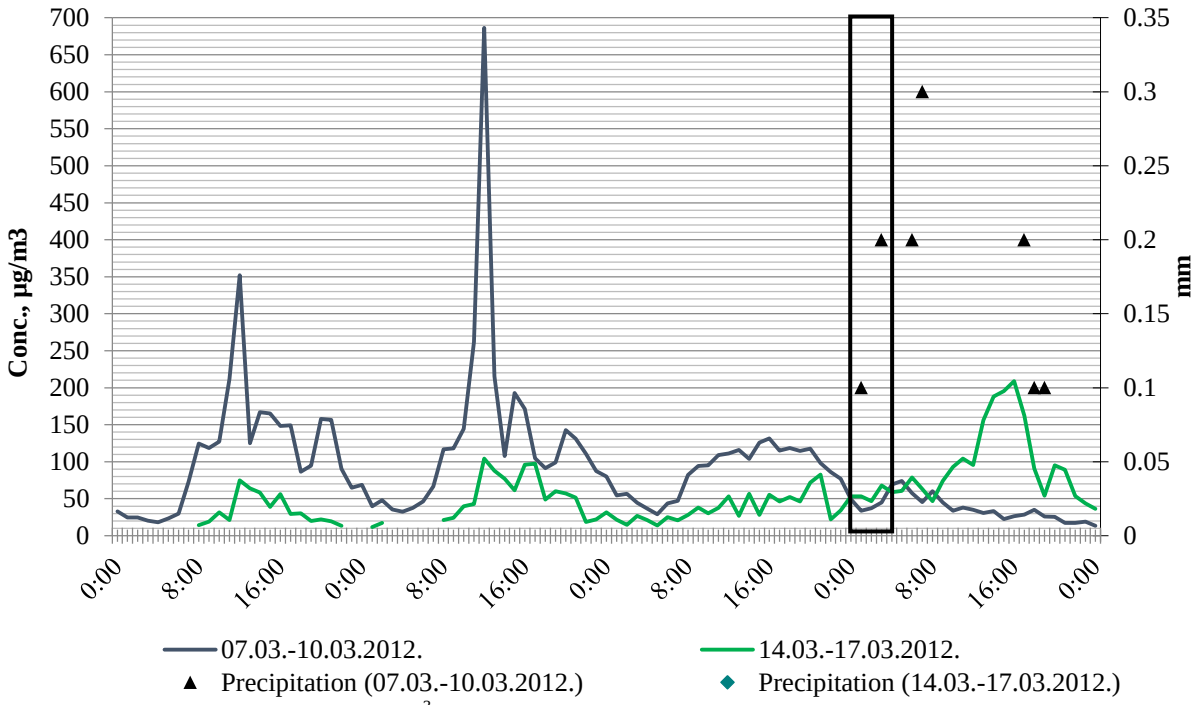

Figure 5. *PM_{10} concentrations ($\mu g/m^3$) on Kr. Valdemara street with (blue)/without (green) sanding with precipitation (triangles)*

To conclude the concentration and distribution of particles depends on various factors, hence it cannot be said that application of sea salt - sand mixture significantly increases PM_{10} concentration in atmosphere, therefore further studies must be carried out.

Street cleaning in city centre is mostly carried out from April to October, 5 - 6 times a week, usually early in the morning or late at night. Unfortunately, the time was not specified in provided information, so in this study it was not possible to examine PM_{10} concentration changes before and right after street cleaning.

Table 1. *Parametrical Pearson's correlation matrix (results from SPSS Statistics program)*

	PM10	Cleaning	Temp	Wsp	Wdir	Precip
PM10	1	,039	,305**	-,095	-,228**	,205**
Cleaning	,039	1	,068	,022	,058	,011
Temp	,305**	,068	1	-,245**	-,248**	0,73
Wsp	,095	,022	-,245**	1	,069	-,014
Wdir	-,228**	,058	-,248**	,069	1	,052
Precip	,205**	,011	0,73	-,014	,052	1

**p=0,01 – correlation is significant at the 0,01 level.

While using correlation (Table 1) there were no significant relevance found between mean daily concentrations and street cleaning activities, so the effects of street cleaning activities must be further examined with additional measurements before, right after and during these activities.

CONCLUSIONS

1. Since 2012 annual average PM_{10} concentration in Riga has increased by about 24% and in city centre daily PM limit values are regularly exceeded, also last year (2014) has been with the highest number of exceedances - 99 days (of the permitted 35).

2. In general there is no significant impact of sanding activities on monthly average PM_{10} concentration levels, although some sanding episodes can increase average daily levels of particulate matter by 28 - 64% and even up to 80% during and immediately after sanding.

3. In all cases the concentration of particles in the atmosphere is also affected by weather conditions, the greatest reduction of PM_{10} concentration was observed on days when there is precipitation.

4. Although effect of salt used for traction control on the environment is undoubtedly essential, but at present moment it is the cheapest option for traction control, and in Riga, unfortunately, it is difficult to use just sand or crushed stone material, because of the poor sewage system. It requires additional studies to find the best solution for street maintenance during winter.

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REFERENCES

1. Amato, F., Pandolfi, M., Moreno, T., Furger, M., Pey, J., Alastuey, A., Bukowiecki, N., Prevot, A. S. H., Baltensperger, U., Querol, X. 2011. Sources and variability of inhalable road dust particles in three European cities. Atmospheric Environment 37, 6777–6787.
2. Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe, Official Journal of the European Union, L 152, 1-44
3. European Environmental Agency (EEA), 2014a. Emissions of primary PM2.5 and PM10 particulate matter, CSI 003/APE 009
4. European Environmental Agency (EEA). 2014b. Air quality in Europe – 2014 report.
5. Keuken, M., van der Gon, D. H., van der Valk, K. 2010. Non-exhaust emissions of PM and the efficiency of emission reduction by road sweeping and washing in the Netherlands. Science of the Total Environment. 408, 4591. - 4599.
6. Querol, X., Alastuey, A., Ruiz, C. R., Artinano, B., Hansson, H. C., Harrison, R. M., Buringh, E., ten Brink, H. M., Lutz, M., Bruckmann, P., Straehl, P. Schneider, J. 2004. Speciation and origin of PM10 and PM2.5 in selected European cities. Atmospheric Environment. 38, 6547. - 6555.

3.8 VARIATIONS IN O3 AND NOX AT COASTAL SUBURBAN, AND URBAN SITES IN ISTANBUL

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ABSTRACT

In this study, the variations of surface ozone (O_3), nitric oxide (NO), nitrogen dioxide (NO_2), and total oxidant (OX) concentrations measured from 1 March 2013 to 1 March 2015 at coastal suburban and urban sites in the megacity of Istanbul are analyzed. In order to understand the contribution of ozone precursors on ozone levels, seasonal and daily variations of ozone and its precursor pollutants were examined. The variation of OX concentrations with NO_x in coastal suburban (Şile) area where the local emissions are very low is examined for the first time due to its new establishment of this monitoring station. OX concentration is also found due to the specious of the NO_x independent regional contribution. The results present that the daily variations of NO_x and OX levels in coastal suburban area indicate that oxidants come from transport processes instead of local emissions.

Keywords: O_3, OX, NOx-dependent, NOx-independent.

INTRODUCTION

The share of aerosols and surface or ground-level ozone pollution among the air quality problems in the city environments are gradually increasing since several decades. Specifically, ozone in the lower troposphere is an important photochemical oxidant and its episodic levels can lead to serious impact on health and ecosystems in urban and rural areas. Especially, children, elderly, and the people having pulmonary disease can be influenced by the surface ozone formation (EPA, 2014). EPA, recently reported that an estimated 25.9 million people have asthma in the U.S., including almost 7.1 million children (EPA, 2014). In the light of these developments, EPA is seeking comment on levels for the health standard of ozone as low as 60 ppb. Therefore, controlling of ozone levels will improve health protection, specifically for children and the elderly people. Furthermore, NO_x ($NO + NO_2$) are one of the main constituents for production of ground-level ozone, which can cause trigger chronic respiratory diseases (Mavroidis and Chaloulakou, 2011, 2012).

Surface ozone is produced photochemically in the presence of intense solar radiation by ozone precursors such as nitrogen oxides and the volatile organic compounds. For example, surface ozone is generated photochemically, when NO_x exceeds 0.05 ppb by NO_2 photolysis, following oxidation of NO to NO_2 (Seinfeld and Pandis, 1998). There is a nonlinear relationship between photochemical ozone production and the concentrations of ozone precursors. In particular, surface ozone is formed through the photolysis of NO_2. NO_2 photolysis generates ozone formation under the effect of solar radiation having the wave length smaller than 424 nm. Reaction mechanism is shown below in (1), (2) and (3). These chain reactions are only a cycle with no total chemistry. For instance, an increase in ozone level, may raise the ambient NO_2 levels because of the NO level's oxidizing to NO_2.

$$NO_2 + h\nu \rightarrow NO + O \quad (1)$$
$$O + O_2 + M \rightarrow O_3 + M \quad (2)$$
$$O_3 + NO \rightarrow NO_2 + O_2 \quad (3)$$

In the NO_x-limited regime, the rate of the photochemical ozone production is determined by the following oxidation of NO to NO_2 with peroxy radicals (HO_2 and RO_2). The reactions are shown by the reactions 4-6:

$$RO_2 + NO \rightarrow RO + NO_2 \quad (4)$$
$$RO + O_2 \rightarrow R'COR'' + HO_2, \quad (5)$$
$$HO_2 + NO \rightarrow OH + NO_2, \quad (6)$$

where R, R' and R'' indicate organic groups.

The trends in surface ozone in urban and rural areas are strongly linked to the changes in man-made emissions of ozone precursors (Wang et al, 2009; Fiore et al, 1998). Ozone precursors, particularly NO and NO_2 seem to be primary indicators of the future ozone levels in major cities. Emissions from sources such as motor vehicles, industrial plants, solvents are among the main sources of ozone forming emissions mainly for nitrogen oxides. In urban areas, diurnal cycle of ozone is controlled by NO. Emissions of anthropogenic ozone precursors from urban and industrialized areas can lead to elevated ozone concentrations in downwind suburban and rural areas (Tang et al, 2009; NRC, 1991).

In the case of low NO_x or NO_x limited regime, an increase in NO increases the ozone production rate (Sadanaga et al, 2012). Specifically, rural areas exhibit similar characteristics for the low NO_x regime. Whereas, in the case of high NO_x mixing ratios, such as traffic dense areas ozone production rates decrease when NO_x concentrations increase. This case is so-called NMHC limited regime and can be occurred in traffic dense areas.

Surface ozone has been measured first time in 1998 at the two traffic dense regions of Istanbul within the new monitoring network. However, the ozone measurements have never been continuous measurements for a long time. In spite of the limited ozone measurements, several studies are conducted (Topcu and Incecik, 2002; 2003; Unal et al, 2010; Anteplioglu et al, 2003). Topcu and Incecik (2002; 2003) examined the ozone and its precursors levels in the city. Later, to address these shortcomings and to understand the ozone variation over the city, Incecik (2007) established three air quality stations on a different locations of the city. For example, Princess Island, Kandilli Observatory and a roadside were selected to represent the rural, semi-rural and traffic areas in the city, respectively. The results of the analysis and model simulations of ozone were published in some journals (Im et al, 2011; Im et al,2013).

In this study, an analysis of ozone and NO_x concentrations based on a coastal/suburban (Şile) site and the urban/traffic (Sultanbeyli) site in the period of March 2013 to March 2015 are presented. For this purpose, variations of oxidant OX (sum of O_3 and NO_2 concentration) are also investigated, contributing to a better understanding of the atmospheric sources of OX at these sites. Furthermore, the variation of O_3 and OX concentrations with NO_x in Şile coastal/suburban area is examined for the first time. First measurement of NO, NO_2, and O_3 can be a considerable challenge to establish the spatial representativeness of the analysis for the ozone trends in coastal/suburban area of İstanbul.

METHODOLOGY

Study Area

Fig. 1 shows the locations of the selected air quality stations in Istanbul. The Greater City of Istanbul which has a population of 15 million within an area of 5400 km^2, making it one of the largest and most densely populated cities in Turkey. Şile suburban site is located at the northern coastal part of the city in Asian side. Sultanbeyli urban and dense traffic site is also located at the Asian part of the city. The air quality stations were established as part of the Twinning Project TR/2007/IB/EN/02 and supported by Instrument for Pre-accession Assistance (IPA) of the EU. The air quality measurements have been performed on the coastal area of Şile, neighbor to the Isık University campus area since March 2013. The monitoring station has subjected regular checks. This area lies just north of the watershed and exhibits typical rural/suburban characteristics within a 712 km^2. The beaches on the coastal area of the Black Sea in the north are attractive regions for the domestic people living in the city environment. About 32,000 population live in this district. However summer population in the area is much greater than winter. The climate of Şile is temperate, mild and warm with 13.3 ^oC. annual average temperature. The hottest month is August and coldest month is January. The annual rainfall amount of this coastal site is 826mm while Sultanbeyli at relatively south of the city is 793 mm. Prevailing winds are generally NE and SW. NE winds can carry the ozone precursor gases from Ukraine and Bulgaria by air masses.

In this study, we used hourly ozone, NO, NO_2, NO_x, O_3 and OX concentration data measured at the coastal/suburban and urban sites from March 2013 to March 2015. Measurement principles of O_3, and NO, NO_2, are based on UV absorption and chemiluminescence technique.

Figure 1. *Location of the air quality stations in Istanbul.*

One of the major NO_x emission sources is the highway extending on the north-south direction connecting Şile to the center of Istanbul with a length of about 70km. Generally, in the summer months highway is very busy due to the summer travelers. Additionally, there is a limited fertilizer use in spring months (March - May) in some agricultural areas around the Şile which may contribute to NO_x emissions. Besides, motor vehicle emissions due to the busy campus traffic may increase NO_x emission in this area.

RESULTS AND DISCUSSION

In this study, variations of surface ozone (O_3), nitric oxide (NO), nitrogen dioxide (NO_2), and total oxidant (OX) concentration at coastal suburban and urban sites of Istanbul are analyzed. Figure 1 represents the annual average daily variation of OX and NO_x at Sultanbeyli and Şile. The highest mean concentration was seen at 09:00 hours LT when the morning traffic activities were started and the second peak was observed during evening traffic flow being less than morning for Sultanbeyli. This behavior is similar to the results of Notario et al (2012) in a metropolitan area of Iberian Peninsula (Notario et al, 2012). Otherwise, OX level as defined the sum of NO_2 and O_3 reaches to peaking just after 08:00 hours LT and even if the O_3 levels decrease after 19:00hours LT, OX levels remain higher due to NO_2 levels.

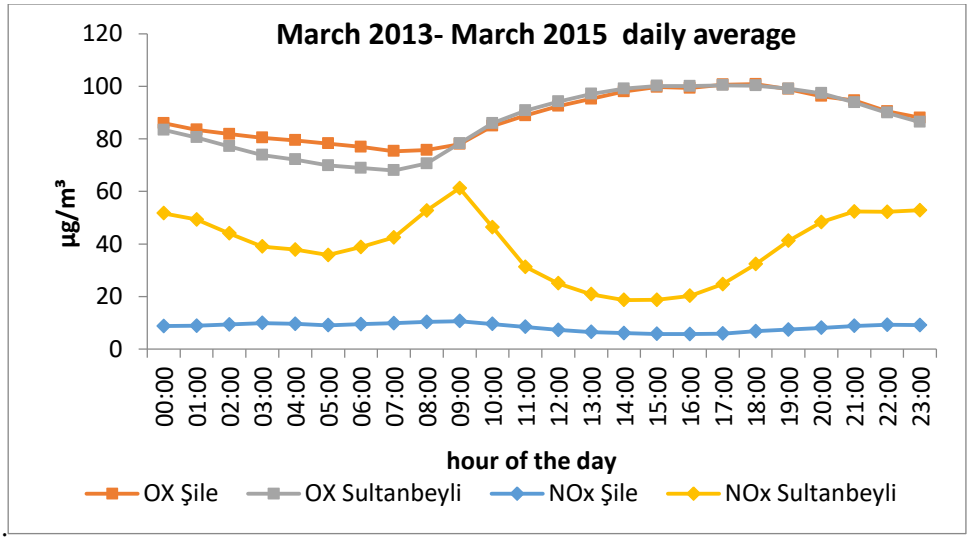


Figure 1. *Annual average daily evolution of OX and NO_x compounds from 1 March 2013 to 1 March 2015 at Sultanbeyli and at Şile.*

Seasonal variations of O_3 concentrations in Şile is shown in Fig. 2a. Ozone levels at early morning hours are relatively low at all seasons. However, after 09:00 LT O_3 levels begin to increase and peaked during 16:00-17:00

LT hours. As expected the lowest levels of ozone are observed in winter season where the solar radiation is the lowest while the highest levels in the summer.

On the other hand, Fig 2a and 2b show that the O_3 levels at the coastal suburban site are less than the urban site. In fact, the peak time is similar in both area. This may be attributed to the solar radiation and the developing of mixing layer (Han et al, 2011).

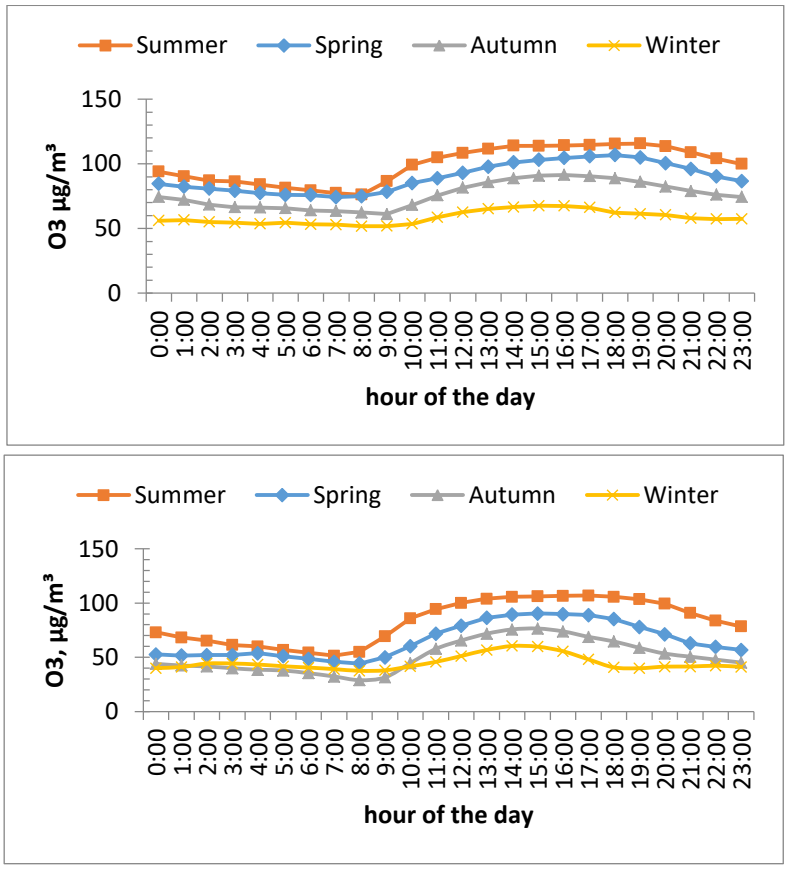
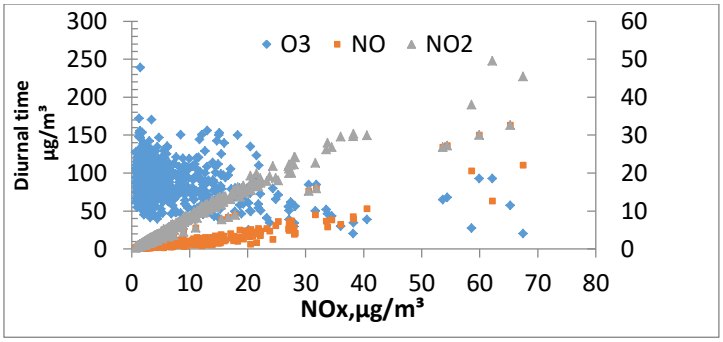


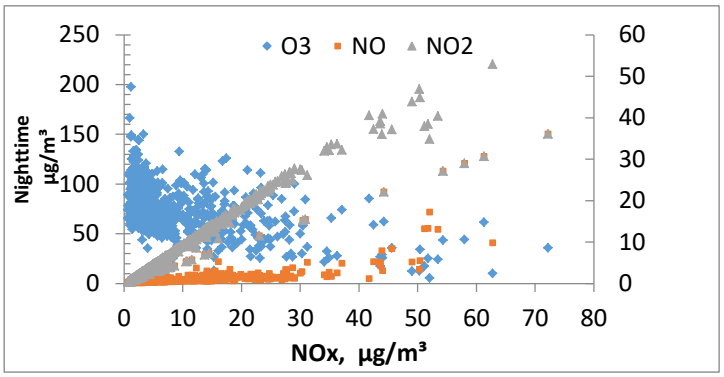
Figure 2. *The average diurnal changes of O_3 concentrations for each season at coastal suburban (Şile) (a) and urban (Sultanbeyli) (b).*

The highest ozone concentrations are appeared where the photochemistry activity of solar radiation reaches to highest limit. Therefore, higher values start on May and continue to October. Furthermore, photochemical activity in the coastal and suburban site is supported by the ozone precursor emissions. This is possibly due to the increases of ozone precursor emissions in the rural environment to support O_3 production occurred on the busy highway for summer travelers connected to the Istanbul. The ozone levels are the lowest at Sultanbeyli urban traffic site due to the ozone destruction process. The annual variation of ozone concentrations in rural areas depends on many factors, such as the geographical location, meteorological factors and the transport from the stratosphere to the troposphere (Junge, 1962;Danielsen, 1968; Fabian and Pruchniewz, 1977). However, we do not expect the stratospheric intrusions at this coastal and suburban area.

As seen in Fig.2, the lowest ozone levels appear in morning between at 6:00 and 8:00 LST and the peak time of the ozone is around 16:00 LST. This behavior is much similar to ozone variations at the crest of the Princes Island in Istanbul (Im et al, 2013). The maximum OX levels are seen in ozone season months (April to October). OX levels are therefore not affected by reactions between NO and ozone. This relationship makes OX a better measure of the true photochemical production rate of ozone (Tang et al, 2009). Therefore the summertime oxidants are higher than wintertime because of the solar radiation effect. The negative relationships between NOx levels and ozone concentrations are clearly seen in Fig.3. At 7:00am in the morning hours, sunlight begins to rise initiating the photochemical reactions. Then, NO is converted to NO_2 via a reaction with O_3, and during daytime hours and vice versa NO_2 is converted back to NO as a result of photolysis, which gives the regeneration of O_3 as seen in Fig 3.



a



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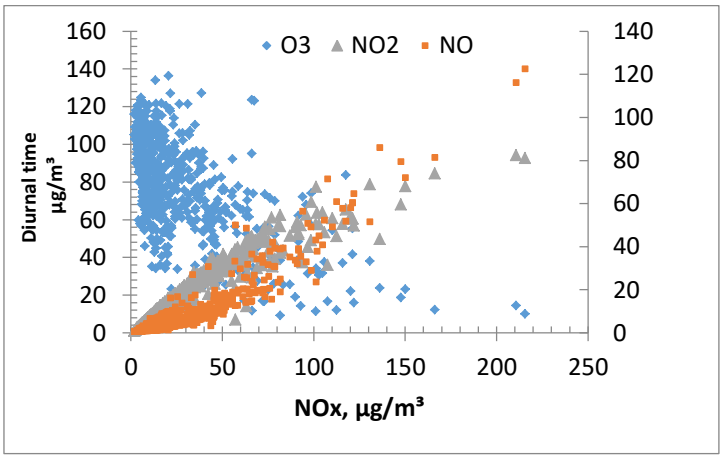
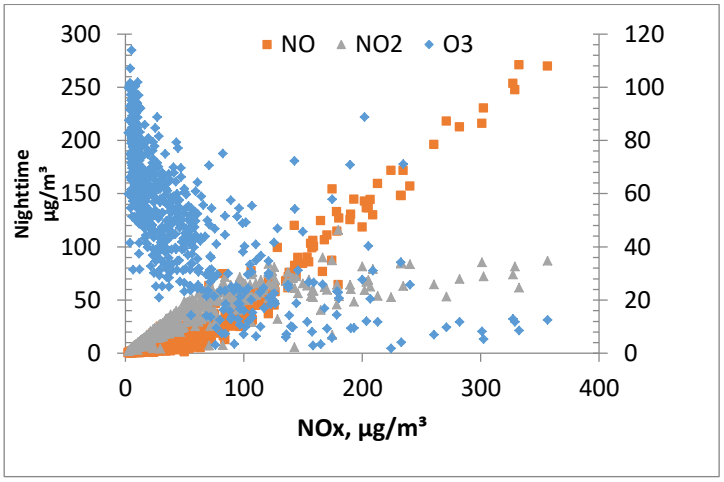


c



d

Figure 3. *Variation of NO, O_3, NO_2, vs NO_x during all period for diurnal (a), nighttime (b) at Şile, and Sultanbeyli (c) and (d).*

CONCLUSIONS

In the present study, the variations of NO, NO_2, O_3 and OX concentrations in ambient air of Şile coastal/suburban site and Sultanbeyli urban /traffic site of Istanbul in the period March 2013 to March 2015 are analyzed. The ozone levels at the coastal and suburban site (Şile) is higher than at the urban/traffic site (Sultanbeyli) in Istanbul.The presented daily variations of NO_x and OX levels in this rural/suburban area indicate that oxidant come through transport processes instead of local emissions.

It is also concluded that the decrease in NO concentrations in Şile coastal/suburban environment is likely associated with the local characteristics in this area. The similar results has been seen before at the crest of Prince Island of Istanbul located at the south part of the city (Im et al, 2013). The possibility that some of these effects might reflect changes in Şile's ozone levels is suggested by the findings of somewhat. However, since the some evidence suggests that the university campus also had an impact on traffic volume on weekdays. Finally, first measurement of NO, NO_2, and O_3 can be a considerable challenge to establish the spatial representativeness of the analysis for the ozone trends specifically at the coastal/suburban area of İstanbul.

Furthermore, although not the aim of this study, it is important to consider how the ozone levels measured at Şile ambient environment might be translated into health effects and ecosystem.

ACKNOWLEDGEMENT

The authors thank to Marmara Clean Air Center for providing the air quality data.

REFERENCES

1. Anteplioğlu.,U., İncecik., S., Topçu, S., 2003. An application of a photochemical model for urban airshed in Istanbul, Journal of Water, Air & Soil Pollution:Focus, 3(5-6), 55-66.
2. Danielsen, E.F., 1968. Stratosphere-troposphere exchange based on radioactivity, ozone and potential vorticity. Journal of Atmospheric Science 25, 502-518.
3. Fabian, P., and Pruchniewz, P. G. 1977. Meridional distribution of ozone in the troposphere and its seasonal variations, J. Geophys. Res., 82, 2063–2073.
4. Fiore, A. M., Jacob, D. J., Logan, J. A., and Yin, J. H., 1998. Long-term trends in ground level ozone over the contiguous United States, 1980–1995, J. Geophysical Research-Atmosphere, 103, 1471–1480.
5. Han, S., Bian, H., Feng, Y., Liu, A., Li, X., Zeng, F., Zhang, X., 2011. Analysis of the Relationship between O_3, NO and NO_2 in Tianjin, China, Aerosol and Air Quality Research, 11, 128–139.
6. Im, U., Poupkou, A., Incecik, S., Markakis, K., Kindap, T., Unal, A., Melas, D., Yenigun, O., Topcu, S., Odman, T., Tayanc, M., 2011. The impact of anthropogenic and biogenic emissions on surface ozone concentrations in Istanbul. Science of the Total Environment 409, 1255–1265.
7. Im, U., Incecik, S., Guler, M., Tek, A., Topcu, S., Unal, Y.S., Yenigun, O., Kindap, T., Odman, T., Tayanc, M., 2013. Analysis of surface ozone and nitrogen oxides at urban, semi-rural and rural sites in Istanbul, Turkey. Science of the Total Environment 443, 920–931.
8. Incecik, S., Im, U., Topcu, S., Yenigün, O., Kindap, T., Odman, T., Tek, A., 2007. Short-term forecasting of ozone over Istanbul,Turkey by MM5-CMAQ, Turkish Scientific and Technical Research Council- Project No:105Y005(in Turkish)
9. Junge, C.E., 1962. Global ozone budget and exchange between stratosphere and troposphere. Tellus 14, 363-377.
10. Mavroidis, I., Chaloulakou, A., 2011. Long-term trends of primary and secondary NO_2 production in the Athens area. Variation of the NO_2/NO_X ratio. Atmospheric Environment 45, 6872–6879.
11. Mavroidis, I., Ilia, M., 2012. Trends of NOx, NO_2 and O_3 concentrations at three different types of air quality monitoring stations in Athens, Greece. Atmospheric Environment 63, 135-147.
12. National Research Council (NRC), 1991. Committee on tropospheric ozone formation and measurement, Re thinking the ozone problem in urban and regional air pollution, National Academy Press.
13. Notario A., Bravo I., Adame J.A., Díaz-de-Mera Y., Aranda A., Rodríguez A., Rodríguez D., 2012. Analysis of NO, NO_2, NOx, O_3 and oxidant ($OX=O_3+NO_2$) levels measured in a metropolitan area in the southwest of Iberian Peninsula. Atmospheric Research 104–105, 217–226.
14. Sadanaga.Y, M. Sengen, N. Takenaka, H. Bandow, 2012. Analyses of the Ozone Weekend Effect in Tokyo, Japan: Regime of Oxidant (O_3 + NO_2) Production, Aerosol and Air Quality Research, 12, 161–168.
15. Seinfeld J.H., and Pandis S.N, 1998. Atmospheric Chemistry and Physics. John Wiley and Sons, Inc., New York: 234-336.
16. Tang G., X. Li, Y.Wang, J. Xin, and X. Ren, 2009. Surface ozone trend details and interpretations in Beijing, 2001–2006, Atmospheric Chemistry Physics, 9, 8813–8823.

17. Topcu.S, İncecik, S., 2003. Characteristics of surface ozone concentrations in urban atmosphere of Istanbul: A Case Study, Fresenius Environmental Bulletin, 12, 413-417.
18. Topcu.S, İncecik, S., 2002. Surface ozone measurements and meteorological influences in the urban atmosphere of Istanbul, Int. Journal of Environment and Pollution 17, 390-404.
19. Unal, Y.S., İncecik, S., Topcu, S., Oztopal, S., 2010. Daily peak ozone forecast in Istanbul. International Journal of Remote Sensing, 31, 551-561.
20. United States Environmental Protection Agency, EPA web site retrieved from: http://www.epa.gov/groundlevelozone/ [07.03.2015].
21. Wang T, X. L. Wei , A. J. Ding , C. N. Poon , K. S. Lam , Y. S. Li , L. Y. Chan , and M. Anson, 2009. Increasing surface ozone concentrations in the background atmosphere of Southern China, 1994–2007, Atmospheric Chemistry and Physics, 9, 6217–6227.

4. ADVANCES IN MONITORING

4.1 NEW SENSING TECHNOLOGIES FOR ENVIRONMENTAL SUSTAINABILITY APPLICATIONS

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ABSTRACT

Air pollution is one of most impacting issues on human health and climate change at worldwide level. Mitigation initiatives based on new accurate low-cost sensing technologies and enhanced awareness of the citizens are extremely urgent to improve the environmental sustainability and quality of life in Europe. This lecture gives an overview of new sensing technologies based on low-cost and low-power sensor-systems for air quality control and environmental sustainability. The smart sensors are shortly reviewed for sustainable applications at the current state-of-the-art. Furthermore, the final goals and objectives of some networking key EU initiatives on enabling sensor applications are detailed such as the European Sensor-System Cluster (ESSC), launched by EC DG R&I, and the running COST Action TD1105 EuNetAir - European Network on New Sensing Technologies for Air-Pollution Control and Environmental Sustainability - funded in the COST framework of European Cooperation in Science and Technology (2012-2016).

INTRODUCTION

Air quality takes a prominent position in discussions on urban environment and health, and it is a concern for many inhabitants of urban areas. About three quarters of the European population lives in urban areas. The urban environment has a profound effect on people's health and well-being. The European Environment Agency (EEA) Report 2015 reported that almost one third of Europe's city dwellers are exposed to excessive concentrations of airborne particulate matter (Guerreiro, 2015). Moreover, the emissions of the main air pollutants in Europe declined in the period 2003-2012, resulting in some improvements in air quality. But particulate matter (PM) and benzo-a-pyrene (BaP) emissions from household combustion have increased considerably, as reported by EEA Report 2015 (Guerreiro, 2015). In particular, the exposure to $PM_{2.5}$, NO_2 and O_3 lead to respectively 431000, 75000, and 17000 premature deaths in Europe based on 2012 concentrations.

Environmental sustainability and energy efficiency of the urban society are key issues in the era of smart cities and information services for the quality of life (Penza, 2015a; US EPA, 2013). Solid-state sensors (Penza, 2014a; Penza et and EuNetAir Consortium, 2014b; Penza, 2014c; Penza et al, 2015b; Penza 2015c) based on advanced functional materials have been developed for several decades and recent improvements in nanotechnology and multifunctional materials have open up the possibility to develop a new generation of sensitive, selective and stable sensors integrated in autonomous systems, with largely improved capacity and enhanced performance to give relevant information both on a personal level and systems level. A summary is reported in Figure 1.

Mitigation policy (AQUILA) of the European Commission in Europe has been realized by European Directive on *Ambient Air Quality*, 2008/50/EC and Daughters [2008]. At the moment, the Directive does not provide for use of sensors in European legislation for regulatory purposes. In fact, the Members States should demonstrate that the Data Quality Objective for Indicative Methods can be met by sensors using *national projects*.

Limitations are still existing for the usage of the air quality (AQ) sensors:

- Lower accuracy compared to high-cost Reference Methods
- Cross-sensitivity and low selectivity
- Low stability and drift to be corrected periodically
- Calibration needs periodically (e.g., at least 1 calibration/month)

- Regular maintenance of the in-field AQ sensor nodes
- Data Quality Objective (European Directive 2008/50/EC) to be addressed for *Indicative Measurements* by demonstration of the equivalence to use low-cost micro-sensors for AQ monitoring.

On the contrary, some advantages and benefits of the AQ sensors:

- Low-cost for deployment in cities at high spatial-temporal resolution
- Suitability for personal exposure studies
- Suitability for emission source information
- Outdoor monitoring of gases (NO_2/NO, O_3, CO, SO_2, H_2S, tVOCs, CO_2, NH_3, etc.)
- Outdoor monitoring of particulate matter (PM_{10}, $PM_{2.5}$, $PM_{1.0}$, UFP)
- Indoor monitoring of gases (CO, VOCs, benzene, formaldehyde, naphthalene, toluene, etc.) and PM (PM10, PM2.5, PM1.0)
- Combination of sensors with modelling for micro-scale analysis (1-2 meters resolution)

At the current stage, the European Commission mainly observes the results of some relevant funded research projects related to micro-sensors for air quality control: *MACPoll, AIRMONTECH, S3-EURUSSIA, KEYVOCs, CITI-SENSE, COST Action TD1105 EuNetAir*, etc).

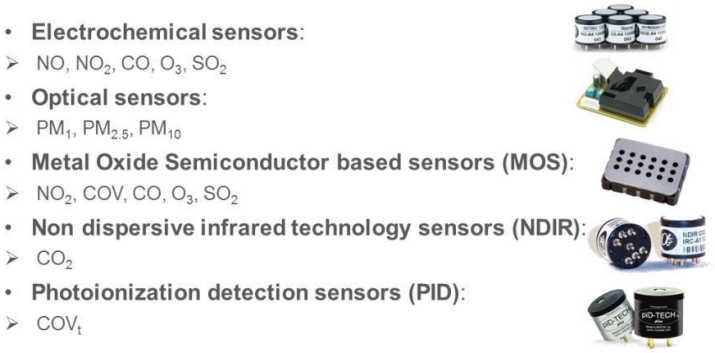

Figure 1. *Set of commercial low-cost sensors for air quality control.*

METHODOLOGY

Two European initiatives, whose logos are shown in the Figure 2, have been recently activated to pursue the development of new sensing technologies, methods, protocols and standards for air pollution control and environmental sustainability: COST Action TD1105 *EuNetAir - European Network on New Sensing Technologies for Air-Pollution Control and Environmental Sustainability* (COST Action TD1105 web portals; Penza, 2015d) and ESSC - *European Sensor-System Cluster* (ESSC web portal; Penza, 2015e) at industrial relevance.

(a)

(b)

Figure 2. *a) Logo of COST Action TD1105 EuNetAir; b) Logo of ESSC*

The COST Action *EuNetAir* aims to establish a top-level Pan-European multidisciplinary R&D platform on a new sensing paradigm for Air Quality Control (AQC) contributing to sustainable development, green economy and social welfare and to create collaborative research teams in the European Research Area (ERA). The challenges addressed by COST Action TD1105, composed by 4 Working Groups and 4 Special Interest Groups with leadership by ENEA (Italy), including about 200 international Experts from outstanding 120 Teams (Academia, Research and Industry) and 31 Countries (*Austria, Belgium, Bulgaria, Croatia, Czech Republic,*

Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Israel, Italy, Latvia, Luxembourg, The Former Yugoslav Republic of Macedonia, Netherlands, Norway, Poland, Portugal, Romania, Serbia, Slovenia, Spain, Sweden, Switzerland, Turkey, United Kingdom) are listed as follows:

- Nanomaterials for AQC sensors
- Low-cost gas sensors
- Low-power sensor-systems
- Wireless technology (*Environmental Sensors Network*)
- Air quality modelling
- Environmental measurements
- Standards and protocols

In the period 2012-2016, the COST Action EuNetAir has organized about 28 meetings and workshops, 4 training schools and supported about 45 young European investigators to carry out challenging research in the field of the environmental sensor technologies and measurements in foreign host institutions of the COST Countries and Associated Countries signing the Memorandum of Understanding EuNetAir. This has created high impact with the establishing of an international network including about 15 SMEs and spin-offs. Several world-class experts from International Organizations such as European Environment Agency (EEA), World Health Organization (WHO) Europe, United Nations Economic Commission for Europe (UNECE) with group devoted to Long-Range Trans-Boundary Air Pollution - European Monitoring and Evaluation Programme (EMEP), Joint Research Center (JRC) - Institute for Environment and Sustainability, US Environmental Protection Agency (EPA), NASA Ames Research Center, MIT, CSIRO and Queensland University of Technology, have been involved with fruitful discussions and long-term cooperation.

Furthermore, the European Sensor Systems Cluster (ESSC) has been launched on November 2014 by European Commission via the DG Research and Innovation to promote clustering policy and avoid defragmentation of the sensor systems research in the Europe. The ESSC cluster is an effective network at industrial relevance to implement the EC research and innovation policy at high impact to maximize the H2020 investment at short, medium and long term in the applicative sectors of the sensor technology such as environment, energy, health and comfort, industrial process control and commercialization of new products for mass-production. The objectives of the ESSC are listed but not limited to:

- Maximize cooperation between projects (avoid duplication and improve efficiency)
- Identify common interests in on-going research and development (e.g. open calls, training)
- Provide a forum for discussion, problem solving and analytical planning R&D activities in Europe
- Establish the EU-wide meeting platform for researchers, industry and end-users
- Remove commercialization barriers to ensure EU leadership in sensor technologies
- Integrate inputs and recommendations from other existing clusters or groups
- Promote connection with external bodies
- Disseminate sensor-related issues/findings to stimulate awareness for the invisible environmental problems and support citizen science.

The ESSC vision can be summarized as follows as: environment and health, including air and water quality, food safety and medicine, pose various challenges to achieve a sustainable development in Europe and worldwide. Collecting information on the status of the environment or the health of an individual is typically the first step to the desired improvement and, thus, sensor systems play a key role to address these challenges. In spite of considerable research efforts over the last decades, sensors and sensor systems to collect and evaluate (bio)chemical information are still not available for many applications, either due to lack of sensitivity, selectivity or stability (3S). The ESSC aims to address the following technological challenges in the field of a full value chain from functional materials, devices, systems, technologies to smart sensor systems integration:

- Improved 3S (Selectivity, Sensitivity, Stability) and *More 3S* of sensors and sensor-systems
- Functional materials for advanced 3S sensors
- Miniaturization and integration
- Integration to systems

Particular challenges of the ESSC for R&D and commercialization are listed as well:

- Indoor sensing
- Environmental sensing
- Biosensors
- Chemo/Bio sensors for liquids
- Modelling and simulation
- Analytical tools and metrology
- Standardization and regulation
- Business models and spin-offs

The ESSC includes more than 100 experts and is mainly based on six Working Groups (WGs) coordinated by a Leader:

✓ WG1: Environmental sensors
✓ WG2: Indoor air quality (sensors)
✓ WG3: Health monitoring and comfort sensors
✓ WG4: Monitoring of industrial processes WG5: Integration and commercialization
✓ WG6: Dissemination and outreach

RESULTS AND DISCUSSION

Here some examples and case-studies of applications for AQ sensor-systems in real-world measurements are shortly reported:

✓ Wireless Sensor Network around Heathrow airport for AQ monitoring by University of Cambridge and Alphasense (UK): about 50 sensor nodes located in and around the airport are operating to measure NO, NO_2, CO, CO_2, SO_2, O_3, VOCs and size-speciated PM. Novel software tools for calibration, data-mining, visualisation/interpretation and network design optimization were applied in the long-term experimental campaign to assess the impact of air pollution and source attribution/model validation of the area.

✓ Mobile Sensors on Public Transportation (e.g., bus, tram) for near real-time pollution detection in the city of Zurich by EMPA, EPFL, ETHZ (Switzerland): a mobile sensor node for air quality monitoring equipped by low-cost sensors of CO, NO_x, O_3, UFP, etc. was operated on public tram in Zurich to complement the stationary city sensor network. Data transfer towards base station was also implemented.

✓ Stationary sensors node and portable sensors for AQ monitoring by ENEA (Italy) in collaboration with JRC-IES (EC): a sensor network based on 11 stationary sensor nodes and 1 mobile sensor node on public bus has been designed and implemented to monitor in real-time the air quality in the city of Bari (Italy). A long-term experimental campaign for a period of more than 1 year is running to monitor mainly NO_2, O_3, CO, SO_2, PM_{10}, tVOCs, CO_2, T and RH under Italian national project RES-NOVAE.

✓ Joint-Exercise *Sensors-versus-Analyzers* in the city of Aveiro (Portugal) by IDAD (Portugal) guiding several *EuNetAir* partners: 15 teams, joined from 12 COST Countries, installed their sensor-systems sideby-side to compare performance with referenced equipment in the Air-Quality Mobile Laboratory by IDAD and parked in the Aveiro city centre. Continuous measurements were realized for two-weeks (1327 October 2014) to monitor CO, benzene, NO_x, SO_2, PM_{10}, VOC, temperature, humidity, wind velocity, wind direction, solar radiation, precipitation with reference instrumentation. Simultaneous measurements of air pollution by low-cost sensors run to assess their accuracy and sensing performance compared to reference data. Indicative measurements of the EU Directive 2008/50/EC were pursued.

CONCLUSIONS

In conclusion, low-cost sensors should not substitute but supplement routine monitoring devices. Use of portable systems based on low-cost solid-state gas sensors to supplement high-cost standard chemical analyzers should be possible for some pollutant gases in the future. Further long-term investigations need in order to extend the range of air-pollutants to be detected by low-cost solid-state gas sensors at higher accuracy. Further sensor-system miniaturization and integration with commercial electronics (e.g., smartphones, tablets, etc.) for community participatory environmental sensing is highly welcomed to enhance environmental awareness in the Europeans

such as air quality control stationary and mobile sensors network for smart cities applications using designed Air Quality Index (AQI) to inform general public.

Some case-studies across Europe give a promising evidence to address pervasive smart sensor network for air quality monitoring in urban context.

ACKNOWLEDGEMENTS

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REFERENCES

1. AQUILA, Network on Air Quality National Reference Laboratories, http://ies.jrc.ec.europa.eu/aquilahomepage.html
2. COST Action TD1105 EuNetAir ESSEM, http://www.cost.eu/domains_actions/essem/Actions/TD1105
3. COST Action TD1105 EuNetAir webpages: www.cost.eunetair.it
4. European Sensor Systems Cluster (ESSC): www.cluster-essc.eu
5. European Union, 2008. Directive 2008/50/EC of the European Parliament and of the council of 21 May 2008 on ambient air quality and cleaner air for Europe. Off. J.Eur. Union L 152, 1-44.
6. Guerreiro C., 2015. Air quality in Europe, EEA, Report No 5/2015
7. Penza M., 2014a. COST Action TD1105: Overview of Sensor-Systems for Air Quality Monitoring, Procedia Engineering 87, 1370-1377.
8. Penza M. and and EuNetAir Consortium, 2014b. The Case-Study of EuNetAir: European Networking on Air Quality Sensors and Environmental Sustainability, Presentation Abstracts and Presenter Biographies from US EPA Air Sensors 2014: A New Frontier, Research Triangle Park Campus, NC, USA, 9-10 June 2014., pp.17, https://sites.google.com/site/airsensors2014/Air%20Sensors%202014_Abstracts%20and%20Bios.pdf?attredirects=0&d=1
9. Penza M., 2014c. COST Action TD1105: New Sensing Technologies for Environmental Sustainability in Smart Cities, IEEE Sensors 2014 Proceedings, Valencia, Spain, 2-5 Nov. 2014. pp. 1-7.
10. Penza M., 2015a. Portable Sensor-Systems for Air Quality Monitoring: The Case-Study of EuNetAir, 2nd Meeting of the Global Platform on Air Quality and Health, Geneva, Switzerland, 18-20 Aug. 2015. Invited Speaker. \
11. Penza M., et al, 2015b. COST Action TD1105: European Network on New Sensing Technologies for Air Pollution Control and Environmental Sustainability, ISOEN Symposium 2015 Proceedings, Dijon, France, 28 June - 1 July 2015.
12. Penza M., 2015c. COST Action TD1105: European Network on New Sensing Technologies for Air Pollution Control and Environmental Sustainability. Overview and Plans, Procedia Engineering 120, 476-479.
13. Penza M., 2015d. COST Action TD1105: European Network on New Sensing Technologies for Air pollution Technologies for Air-Pollution Control and Environmental Sustainability –EuNetAir, Linkoping, Sweden, 3-5 June 2015., p. 1-4 DOI: 10.5162/4EuNetAir2015/01. URL: http://www.amascience.org/proceedings/details/2116
14. Penza M., 2015e, The European Sensor Systems Cluster - ESSC: A New EC Initiative, Linkoping EuNetAir Meeting, AMA Science 2015 Proceedings, Linkoping, Sweden, 3-5 June, 2015., pp. 1-4, DOI:10.5162/4EuNetAir2015/08. URL: http://www.ama-science.org/proceedings/details/2123
15. US EPA, 2013. Draft Roadmap on Next Generation of Air Monitoring (NGAM): https://www.epa.gov/sites/production/files/2014-09/documents/roadmap-20130308.pdf, assessed October 2016.

4.2 AN EXAMPLE OF FIELD VALIDATION OF A CITIZEN-ORIENTED CHEAP PARTICLE MATTER COUNTER COLLOCATED WITH REFERENCE INSTRUMENTS

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ABSTRACT

There is a strong evidence related to the adverse health impacts of respirable particulate matter (RPM) fraction. Increasing attention has been paid in last decades to RPM monitoring not only in area of occupational environment, but to ambient outdoor and indoor environment in the aim to bring changes to lifestyle of air pollution aware population. Low cost sensor networks could provide additional information for risk management, if the quality of output is sufficient for the purpose of monitoring. In this work, we tested intra device variability of cheap RPM DC1700 (Dylos) monitors. In addition, we tested inter device variability when DC1700 monitor is collocated with conventional RPM monitors including reference and equivalence PM detectors. Total of ten DC1700 devices were tested and when the devices functioned properly, no deviation in response was detected. In the field, during campaigns, the correlation between minute and daily measurement done by the DC1700 low-cost devices and conventional device were above 0,5 for each of the DC1700 units over a period of 15 days. This is comparable with other published results.

***Keywords**:* air pollution, PM_{10}, $PM_{2.5}$, low-cost sensors, control test atmosphere, field testing

INTRODUCTION

There is a strong evidence related to the adverse health impacts of respirable particulate matter (RPM) fraction. Air pollution, where currently the largest health risks are attributed to RPM, stems from both anthropogenic and natural emissions that undergo further changes in the atmosphere. It is a mixture of mixtures that is not constant in level and composition, and varies through space and time. RPM with high specific surface area have greater possibility to absorb and carry compounds that pose risk to human health, and RPM's ability to enter lower parts of the human lung increases as size of particles gets smaller.

Premature death attributable to air pollution happen most due heart disease and stroke, followed by lung diseases and cancer (WHO, 2014; IACR, 2013a). In addition, air pollution is associated with increase in incidence of numerous additional diseases. The International Agency for Cancer Risk IARC designated outdoor air pollution as a Group 1 carcinogenic substance, i.e., proven human carcinogen (IACR, 2013b). RPM mixture, as a major component of outdoor air pollution, was evaluated separately and was also classified as carcinogenic to humans, Group 1 (IACR, 2013b). Current health risk literature does not distinguish between RPM in indoor environment and outdoors as the metric used is mainly related to mass for each size fraction. In the presence of indoor sources of RPM, levels of RPM fractions indoors can be higher than outdoors, so both environments are of importance.

Monitoring networks at local and state level provide information that is comparable between networks with similar technologies and quality systems. The prescribed spatial coverage of compliance networks does not information on local gradients, and thus does not give enough information for personal exposure to air pollutants. Information on size fractions of RPM is also often not available. Such detailed information together with information on variability of air quality encountered when moving and spending time in different microenvironments is important for citizen in order to minimize personal exposure (Steinle et al, 2015, Jovašević-Stojanović, 2015).

Current commercial low-cost RPM devices are based on optical and light scattering counters, that detected PM above 0,5 or 0,3 μm, and provide data in near real time. In order to inform the general public about the actual performance of commercially available low-cost air quality sensors, the Air Quality Performance Evaluation Center (AQ spec, 2016) evaluated performances of 13 such devices in the price range of $150-$2000. According to their preliminary reports, in controlled test atmosphere (chamber), the devices give data that are usually highly correlated with reference or equivalent PM monitors.

There have also been efforts to develop lower cost monitors to detect particles below 0,5 μm diameter, including nanoparticles (Wasisto et al, 2016). Research projects are in progress which develop novel low-cost RPM mass monitors on light scattering principle (Donga et al,2016), but also different principles are used, such as acoustic wave sensor (Paprotnya, 2013; Thomas et al, 2016; Thomas et al, 2016).

Significant effort is put into testing the low-cost PM devices in laboratory conditions, control test atmosphere. Evidence shows that the environment in which the device is operating influences the outcome, and it is equally important to test in the field conditions, covering different indoor and outdoor microenvironment (Jovašević-Stojanović, 2015; Northcross, 2013; Dacunto et al, 2015; Jiao et at, 2016; Han et at, 2016; Wang et al, 2015; Austin et al, 2016; Holstius et al, 2014; Johnson et al, 2016; Prabakar et al, 2015).

In this work we investigated intra and inert device type variability (Polidori et al, 2016), of cheap RPM device for detecting coarse and fine particulate matter. The aim was to evaluate relationship between the RPM fractions detected with a commercially available cheap PM counter colocated with reference/equivalence instruments. In addition, before comparing the low-cost and reference/equivalent devices, we show that that concentrations obtained by several low-cost devices in parallel are comparable. We also tested intra-device variability in chamber, for three low-cost pods.

METHOD

In this paper we present the results of in the field testing, which includes comparison of PM_{10} and $PM_{2.5}$ measured concentration collected using heterogeneous group of instruments which included reference instruments, equivalence PM monitors and a laser based optical particle counter DC1700 (Dylos Corp). Since the testing occurred outdoors, DC1700 was integrated into the EB-700 platform (DunavNet, Serbia) that ensure wireless data transfer and recording, shown in Figure 1. This platform was later distributed over Belgrade Master Plan area (total of ten units with integrated DC1700 device), for purposes of near real time, indicative level monitoring.

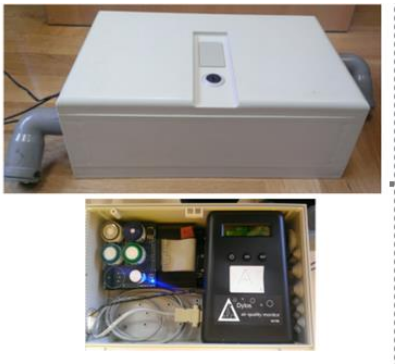

Figure 1. *EB-700 platform with Alphasense sensors for gases and Dylos 1700 for PM10 and PM2.5*

Figure 2. *ATM Novi Beograd*

Data were collected at ATM in Belgrade (shown in Figure 2) which belongs to the State Network, operated by Serbian Environmental Protection Agency (SEPA). Ten EB-700 platforms with integrated DC1700 monitor for registering air pollutants with time resolution and averaging interval for concentration of 1 minute were collocated with following conventional devices:

- Reference device for PM monitoring, SVEN Leckel low volume samplers equipped with sampling heads for $PM_{2.5}$ and PM_{10}, resolution 24h. .
- Equivalence device, integrated in ATM, Grim Model 1.108 monitor, instrument as a part, resolution 1 minute.

During 2014, we performed two campaigns at ATM Novi Beograd. The first campaign was performed in March (15 days duration) and the second campaign spanned end of October and beginning of November (10 days duration).

Low-cost PM devices which are capable of providing higher time-resolution signal were co-located with more sophisticated optical instruments. Both reference and equivalence instruments give data in $\mu g/m^3$, in accordance with the legislation requirements.

RESULTS

To quantify and compare the strengths of correlations, we used the coefficients of correlation (*R*) from ordinary least-squares regression models fitted within ten DC1700 monitors and between low-cost devices and reference instruments Grimm Model 1.108 monitor, for period when all devices were located at the AMS Novi Beograd. For the statistical analysis, we used data recorded with the DC1700 device and GRIMM Model 1.108 monitor, with same time resolution. First step in the analysis was to perform filtering of the signals from the DC1700 devices by using a smoothing function described by Gracia (2010). This step was followed by conversion of the $PM_{0.5-2.5}$ and $PM_{2.5-10}$ counts to mass concentration based on conversion procedure described in (Tittarelli et al, 2008; Lee 2008). Applied smoothing procedure improves the correlation coefficient between the signals from the DC1700 and the Grimm PM monitors.

Figures 3 and 4 depict daily average concentrations for nine DC1700 devices for PM_{10} and $PM_{2.5}$. Nine EB 700 unit with integrated DC1700 device are assigned in legend with P1, P2, P3, P5, P6, P7, P8, P9, P10 and P13. Coefficient of correlation within the nine DC1700 devices was higher than 0.8 and 0. 9 for fine and coarse PM fractions respectively. A degradation of the signals has not been noted between two campaigns.

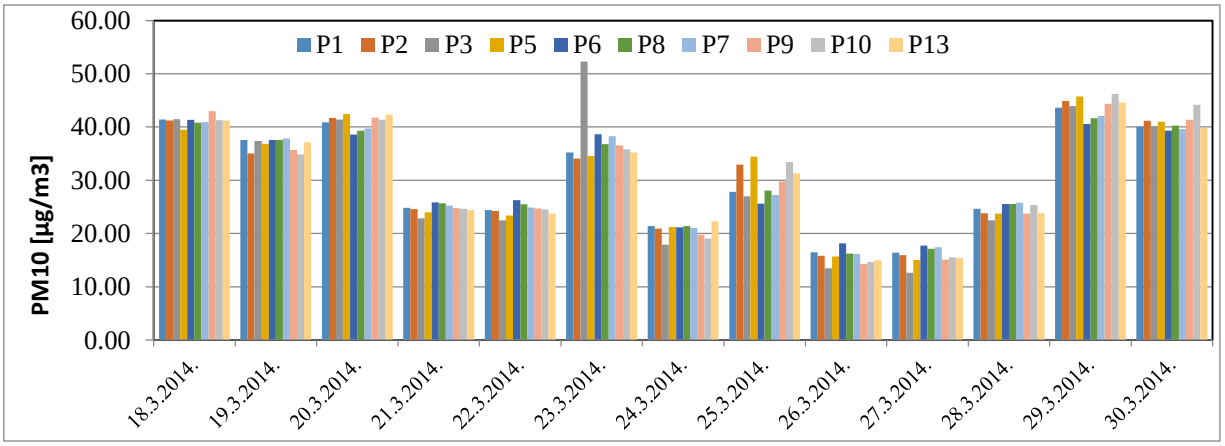

Figure 3. *PM_{10} daily average levels at ten EB700 units collected with DC 1700 monitor during second field campaign in framework of CITI-SENSE pilot study in Belgrade*

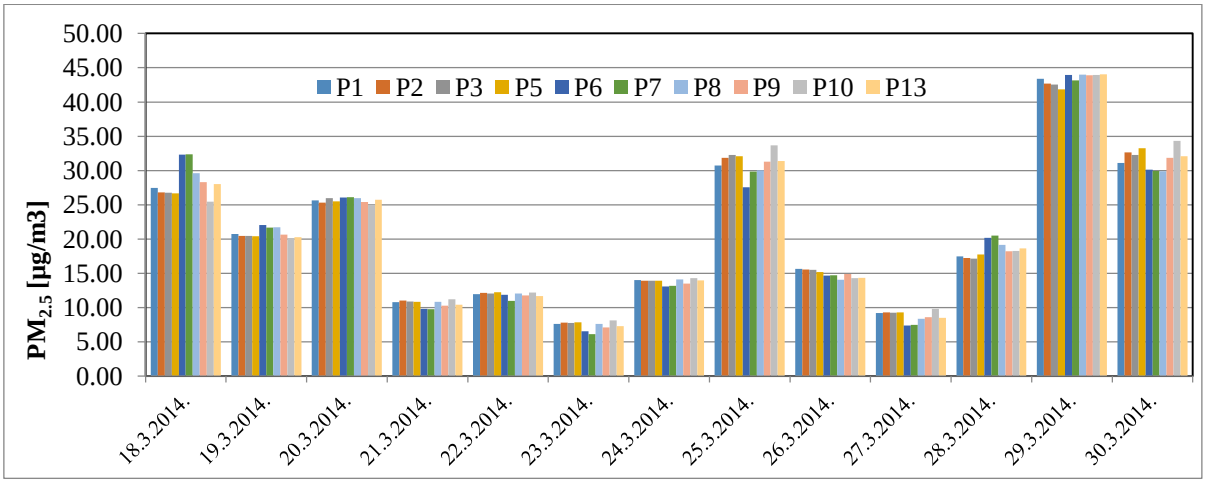

Figure 4. *$PM_{2.5}$ daily average levels at ten EB 700 units collected with DC1700 monitor during second field campaign in framework of CITI-SENSE pilot study in Belgrade*

During the first campaign, R between each of the nine DC1700 and Grim monitor was higher than 0,90 and between 0,72 and 0.87 for $PM_{2.5}$ and PM_{10} respectively. During the second campaign, R for both fractions was higher than 0.95 for 7 of the 9 devices, and only for one of the DC1700 units correlation was less than 0.6 and only for PM_{10} fraction.

Beside comparison of DC1700 and Grim monitor, both group of devices were compared with daily concentrations collected using LVS Sven Leckel gravimetric pumps. Figures 5 and 6 depict daily average for PM_{10} and $PM_{2.5}$ for data collected with reference LVS Sven Leckel,

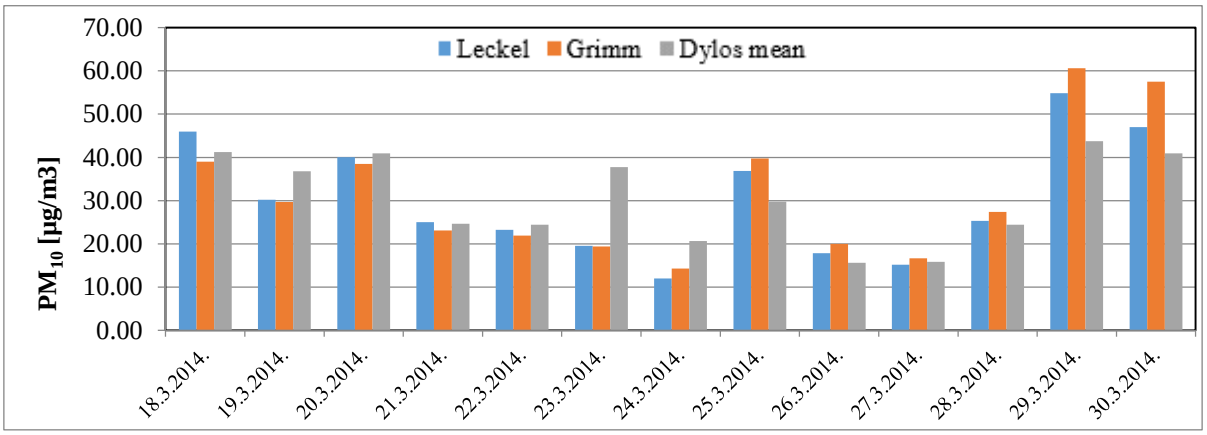

***Figure** 5. PM10 daily average levels with conventional and low-cost device during second field campaign in framework of CITI-SENSE pilot study in Belgrade.*

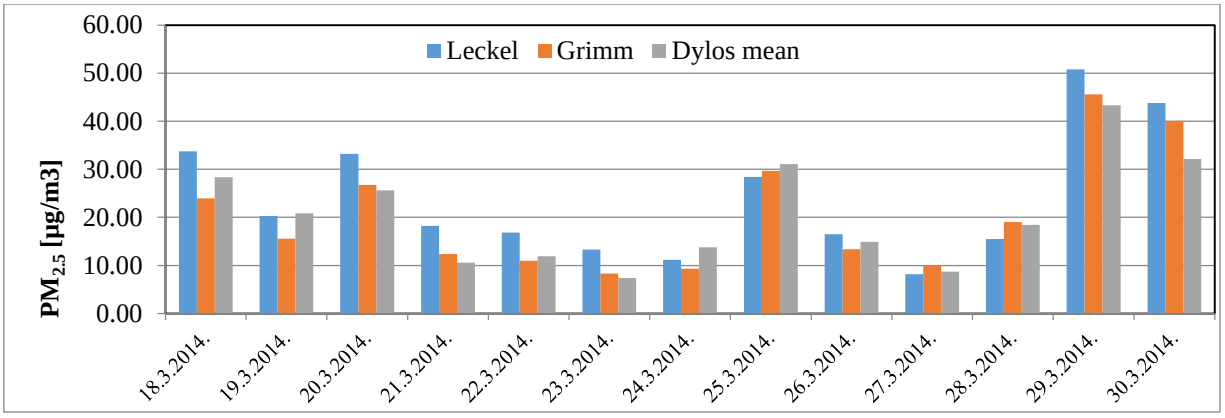

***Figure 6.** PM2.5 daily average levels with conventional and low-cost device during second field campaign in framework of CITI-SENSE pilot study in Belgrade*

Similar efforts for evaluating performance of low cost particulate matter monitors (4 out of 5 campaigns used Dylos monitor), which were conducted and published after finish of our campaign are listed below, along with the correlation coefficients. This summary aims to provide suitable context for comprehensive comparison of our campaign results with other published results known at the time of publication.

A modified Dylos monitor, BAIRS device was tested in the laboratory conditions by Northcross et al (2013). In a chamber with controlled test atmosphere a very wide range of aerosol concentrations was generated. Pearson correlation coefficient between the TSI Dust Track compared with BAIRS was 0.99 for polystyrene latex spheres and NH_4NO_3 aerosol and 0.97 for wood smoke particles.

Steinle et al (2015) tested Dylos monitor collocated with reference device in rural and urban environment and obtained R 0.9 and 0.7 respectively. They transformed PNCs (particle number concentration) into $PM_{2.5}$ mass concentration based on co-location experiments and calculated for 5 days colocation studies with TEOM-FDMS at ATM, R at rural and urban site 0.9 and 0.7 respectively.

Dacunto et al (2015) calculated calibration factors of $PM_{2.5}$ Dylos Pro 1100 in comparison with TSI SidePak and gravimetric pump in test atmosphere were emissions from 17 different common indoor sources including cigarettes, incense, fried bacon, chicken, and hamburger were used. Conclusion was that the Dylos might be used to provide a qualitative measure of near instantaneous $PM_{2.5}$ concentration indicating whether it is generally in a "high," "medium," or "low" category.

Jiao et al (2016) presented results of comparison of adjusted coefficients of correlation (R_{adj}) of Multiple Linear Regression Models (MLR) between D and Federal Reference Method with MetOne BAM 1020 device. When R_{adj} takes into account influence of ambient temperature, humidity, and/or number of measurement days it is improved from 0,67 to 0,77.

Han et al (2016) found that relative humidity (RH) significantly changes the association between the DC 1700 PNC and PM mass concentrations detected with the Grimm 11-R, which can be summarized as follows. For situations with RH < 60 % the mass concentration ratios of the DC 1700 to the Grimm 11-R were close to 1, while for RH > 60%, the ratios were larger than 1 for both fine and coarse fraction.

CONCLUSION

During campaigns it was noticed that the design of the DC1700 monitor has to be improved to eliminate the possibility of the fan blockage. Coefficient of correlation within DC1700 monitors and between DC1700 monitors and reference PM devices in the field condition were high taking in account that in all cases correlation were higher than 0.5. This is comparable to other published results. This work has contributed to testing of intra- and inter variability of DC1700 monitor and proved that if the devices work properly, the response of units is to a high degree comparable. Future research will be oriented toward proving usability of a low cost PM sensors for monitoring with higher spatial and temporal resolution for personal exposure assessment and comparing data collected at different type of ATMs e.g. traffic, residential, industrial sites, background, etc.

ACKNOWLEDGEMENTS

This work is supported by CITI-SENSE project, EU FP7-ENV-2012 (# 308524) and project III41028, Ministry of Education, Science and Technological Development of the Republic of Serbia,

REFERENCES

1. AQ spec-Air Quality Sensors performance Evaluation Center , http://www.aqmd.gov/aq-spec/home, accessed October 2016.
2. Austin E. , Novosselov I., Seto E., Yost M. G., 2016. Laboratory Evaluation of the Shinyei PPD42NS Low-Cost Particulate Matter Sensor, PLoS ONE 10(9), e0137789. doi:10.1371/journal.
3. Dacunto P. J., Klepeis E., Cheng K.-C., Acevedo-Bolton V., Jiang R.-T. , Repace J. L., Otta W.R. , Hildemanna L.M., 2015. Determining PM2.5 calibration curves for a low-cost particle monitor: common indoor residential aerosols", Environ. Sci.: Processes Impacts, 17, 1959-19
4. Donga M., Iervolino E., Santagata F., Zhang, G., Zhange G., 2016., Silicon microfabrication based particulate matter sensor, Sensors and Actuators A: Physical, 247,115-124
5. Gracia, D., 2010. Robust smoothing of gridded data in one and higher dimensions with missing values. Comput. Stat. Data Anal. 54, 1167e1178.
6. Han I., Symanski E., Stock T.H., 2016. Feasibility of Using Low-cost Portable Particle Monitors for Measurement of Fine and Coarse Particulate Matter in Urban Ambient Air, Journal of the Air & Waste Management Association, DOI: 10.1080/10962247.2016.1241195
7. Holstius, D., Pillarisetti, A., Smith, K., Seto, E., 2014. Field calibrations of a low-cost aerosol sensor at a regulatory monitoring site in California. Atmos. Meas. Tech. Discuss. 7, 605–632.
8. IACR, 2013, Air pollution and cancer, ed. Straif K., Cohen A., Samet J. , IARC scientific publication no. 161
9. IARC, 2013. "Outdoor air pollution a leading environmental cause of cancer deaths", Press Release No 221, 2013. https://www.iarc.fr/en/media-centre/pr/2013/index.php , accessed October 2016.
10. Jiao W., Hagler J.W., Williams G., Sharpe R., Brown R., Garver D., Judge R., Caudill M., Rickard J., Davis M., Weinstock L., Zimmer-Dauphinee S., Buckley K. 2016., Community Air Sensor 1 Network (CAIRSENSE) project: Evaluation of low-cost sensor performance in a suburban environment in the southeastern United States, Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-131, in review
11. Johnson K.K., Bergin M.H., Russell A.G., Hagler G.S.W., 2016. Using Low Cost Sensors to Measure Ambient Particulate Matter Concentrations and On-Road Emissions Factors, Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2015-331

12. Jovašević-Stojanović M., Bartoňová A. , Topalović D., Lazović I., Pokrić B., Ristovski Z., 2015. On the use of small and cheaper sensors and devices for indicative citizen-based monitoring of respirable particulate matter, Environmental Pollution 206, 696-704.
13. Laboratory Setup and Testing Protocol, Air Quality Performance Evaluation Center, August 2016,
14. Lee, J.Y., Shin, H.J., Bae, S.Y., Kim, Y.P., Kang, C.-H., 2008. Seasonal variations of particle size distributions of PAHs at Seoul, South Korea. Air Qual. Atmos. Health 1, 57-68.
15. Northcross, A.L., Edwards, R.J., Johnson, M.A.,Wang, Z.-M., Zhu, K., Allen, T., et al, 2013. A low-cost particle counter as a realtime fine-particle mass monitor. Environ. Sci. Process. Impacts 15, 433–439.
16. Paprotnya, I., Doeringa, F., Solomon, P., Whitea, R.M., Gundel, L.A., 2013. Microfabricated air-microfluidic sensor for personal monitoring of airborne particulate matter: design, fabrication, and experimental results. Sens. Actuators A 201,506-516.
17. Polidori A., Papapostolou V., Zhang H., 2016. Laboratory Evaluation of Low-Cost Air Quality Sensors, www.aqmd.gov/docs/default.../aq.../sensors-lab-testing-protocol.pdf , accessed October 2016.)
18. Prabakar J., Mohan V., Ravisankar K., 2015. Evaluation of Low Cost Particulate Matter Sensor for Indoor Air Quality Measurement, International Journal of Innovative Research in Science, Engineering and Technology, 4/2, 366-369.
19. Steinle S., Reis S., Sabel C. E, Semple S.,.Twigg M. M, Braban C. F. , Leeson S. R., Heal M. R., Harrison D. , Lin C., Wua H., 2015. Personal exposure monitoring of PM2.5 in indoor and outdoor microenvironments, Science of the Total Environment 508, 383–394.
20. Thomas S., Cole M, , Villa-López F.H., Gardner J.W., 2016b. High frequency surface acoustic wave resonator-based sensor for particulate matter detection, Sens. Actuators A 244, 138–145
21. Thomas S., Villa-López F.H., Theunis J., Peters J., Cole M., Gardner J.W., 2016a. Particle Sensor using Solidly Mounted Resonators, IEEE Sensors, 16(8) 2282 – 2289
22. Tittarelli, A., Borgini, M., Bertoldi, E., De Saeger, A., Ruprecht, R., Stefanoni, G., Tagliabue, P., Contiero, P., Crosignani, 2008. Estimation of particle mass concentration in ambient air using a particle counter. Atmos. Environ. 42,8543-8548.
23. Wang Y. Jing J. Li. H. , Zhang Q., Jiang J., Biswas P., 2015. Laboratory Evaluation and Calibration of Three Low-Cost Particle Sensors for Particulate Matter Measurement, Aerosol Science and Technology, 49(11) 1063-1077.
24. Wasisto H.S., Uhde E., Peiner E., 2016. Enhanced performance of pocket-sized nanoparticle exposure monitor for healthy indoor environment, Building and Environment, Building and Environment 95, 13-20
25. WHO, 2014. Burden of disease from Ambient Air Pollution for 2012 - Summary of results, World Health Organization , http://www.who.int/phe/health_topics/outdoorair/databases/AAP_BoD_results_March2014.pdf , accessed October 2016

5. AIR POLLUTION IN INDOOR MICROENVIRONMENTS

5.1 PARTICULATE MATTER POLLUTION INDOORS FROM SMOKING

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ABSTRACT

Nowadays one of the most important risks of indoor air quality is related with smoking – it affects not only health of smokers, but also passive non-smokers. People more time spend indoors, where dispersion of pollutants are limited, because of quasistable temperature and relative humidity regime and very often in the buildings are not provided effective ventilation rate. Increasing is number of people, who prolonged spending time indoors with poor air quality, therefore more and more people are at high risk to be affected by cardiovascular diseases, vascular and pulmonary cancer, bronchitis and other serious health issues.

This paper introduce with the data about regularities between particulate matter pollution from smoking indoors and various environmental conditions and ventilation effectiveness. Study shows how significant is particle pollution indoors compared with outdoor concentration limits from guidelines and that regulations is also necessity for indoor environments.

INTRODUCTION

Smoking is stated as one of the biggest problems in public health field. World Health Organization has calculated that smoking every year causes six million people deaths and every tenth of them is from environmental tobacco smoke (second-hand), which highly affects non-smokers. The number of smokers in the world is increasing every year, it also contributes to increase the level of morbidity. General statistics are controversial, it shows that the prevalence of smoking is declined in a number of high level of development countries, but increased in countries with low and middle incomes (Wu et al, 2013). Restrictions on smoking and the prevalence vary in different European countries, because currently lack of uniform rules. In all European Union member states has restrictions on smoking, but they vary according to national law.

Cigarettes are tobacco products, which harmfulness depends of combustion processes, compounds, additives and many other parameters. Smoke of cigarettes contains more than 5000 chemical substances (for example, formaldehyde, carbon monoxide) and approximately 70 of them are carcinogenic. During cigarette combustion process chemical substances changes physically and chemically increasing toxicity of the smoke (Al-sarraf et al, 2015).

In the result of smoking air is polluted with aerosols (including particulate matter), that are mixture of wide chemical spectra and size particles. The most hazardous are particles with aerodynamic diameter smaller than 2.5 mm, which has ability to penetrate into a deeper parts of respiratory system (Slezakova et al, 2009). Particulate matter has not known exposure threshold below which cannot adverse health effects occur and for indoor environment there are no guidelines for concentration limits as it is for outdoors. Therefore, in this study aim was to identify aerosol fractional distribution depending on ventilation effectiveness during and after smoking. Under various environmental conditions were tested different brands of cigarettes and their relevance with amount of emissions.

METHODOLOGY

Research part was based on particulate matter measurements using mobile optical counter (DT-9881), which main principle of operation is to detect particles using laser and specific optical components. Particles were counted in six size channels: 0.3, 0.5, 1.0, 2.5, 5.0, 10.0 microns for 21 second with pumping intensity of 2,38 l/min. This device allows to identify particle pollution from cigarette combustion, because it counts also fine particles, which mainly forms hazardous smoke. Device were used also to determine microclimatic parameters: air temperature, relative humidity, dew point and wet bulb temperature.

To detect changes of particle amount in the air were investigated four main cases within intervals of five minutes: 1) before smoking; 2) during smoking; 3) after smoking and 4) after smoking with opened window. For data reliability and comparability, the measurement was performed several times in different seasons.

As a place of study was chosen kitchen in of one of the apartments in high-rise building (area: 8 m^2), where regularly are big influence of active smokers and for indicative data were obtained measurements also in the

living room. In this study smoker used four cigarette brands – Kent, L&M, Parliament, Candlelight – which particle emissions were compared to determine, if there are some relevance between cigarettes, their price and emitted pollution.

Mobile optical counter measures number of particles, which are emitted, but for the comparing with other research materials data were recalculated to concentrations using this formula, where amount of particulate matter is mathematically extrapolated using correction factor (Cheng and Lin, 2010):

$$m(d_{pi}) = C_F \frac{\pi}{6} {d_{pi}}^3 n(d_{pi}), \quad (1)$$

Where:

i – channel number of the optical particle counter,
d_{pi} – the arithmetic mean diameter of the upper and lower boundaries for channel i,
$m(d_{pi})$ – the mass concentration in channel i,
$n(d_{pi})$ – the number concentration in channel i,
C_F – correction factor (in this study it is default 1.0).

For further data processing and analysis were used statistical program IBM SPSS Statistics 22.0, which allows to analyze large data sets, create the appropriate tables and graphs of regularities between various influencing factors. Statistical analysis were done using Pearson`s correlation coefficient, Kendall rank correlation coefficient, Spearmens`s rank correlation coefficient, factor analysis with number of particles and concentrations, hierarchical cluster analysis and two sample t-Test between different cigarette brand emitted particles.

RESULTS AND DISCUSSION

Results indicated significant increase of small particles (with aerodynamic diameter 0.3 – 0.5 microns) – more than five times – which confirms the fact relating to emissions of cigarette smoking in other published studies: the most rapid growth of number of particles from 0.01 to 1.0 micrometre range. Data showed that after smoking indoor air pollution is determined by smaller particles (up to 2.5 microns) and the pollution level is even higher than it is recommended for outdoors.

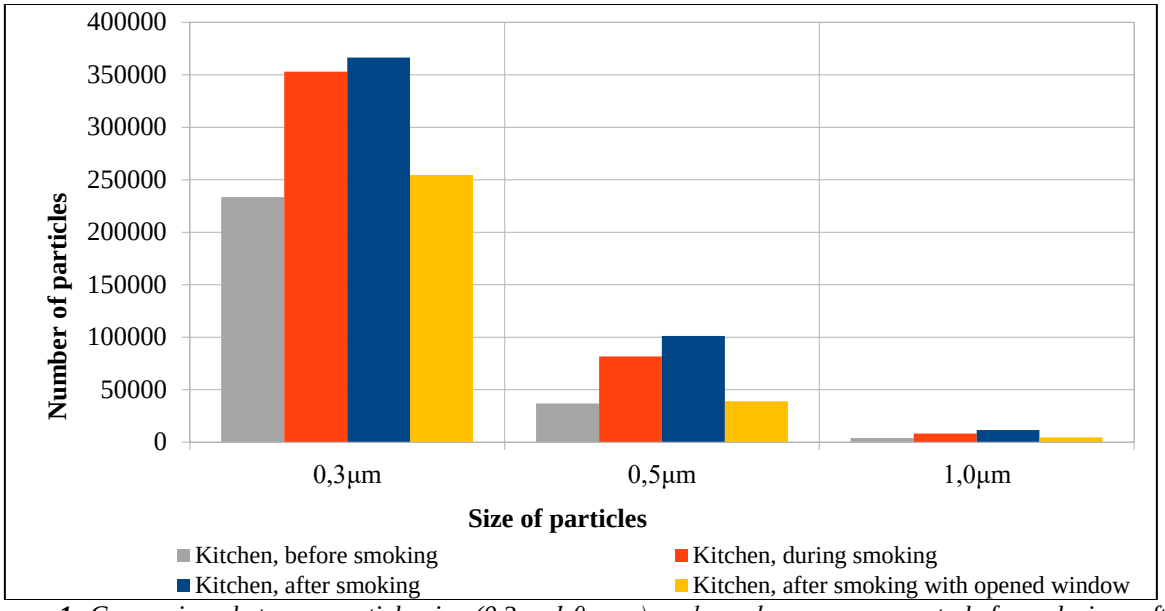

Figure 1. *Comparison between particle size (0,3 – 1,0 µm) and number measurements before, during, after smoking and with case with opened window in the kitchen (spring season data)*

Figure 1. shows that in kitchen (main control location) number of small particles increases slower, but the pollution remains for a longer time, because of specific other room parameters: free space area is smaller, window size is smaller, poor air circulation, low ventilation rate, greater is influence from household activities (more frequent smoking, cooking etc.). Coarser particles (2,5 – 10,0 µm) are not shown in this graph, because increase are not so rapid.

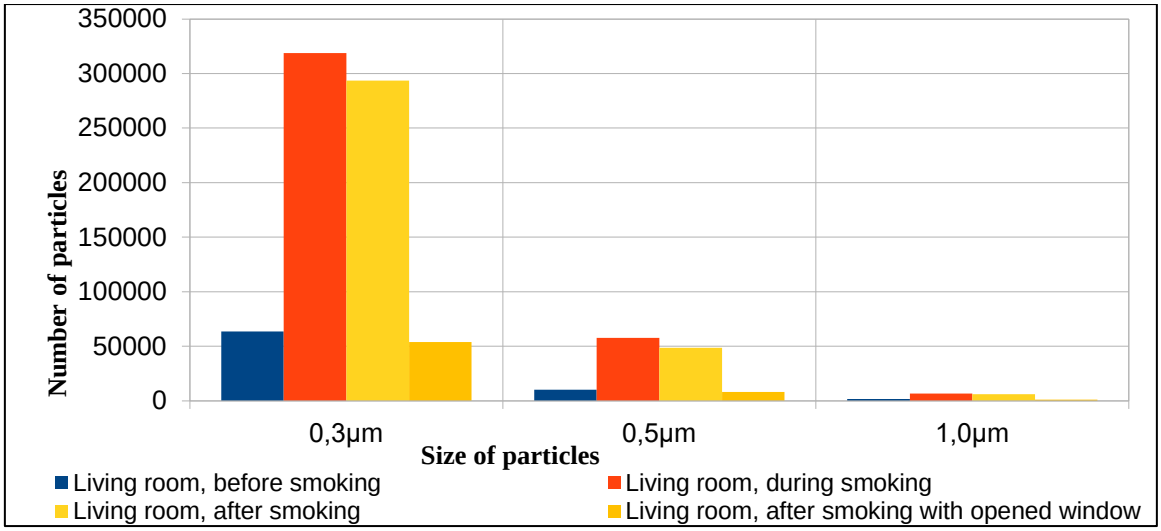

Figure 2. *Comparison between particle size (0,3 – 1,0 µm) and number measurements before, during, after smoking and with case with opened window in the living room (spring season data)*

Indicative data were analysed using measurements also in living room. Figure 2. represents situation in living room, where air exchange with outdoor environment is more active. Contrary to the situation of kitchen in living room before smoking number of particles is approximately four times less.

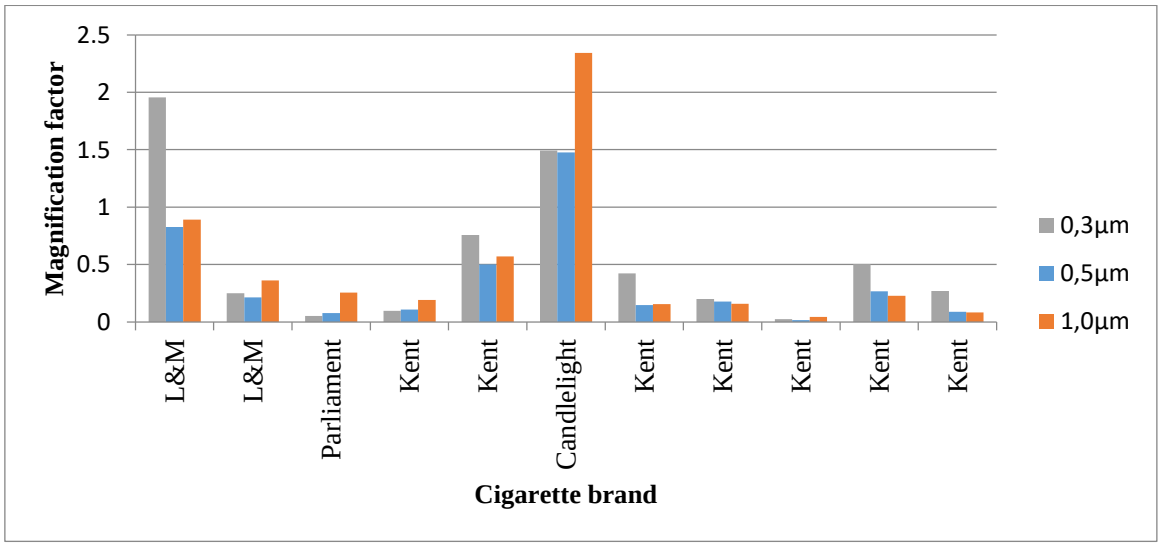

Figure 3. *Factious particle number (with size 0,3 – 1,0 µm) distribution before – during smoking, using different cigarette brands*

In figure 3. is shown magnification factor for emitted amount of particles depending on various cigarette brands. In this study the most often were used Kent brand, but this analyse shows that between these indicators there is no link, because the measurements are different and vary depending on other influencing factors. Although Candlelight cigarette brand has the most higher magnification factor, but other brand results shows that after more than one measurement with equal cigarettes, there are no relevance between them.

In order to determine not only the cigarette brands influence of particulate emissions formation was analyzed particle concentration dependence on the average prices of different cigarette brands. It was found that the price does not affect the number of particles, which means that more expensive cigarettes are not more qualitative - they do not produce less harmful emissions during smoking, but verify the complete veracity contention would be possible only after the chemical analyses of particulate matter.

Statistical analysis using parametric and non-parametric methods were used to evaluate correlation between the various factors (both – quantitative and qualitative) and obtained matrix showed that statistically significant

between them have almost all the studied factors, though the strongest correlation was observed between the largest particles (5.0 μm and 10.0 μm) and cigarette brands, as well for coarser particles room is more influencing factor.

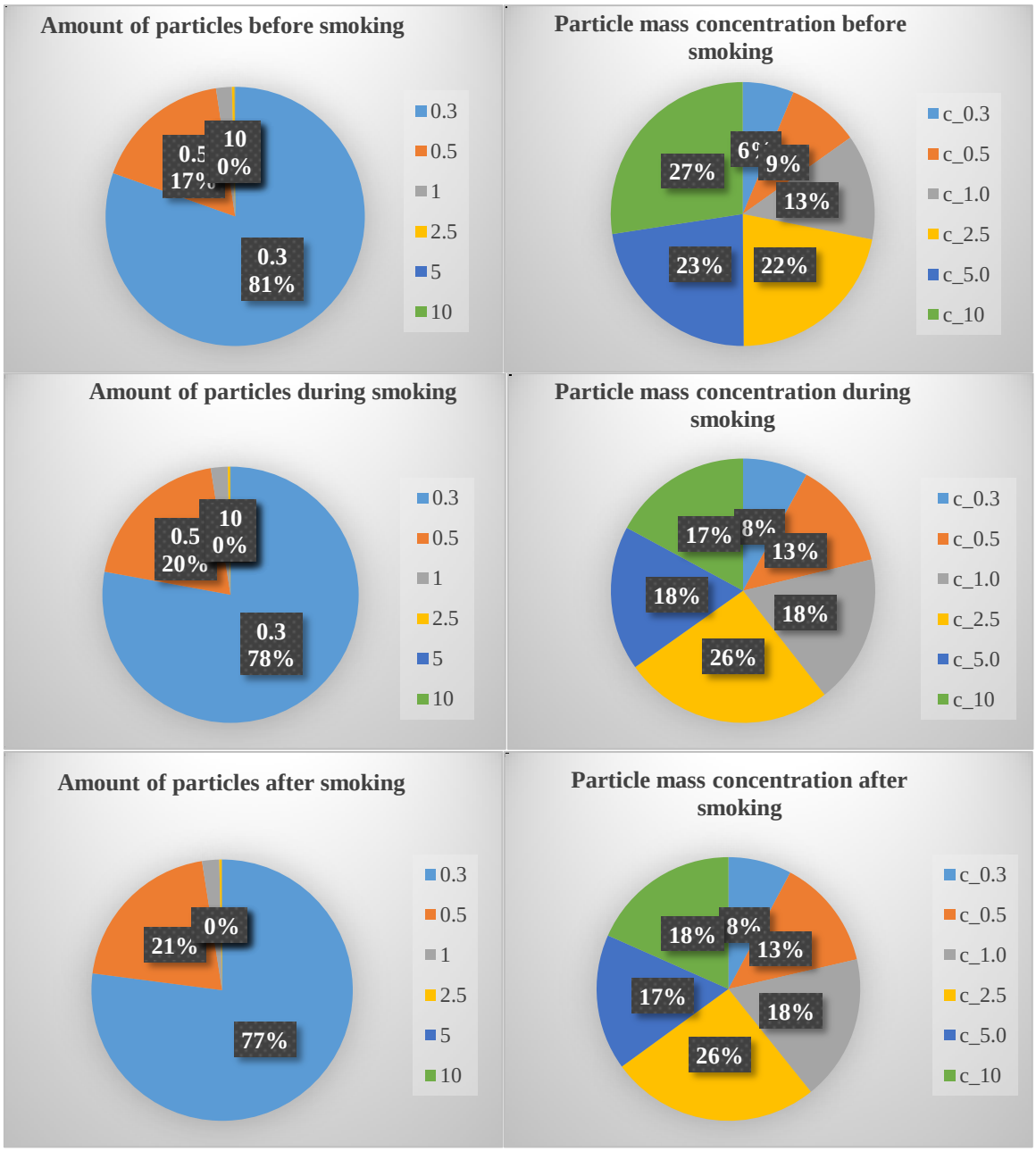

Figure 4. *Comparison between amount of particles and particle mass concentration before, during and after smoking*

Through calculations using mathematical extrapolation were obtained mass concentrations for different particulate matter size channel. Figure 4. shows that number of particles is highest for the fine particulate matter, but the most significant mass concentration of pollution forms coarser material.

Comparing of the particle number and mass concentration before, during and after smoking showed that in the cigarette burning process the highest levels of emissions reach $PM_{2.5}$ particles (26 %), although the amount of them was not the highest. Particles with aerodynamic size 0.3 μm forms most of the amount, but their concentration is lowest.

Case	Sum of particle number	Sum of particle mass concentration
Before smoking	20811	80,088
During smoking	921042	309,737
After smoking	534627	165,343
After smoking with opened window	196131	51,006

Table 5. *Comparison of sum of particle number and mass concentration in four study cases (fall season data)*

Magnification factor for number of particles vary more for measured particle number, but also for PM mass concentration it is particularly high. Table 5 shows sums of particle number and mass concentration in one of the measurements in fall season, where increase in particle number is significantly high.

For a more detailed understanding of the correlations, we also conducted factor analysis, using number of particles and mass concentrations separately. The results are similar for both variables; this could be considered as a confirmation that the algorithm, which was used for calculation of particulate mass, is correct.

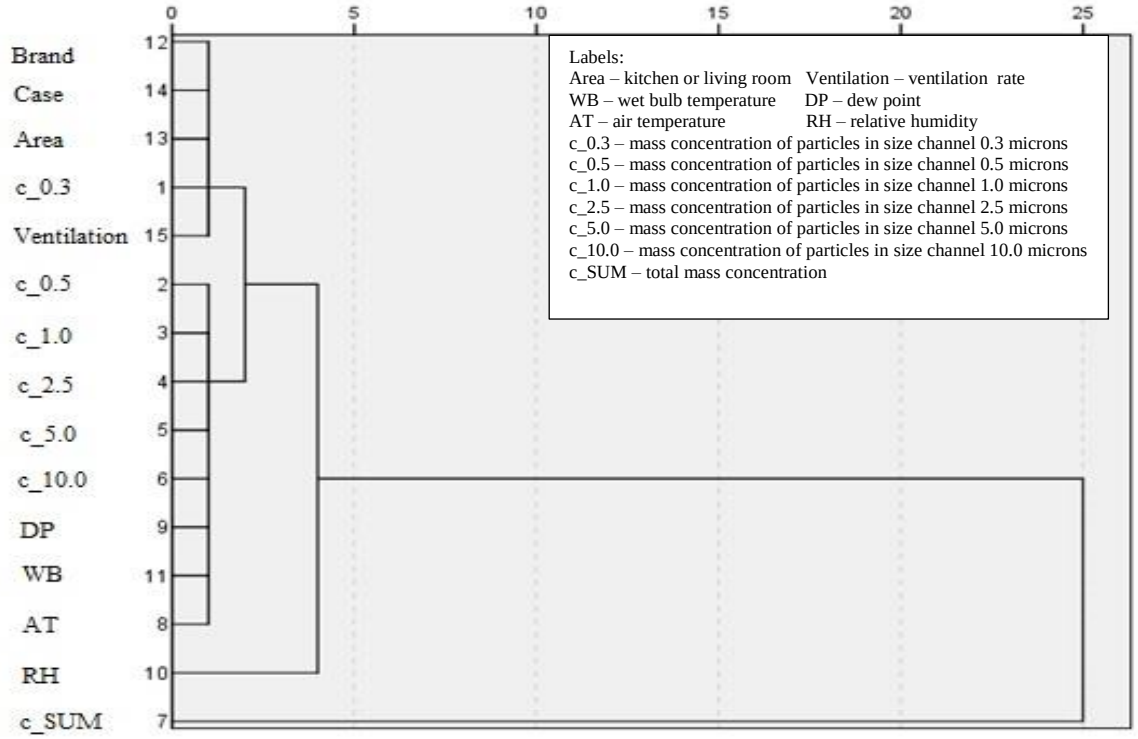

Figure 6. *Results of cluster analysis*

In Figure 6 is shown cluster analysis using particle mass concentration in different size channels, microclimatic parameters, ventilation rate, area, brand and case. Microclimatic conditions is not influencing for the finest particles (0,3 microns), but with the coarser particulate matter there is a little bit stronger bond. Hierarchical cluster analysis results indicates that the finest particles (0,3 μm) correlate with ventilation rate, room (area), case and brand. The correlation tests with parametric and non-parametric methods did not indicate such a significant mathematical dependence, therefore in addition was made also t-Test for two independent variables verifying cigarette brands and particle mass concentration linkage, but the results did not prove this statement.

During the study was conducted one exceptional case, which was not included in the full analysis, because the obtained data cannot be compared with other measurements. In this case two people smoked simultaneously in the kitchen with opened window during cigarette burning. The results indicates decrease in the number of

particles that is completely contrary to all other cases. These measurements were done ten minutes after previous smoking case, therefore at the beginning in the air is particle pollution with high concentration.

CONCLUSIONS

1. Smoking indoors significantly influences particulate matter factious composition and their concentration in the air – the average magnification factor for number of particles is in the range of 1.3 – 3.2, but the concentration increase is twofold.

2. In the naturally clean environment indoor air pollution level is determined by coarser particles, dust with a size 5.0 – 10.0 microns, while during smoking significantly increases the finest particles (up to 2.5 microns), that defines the total level of pollution.

3. Natural ventilation in research site is installed according to construction standards, but during and after smoking it is ineffective and does not reduce the amount of particles and their mass concentration, which means that for the premises, where smoking is regular, it is necessary to provide more stringent requirements for ventilation.

4. Test results with different cigarette brands showed that, regardless of the price and selected brand, aerosol pollution levels are equivalent.

5. In this study founded that the World Health Organisation recommended air quality limit value was exceeded before smoking, but during and after smoking excess is even 3 – 4 times.

ACKNOWLEDGEMENTS

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REFERENCES

1. Al-sarraf, A., A., Yassin, M., F., Bouhamra, W. 2015. Experimental and computational study of particulate matter of secondhand smoke in indoor environment. International Journal of Environmental Science and Technology, 12, 73-86.
2. Cheng, Y.-H., Lin, Y.-L. 2010. Measurement of Particle Mass Concentrations and Size Distributions in an Underground Station. Aerosol and Air Quality Research. 10 (1), 22 – 29.
3. Slezakova, K., Castro, D., Pereira, M., C., Morais, S., Delerue-Matos, C., Alvim-Ferraz, M., C. 2009. Influence of tobacco smoke on carcinogenic PAH composition in indoor PM10 and PM2.5. Atmospheric Environment. 43, 6376-6382.
4. Wu, F., Chen, Y., Parvez, F., Segers, S., Argos, M., Islam, T., Ahmed, A., Rakibuz-Zaman, M., Hasan, R., Sarwar, G., Ahsan, H. 2013. A Prospective Study of Tobacco Smoking and Mortality in Bangladesh, PLoS One. 8(3):e58516. https://dx.doi.org/10.1371/journal.pone.0058516

5.2 THE INFLUENCE OF HUMAN ACTIVITIES ON PM LEVELS IN THE APARTMENTS IN BOR, SERBIA

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ABSTRACT

The influence of the human activities on PM (PM_{10} and $PM_{2.5}$) concentration was examined in four apartments in the town of Bor, eastern Serbia. The measurements were carried out in 2014 for a period of at least 60 days per apartment. Each apartment was occupied with 3-4 non-smoking persons. An optical scattering device (Turnkey OSIRIS) was used to continuously measure PM concentrations. The device was placed in the participants' living area. In each apartment, during the first week of measurements, 24-h gravimetric samples of PM_{10} and $PM_{2.5}$ were collected by the reference gravimetric samplers concurrently with the OSIRIS measurements. The PM concentrations were calculated and classified as daily averages and averages of PM concentrations encountered in five main activity categories: morning activities (getting up and breakfast), cooking, washing, cleaning and sleeping. The average daily PM_{10} and $PM_{2.5}$ concentrations in the apartments were 37.4 $\mu g/m^3$ and 16.6 $\mu g/m^3$ respectively. The highest average PM concentrations during an activity were found to occur during the activity of cooking with a PM_{10} concentration of 332.7 $\mu g/m^3$ and $PM_{2.5}$ concentration of 94.1 $\mu g/m^3$. The lowest PM concentrations were detected during the activity of sleeping, in the time interval from midnight to 6 AM. The average ratios of the PM_{10} concentration during certain activity and the average daily PM_{10} concentration ranged from 0.6 (sleeping) to 2.9 (cooking). The average ratios of the $PM_{2.5}$ concentration during certain activity and the daily mean $PM_{2.5}$ concentration ranged from 0.8 (sleeping) to 2.6 (cooking). The presented results indicate that the activities of cooking and cleaning are the most responsible for the increase of the PM concentrations in the observed apartments.

INTRODUCTION

Exposure to particulate matter (PM) pollution has been associated with respiratory and cardiovascular disease (Anderson et al, 2001; Atkinson et al, 2010; Pope et al, 2002, 2006, 2009). The influence of indoor air pollution on health is complex and still unexplored in detail. 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. However, for health impact assessment studies, it is important to characterize mass concentration, particle size distribution and chemical composition of PM in indoor microenvironments. It is very important to determine the impact of indoor PM concentrations on human health because that people spend most of their lives indoors (Franck et al, 2011).

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 as representative hot spot of urban-industrial environments in the country. The main source of air pollution with sulfur dioxide, toxic metals, and metalloids in particulate matter is the Copper Mining and Smelting Complex Bor. 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 (Tasić et al, 2010). According to SEPA annual report for 2010 (SEPA, 2010), annual mean PM_{10} concentration in Bor at sampling site Town Park was 31 $\mu g/m^3$. In fact, annual mean PM_{10} concentration recorded in Bor were among the lowest compared with PM_{10} concentrations in other Serbian cities (SEPA, 2010). In the most of Serbian cities, PM_{10} concentrations have been much higher in the cold than in the warm period of the year. However, in the Bor town, PM_{10} concentrations were just 10% higher in the cold period than in the warm period (Tasić et al, 2012).

In the Republic of Serbia, the PM concentrations inside the residential buildings are still insufficiently known. As the result, relations between the PM concentrations inside and outside such buildings are insufficiently well known and explored. As the fate of particles in the indoor environment is influenced by a series of physical and chemical processes, this leads to certain changes in their chemical composition and physical characteristics. This work presents part of the results of an ongoing research aimed to determine the influence of the human activities on PM (PM_{10} and $PM_{2.5}$) concentration inside the apartments in the Republic of Serbia.

METHODOLOGY

The influence of human activities on PM (PM_{10} and $PM_{2.5}$) concentrations was examined in four apartments in the urban area of Bor town. The measurements were conducted in 2014, with a total of 240 days of measurements, approximately 60 days in each apartment. Apartments were selected on such way to be at the different distances from the copper smelter, as shown in Figure 1. The nearest apartment is about 500 m and the furthest 2.5 km away from the copper smelter fence. The apartments were occupied with 3-4 non-smoking persons.

The real-time measurements of PM concentrations were provided by Turnkey OSIRIS air particulate monitor (Model 2315). This monitor provides continuous real-time readings of TSP, PM_{10}, $PM_{2.5}$ and PM_1 mass fractions. 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. An air sample is continuously drawn into the instrument by a pump with a flow rate set by a microprocessor. The incoming aerosol passes through a laser beam in a photometer, and then through a filter which removes particles before reaching the pump. It should be noted that the intensity of light scattered by reflection or refraction depends on the type of particle while the diffracted component depends only on the particle size.

The OSIRIS monitor was placed in the middle of the living room at breathing height. The living rooms were carpeted, without air conditioning system. The area of the windows in the living rooms covered approximately 2.5 m^2. During the measurements in the time interval April-September, a window in the living room remained open most of the time. The living room volumes were approximately 15-25 m^3.

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 gravimetric samples were collected on a daily bases (8 AM to 8 AM) on Quartz fiber filters (Whatman QMA 47 mm diameter filters). The PM concentrations from the OSIRIS monitor were originally available as 15-min averages. For the calculation of daily averages, a minimum capture of 90% of 15-min averages was required. The results obtained by the OSIRIS monitor were corrected as it was suggested by (Ramachandran et al, 2003) by using the daily average PM concentrations obtained by gravimetric method.

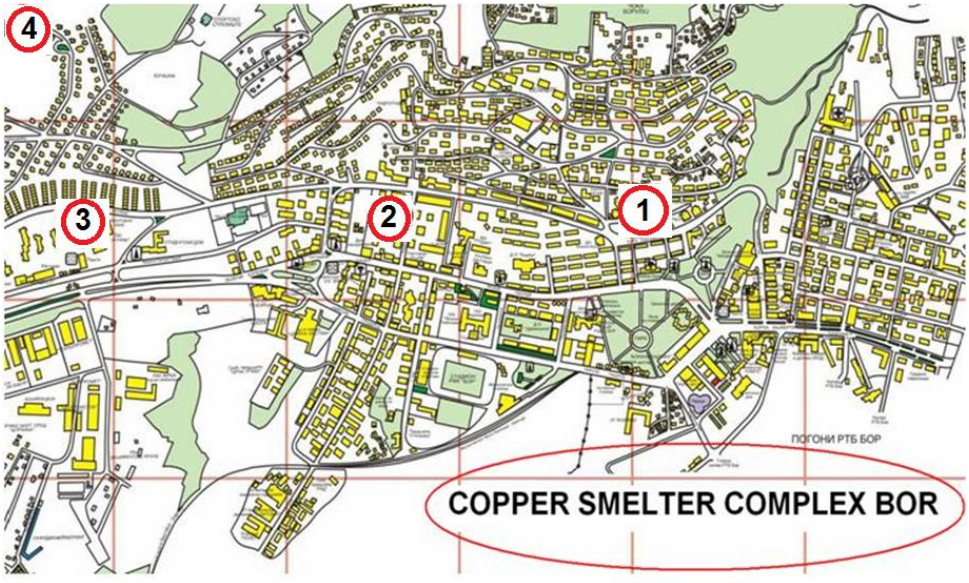

Figure 1. *Bor town map with the apartment locations marked*

The average daily PM concentrations were calculated, as well the averages of PM concentrations encountered in the five main activity categories: morning activities (getting up and breakfast), cooking, washing, cleaning and sleeping. The duration and frequency of each activity are highly dependent on habits of the occupants of the

selected apartments. A time-activity diary was kept by the occupants with the aim to collect quantitative data on each activity.

RESULTS AND DISCUSSION

For each apartment PM concentrations were calculated and classified as average daily PM concentrations, followed by the average PM concentrations encountered in the five main activity categories: morning activities (getting up and breakfast), cooking, washing, cleaning and sleeping (Table 1 and Table 3).

Table 1. *Average PM_{10} concentrations detected during an activity ($\mu g/m^3$)*

Apartment	PM_{10} average daily conc.	Morning activities	Cooking	Washing	Cleaning	Sleeping
1	41.7	66.5	68.0	76.7	101.3	26.2
2	17.2	20.0	21.8	27.4	37.6	12.0
3	44.8	34.9	332.7	36.1	37.7	17.1
4	45.7	50.1	66.6	58.3	73.2	26.5
Average	37.4	42.9	122.3	49.6	62.5	20.5

The average daily PM_{10} concentration in the apartments was 37.4 $\mu g/m^3$. The highest average PM_{10} concentration during an activity was found to occur during the activity of cooking (Apartment 3, 332.7 $\mu g/m^3$). This was followed by the activity of cleaning (Apartment 1, Apartment 4 and Apartment 2). This value is about 50% higher than measured in the same apartments in the time interval 2010-2012 (Tasić et al, 2013). The coarse airborne particles were positively affected by the presence of a large number of occupants and by cleaning activities (Urso et al, 2015; Spengler et al, 1981). It is known that human activities lead to the resuspension of deposited particles from horizontal surfaces, such as floors, carpets and furniture (Thatcher et al, 1995). The resuspension rates increase with particle size (Abt et al, 2000). Also, PM emissions vary considerably with the method of cooking (grilling, frying, boiling) contributing to higher PM levels (Abt et al, 2000).

Considering all the facts mentioned before, we assumed that the main reason for highest PM_{10} concentrations observed in the Apartment 3 is the position of the kitchen. Namely, in the Apartment 3, the kitchen is closer to the living room than in the other apartments.

Table 2. *Average ratios of PM_{10} concentration, activity PM_{10} vs. daily average PM_{10}*

Apartment	Morning act./Daily average	Cooking/Daily average	Washing/Daily average	Cleaning/Daily average	Sleeping/Daily average
1	1.6	1.6	1.8	2.4	0.6
2	1.2	1.3	1.6	2.2	0.7
3	0.8	7.4	0.8	0.8	0.4
4	1.1	1.5	1.3	1.6	0.6
Average	1.2	2.9	1.4	1.8	0.6

The average ratios of PM_{10} concentration for specific activities and the daily average PM_{10} concentration ranged from 0.6 (sleeping) to 2.9 (cooking) as shown in Table 2.

The average daily $PM_{2.5}$ concentration in the apartments was 16.6 $\mu g/m^3$ as shown in Table 3. The highest average $PM_{2.5}$ concentration during an activity was found to occur during the activity of cooking (Apartment 3, 94.1 $\mu g/m^3$). This was followed by the activity of cooking (Apartment 1), then by the morning activities (Apartment 4), and washing activity (Apartment 2).

Table 3. *Average $PM_{2.5}$ concentrations detected during an activity ($\mu g/m^3$)*

Apartment	$PM_{2.5}$ average daily conc.	Morning activities	Cooking	Washing	Cleaning	Sleeping
1	31.6	39.6	41.3	40.9	39.4	19.9
2	9.2	10.3	10.0	10.7	10.6	8.2
3	14.0	14.1	94.1	8.6	11.8	9.9
4	11.4	15.2	14.0	13.1	14.4	11.0
Average	16.6	19.8	39.9	18.3	19.1	12.3

As mentioned before, the resuspension of deposited particles from horizontal surfaces contributes to an increase in the indoor $PM_{2.5}$ concentrations (Thatcher et al, 1995). As in the case of the PM_{10} concentrations, we assumed that the main reason for the highest $PM_{2.5}$ concentrations observed in Apartment 3 is the position of the kitchen relative to the position of the living room (measuring equipment position). Also, as shown in Table 5, the average duration of cooking for Apartment 3 is longer relative to other apartments.

The average ratios of $PM_{2.5}$ concentrations for specific activities and the daily average $PM_{2.5}$ concentration ranged from 0.8 (sleeping) to 2.6 (cooking) as shown in Table 4. The averages of PM concentrations for each activity were determined based on the time-activity diary that was kept by occupants of the apartments. Descriptive statistics of activities performed by the occupants are shown in Table 5.

Table 4. *Average ratios of $PM_{2.5}$ concentration, activity $PM_{2.5}$ vs. daily average $PM_{2.5}$*

Apartment	Morning act./Daily average	Cooking/Daily average	Washing/Daily average	Cleaning/Daily average	Sleeping/Daily average
1	1.3	1.3	1.3	1.2	0.6
2	1.1	1.1	1.2	1.2	0.9
3	1.0	6.7	0.6	0.8	0.7
4	1.3	1.2	1.1	1.3	1.0
Average	1.2	2.6	1.1	1.1	0.8

Table 5. *Descriptive statistics of daily activities performed by the occupants during the measurements campaign (AM = Arithmetic mean; SD = Standard deviation)*

Indoor activities	Apartment 1 AM±SD	Apartment 2 AM ±SD	Apartment 3 AM ±SD	Apartment 4 AM ±SD
Morning activities (h)	2.5 ± 0.5	1.6 ± 0.3	2.0 ± 0.4	2.2 ± 0.6
Cooking (h)	1.4 ± 0.2	1.1 ± 0.3	2.2 ± 0.4	1.8 ± 0.2
Washing (h)	1.2 ± 0.3	0.6 ± 0.4	1.2 ± 0.3	1.6 ± 0.5
Cleaning (h)	0.5 ± 0.6	0.5 ± 0.5	0.7 ± 0.4	0.7 ± 0.5
Sleeping (h)	7.2 ± 1.1	7.5 ± 0.4	7.8 ± 0.6	7.1 ± 1.2

CONCLUSIONS

In the scientific literature, a large number of measurements of PM concentrations in indoor air are described. In the Republic of Serbia, the PM concentrations inside the residential buildings are still insufficiently known. This

work presents a part of the results of an ongoing research aimed to determine the influence of the human activities on PM concentration (PM_{10} and $PM_{2.5}$) inside residential buildings in the Republic of Serbia. The PM concentrations were examined in four apartments in the town of Bor in 2014. An optical scattering device was used to continuously measure PM concentrations. The device was placed in the participants' living area. The measurement results indicate that the most important PM_{10} and $PM_{2.5}$ source, in the selected apartments, was cooking (particularly frying). A second, less powerful source of PM_{10} particles was cleaning. The lowest PM_{10} and $PM_{2.5}$ concentrations were detected during sleeping, in the time interval from midnight to 6 AM. Further investigation in this area should be continued with the aim of characterization of the chemical composition of PM in a residential environment since most individuals spend the majority of their time indoors.

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REFERENCES

1. Abt, E., Suh, H.H., Allen, G., Koutrakis, P., 2000. Characterization of indoor particle sources: a study conducted in the metropolitan Boston area. Environ. Health Perspect., 108, 35-44.
2. Anderson, H.R., Bremner, S.A., Atkinson, R.W., Harrison, R.M., Walters S. 2001. Particulate matter and daily mortality and hospital admissions in the West Midlands conurbation of the United Kingdom: associations with fine and coarse particles, black smoke and sulphate, Occup. Environ. Med., 58, 504–510.
3. Atkinson, R.W., Fuller, G.W., Anderson, H.R., Harrison, R.M., Armstrong, B. 2010. Urban ambient particle metrics and health: a time series analysis, Epidemiology, 21, 501–511.
4. Franck, U., Herbath, O., Roder, S., Schlink, U., Bote, M., Diez, U., Kramer, U., Lehmann, I., 2011. Respiratory effects of indoor particles in young children are size dependent. Sci. Total Environ., 409, 1621-1631.
5. Pope, C.A., Burnett, R.T., Krewski, D., Jerrett, M., Shi, Y., Calle, E.E., et al. 2009. Cardiovascular mortality and exposure to airborne fine particulate matter and cigarette smoke. Shape of the exposure–response relationship, Circulation, 120, 941–948.
6. Pope, C.A., Burnett, R.T., Thun, M.J., Calle, E.E., Krewski, D., Kazuhiko, I., et al., 2002. Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air pollution, J. Am. Med. Assoc., 287, 1132–1141.
7. Pope, C.A., Dockery, D.W. 2006. Health effects of fine particulate air pollution: Lines that connect, Journal of the Air and Waste Management Association 56, 709-742.
8. Ramachandran, G., Adgate, J.L., Pratt, G.C., Sexton, K., 2003. Characterizing indoor and outdoor 15-minute average $PM_{2.5}$ concentrations in urban neighbourhoods, Aerosol Sci. Technol., 37, 33-45.
9. Serbian Environmental Protection Agency (SEPA), 2010. State of Environment in the Republic of Serbia during 2010 (annual report), http://www.sepa.gov.rs/download/Izvestaj_o_stanju_zivotne_sredine_za_2010_godinu.pdf [accessed 24 October 2015]
10. Spengler, J.D., Dockery, D.W., Turner, W.A., Wolfson, J.M., Ferris, B.G., 1981. Long-term measurements of respirable sulphates and particles inside and outside homes, Atmos Environ., 15, 23-30.
11. Tasić, V., Kovačević, R., Maluckov, B., 2013. Preliminary Measurements of PM_{10} in Apartments in Bor, Serbia, Proceedings from the 4th International WeBIOPATR Workshop&Conference Particulate Matter: Research and Management WeBIOPATR2013, 02.10.-04.10.2013, Belgrade, Serbia, pp. 117-120, ISBN: 978-86-83069-40-8
12. Tasić, V., Milošević, N., Kovačević, R., Jovašević-Stojanović, M., Dimitrijević, M., 2012. Indicative Levels of PM in The Ambient Air in The Surrounding Villages of The Copper Smelter Complex Bor, Serbia, Chemical Industry & Chemical Engineering Quarterly, 18, 643-652.
13. Tasić, V., Milošević, N., Kovačević, R., Petrović N., 2010. The analysis of air pollution caused by particle matter emission from the copper smelter complex Bor (Serbia), Chemical Industry & Chemical Engineering Quarterly, 16, 219−228.
14. Thatcher ,T.L., Layton, D.W., 1995. Deposition, resuspension, and penetration of particles within a residence. Atmos Environ., 29, 1487-1497.
15. Urso, P., Cattaneo, A., Garramone, G., Peruzzo, C., Cavallo, D.M., Carrer, P. 2015. Identification of particulate matter determinants in residential homes, Building and Environment, 86, 61-69.

5.3 THE ASSESSMENT OF PARITICULATE MATTER CONCENTRATIONS IN THE LIBRARY, IN BOR, SERBIA

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ABSTRACT

This study aims to assess PM (PM_{10} and $PM_{2.5}$) concentrations and their indoor/outdoor relation in the public library, in Bor, eastern Serbia. The measurement was conducted from June 12th to June 19th of 2015. The results showed that daily PM_{10} and $PM_{2.5}$ concentrations in the ambient air do not exceed daily limit values. Daily limit value for $PM_{2.5}$ concentration in the indoor air was exceeded once. The averages of daily PM_{10} and $PM_{2.5}$ concentrations in the library were 33.2 μg/m^3 and 22.2 μg/m^3, respectively. The averages of daily PM_{10} and $PM_{2.5}$ concentrations in the ambient air were 31.2 μg/m^3 and 20.4 μg/m^3, respectively. The averages of daily PM_{10} and $PM_{2.5}$ I/O ratios were 1.06 and 1.09, respectively. There was no significant difference between the average daily PM_{10} concentrations in the indoor and outdoor air (at the level of significance 0.05). It also applies to the average daily $PM_{2.5}$ concentrations. The average daily $PM_{2.5}/PM_{10}$ ratio in the ambient air was 0.66 while in the library it was 0.67. Such high $PM_{2.5}/PM_{10}$ ratio points out to considerable influence of the pollution sources of anthropogenic origin, such as fossil fuels combustion and traffic. All these findings point to the absence of significant additional sources of PM in the library, so the most of indoor PM particles originates from outdoor air.

INTRODUCTION

The town of Bor with the population of about 40,000 people is situated in the eastern part of the Republic of Serbia. It was a major center for mining and processing of copper for more than a century. Because of the emissions of sulfur oxides and particulate matter from the copper smelter, situated close to the urban area, air pollution is the main environmental problem in Bor (Tasić et al, 2010). Monitoring of the PM pollution in the ambient air has been carried out in Bor since 2003. The measurements were conducted at several sites in the urban area with a different kind of measuring equipment (Tasić et al, 2012).

The exposure to PM pollution has been associated with respiratory and cardiovascular disease (Anderson et al, 2001; Atkinson et al, 2010; Pope et al, 2002, 2006, 2009). Considering that people spend most of their lives indoors (Franck et al, 2011), it is very important to determine the impact of indoor PM concentrations on human health. In the Republic of Serbia, as well in Bor, there is luck of information about the PM concentrations inside the buildings where people work and live. As the result, relations between PM inside and outside the buildings are also not sufficiently known and explored.

This study is part of research of the characterization of suspended particles inside the educational and public institutions in the Republic of Serbia. In the past few years (2010-2014) measurements of indoor PM concentrations in Bor were carried out in the kindergarten, primary and secondary school, hospital, and in a few select apartments (Tasić et al, 2011, 2013). This work presents the results of measurements of PM (PM_{10} and $PM_{2.5}$) concentrations and their indoor/outdoor relation in the public library in Bor.

METHODOLOGY

The library is housed in, so called, house of culture, at a distance less than 500 m from the town's old center and from the Copper Smelter Complex Bor. It is situated between the two main streets (less than 100 m far from the library) and Town Park, as shown in Figure 1. It has a collection of around 80000 books situated in a purpose-built area of 1113 m². The library occupied four levels that enable the efficient organization of the departments and services:

- Children's Department with reading room,
- Informative department with reading room, exhibition hall, and a hall for public events,
- Department for adults,
- Department with special funds with reading room.

The referent low-volume samplers, Sven/Leckel, were used to simultaneously collect the PM inside the library and in the outdoor air. As well, an optical scattering device, Turnkey OSIRIS Particle Monitor (Model 2315 was used to continuously measure PM (PM_{10} and $PM_{2.5}$) concentrations inside the library. The measurements of PM concentrations in the library were carried out from June 12th to June 19th of 2015. The samples were collected during working hours from 8 AM to 8 PM, and also during nonworking hours from 8 PM to 8 AM. Two samplers were placed in the middle of department for adults, at the third level. The department has a volume of approximately 275 m^3. The room was carpeted, without air conditioning system with windows surface of approximately 15 m^2. During the measurements one window was constantly remained open. The other two samplers were placed at the balcony (same department) at height of 10 m above ground.

The flow rate of the LVS3 samplers (38.3 l/min) was calibrated at the beginning of measurements using certified flow meter. PM mass concentrations were obtained from gravimetric analysis of filters. Quartz fiber filters (Whatman QMA 47 mm diameter filters) were used to collect the PM. Approximately 10% (6 filters) of all gravimetric samples (56 filters) was collected as field blanks. Pre-conditioning and post-conditioning of filters was undertaken in accordance with the general requirements of SRPS EN 12341:2008 standard. After preconditioning in a clean room, filters were weighing using the Mettler Toledo semi-micro balance (10 μg mass resolution). PM mass concentrations were calculated using average (each filter is measured three times) weight of filters. Average change in the field blank weight (1.9 μg) was subtracted from net mass of the sample filters. The detection limit was 2.1 $\mu g/m^3$ calculated as three times the standard deviation in net mass of the field blanks divided by the nominal sample volume.

The direct reading aerosol monitoring device, Turnkey OSIRIS Particle Monitor (Model 2315), was placed near the LVS3 devices in the library. Monitoring data from the OSIRIS were originally available as 15-min averages. For the calculation of daily averages, a minimum capture of 90% of 15-min averages was required. The results obtained by OSIRIS were corrected as it was suggested by (Ramachandran et al, 2003) by using the average daily indoor PM concentrations obtained by gravimetric method.

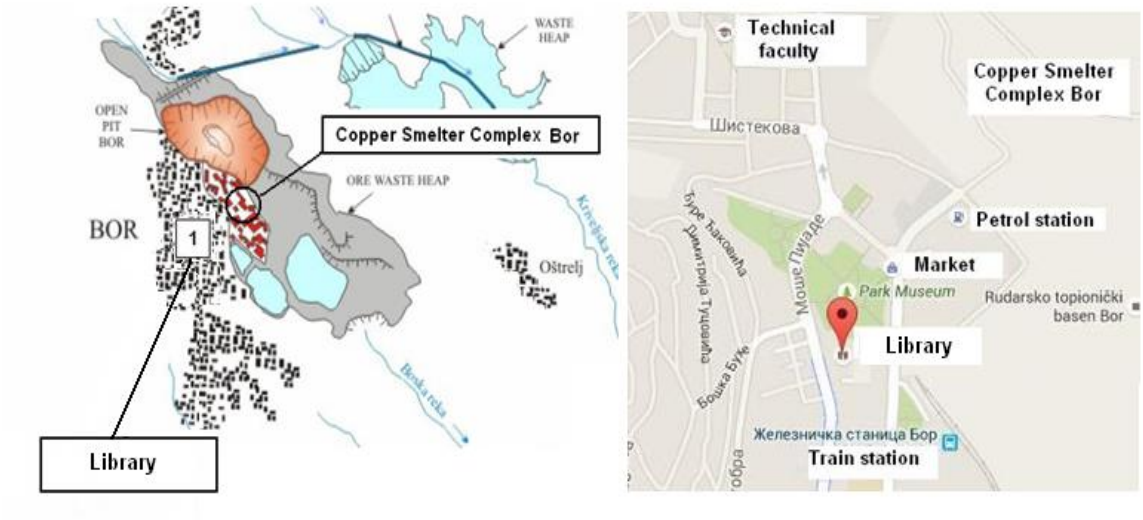

Figure 1. *Location of the Bor town library*

RESULTS AND DISCUSSION

The weather has been mostly calm and stable during the measurements. Daily averages of meteorological parameters are shown in Table 1. The meteorological data were taken from the automatic monitoring station (AMS Bor Park) situated in the Town Park some 150 m north from the library (Tasić et al, 2012). During the measurements campaign, the wind was blowing mostly from the west - southwest direction (with the frequency above 80%).

Table 1. *Statistics of meteorological parameters during the measurements campaign (daily averages ± standard deviation): temperature (T), relative humidity (RH), wind speed (WS) and pressure (P)*

Period	T (^{0}C)	RH (%)	WS (m/s)	P (mbar)
12.06. - 19.06.2015.	21.5±4.7	67.5±15.9	2.2± 1.3	967.8±2.3

Average daily PM_{10} and $PM_{2.5}$ concentrations and their I/O ratios are summarized in Table 2. The average of daily PM_{10} concentrations in the library was 33.2 μg/m^3 and 31.2 μg/m^3 in the ambient air. The average of daily $PM_{2.5}$ concentrations in the library was 22.2 μg/m^3 and 20.4 μg/m^3 in the ambient air. There was no significant difference between the average daily PM_{10} concentrations in the indoor and outdoor air (at the level of significance 0.05). It also applies to the average daily $PM_{2.5}$ concentrations. The results showed that daily PM_{10} concentrations in the ambient air and in the library as well, do not exceed daily limit value. The daily limit value for $PM_{2.5}$ concentration (25 μg/m^3) wasn't exceeded in the ambient air, but was exceeded once in the library.

In the recent years, a similar PM concentrations were recorded in the Bor town during the warm period (April – September). For example, average daily PM_{10} and $PM_{2.5}$ concentrations in the ambient air measured in the warm periods in two consecutive years (2009 and 2010) were 28.7 μg/m^3 and 19.1 μg/m^3, respectively (Tasić et al, 2011). Also, averages of daily PM_{10} and $PM_{2.5}$ concentrations in the warm period inside the Museum that is situated in the same building as the library were 24.8 μg/m^3 and 9.1 μg/m^3, respectively (Tasić et al, 2011).

The indoor/outdoor (I/O) PM concentration ratio is used to justify presence of indoor sources (I/O >1) or infiltration of ambient air (I/O≤ 1). According to Table 2, the average I/O ratio for daily PM_{10} concentrations was 1.06. Similarly, an I/O ratio for daily PM2.5 concentrations was 1.09. This indicates the presence of some indoor sources such as resuspension of particles caused by the activity of people that passing through the library.

The PM size distribution is helpful in understanding the source of PM. For example, particles emitted as part of combustion are almost always entirely in the fine fraction. Also, windblown dust is almost entirely in the coarse fraction, with a small percentage of windblown dust in the fine fraction. The average of daily PM2.5/PM10 ratio in the ambient air was 0.66 and 0.67 inside the library. These findings are consistent with the previously published value of 0.53 for average daily $PM_{2.5}/PM_{10}$ ratio determined in the ambient air in the Bor town in the warm periods from 2005 to 2010 (Tasić et al, 2012). Such high $PM_{2.5}/PM_{10}$ ratio points out to considerable influence of the air pollution sources of anthropogenic origin, such as fossil fuels combustion and traffic.

Table 2. *Average daily PM concentrations (μg/m^3), ranges and I/O ratios (SD - standard deviation, n – number of days)*

Sampling site	$PM_{10\ INDOOR}$			$PM_{10\ OUTDOOR}$			PM_{10} I/O ratio	n
	Average	Range	SD	Average	Range	SD		
Library	33.2	25.5-43.6	5.8	31.2	26.0-35.1	3.4	1.06 (0.91-1.25)	7

Sampling site	$PM_{2.5\ INDOOR}$			$PM_{2.5\ OUTDOOR}$			$PM_{2.5}$ I/O ratio	n
	Average	Range	SD	Average	Range	SD		
Library	22.2	18.6-29.0	3.5	20.4	17.3-24.5	2.5	1.09 (0.96-1.24)	7

Pearson correlation coefficients of average daily PM concentrations are presented in Table 3. Very strong correlations (r>0.8) were observed between the indoor PM_{10} concentrations and all other PM concentrations that were measured. As well, a strong correlation (0.8>r>0.6) between indoor $PM_{2.5}$ and outdoor PM concentrations was observed. Such correlations indicate that the major part of air pollution with PM in the library comes from the outdoor air.

The average ratio between daily PM_{10} concentrations obtained by the OSIRIS monitor and PM_{10} concentrations obtained by the gravimetric method was 0.82 (range from 0.75 to 0.94, r=0.92). Similar, the average ratio between daily $PM_{2.5}$ concentrations obtained by the OSIRIS monitor and $PM_{2.5}$ levels obtained by the gravimetric method was 0.63 (range from 0.56 to 0.89, r=0.74).

Table 3. *Pearson correlation coefficients of average daily PM concentrations*

	$PM_{10\ INDOOR}$	$PM_{10\ OUTDOOR}$	$PM_{2.5\ INDOOR}$	$PM_{2.5\ OUTDOOR}$
$PM_{10\ INDOOR}$	1			
$PM_{10\ OUTDOOR}$	0.84	1		
$PM_{2.5\ INDOOR}$	0.95	0.74	1	
$PM_{2.5\ OUTDOOR}$	0.86	0.72	0.76	1

Such results show that automatic monitor underestimated PM_{10} concentrations by approximately 18% and $PM_{2.5}$ concentrations by approximately 47%, relative to the reference gravimetric sampler. Figure 2 shows PM mass concentrations in the library measured by the OSIRIS monitor and calibrated as it was suggested by Ramachandran et al (Ramachandran et al, 2003). Figure 2 clearly shows that variations of PM concentrations in the library follow almost similar pattern during most of the measurement days. PM concentrations in the library rise with the start of working hours, at 8 AM, and declining upon closing of the library, after 8 PM.

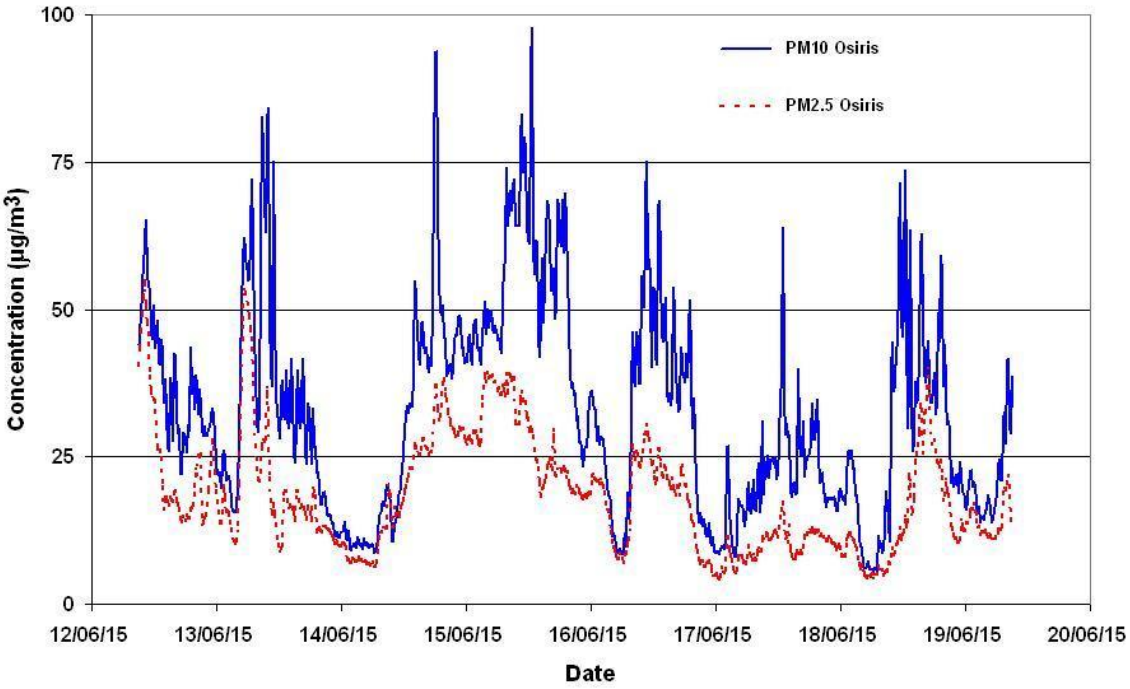

Figure 2. *15-min average PM mass concentrations in the library during the measurements campaign*

CONCLUSIONS

This work presents the results of measurements of PM_{10} and $PM_{2.5}$ concentrations and their indoor/outdoor relations in the library in Bor, Republic of Serbia. The results show that daily PM concentrations in the ambient air weren't exceeded daily limit value. Daily limit value for $PM_{2.5}$ concentration in the indoor air was exceeded once. There is no significant difference between the daily PM concentrations in the indoor and in the outdoor air (level of significance 0.05). PM_{10} concentrations in the library were very strongly correlated with the outdoor PM concentrations. Similarly, $PM_{2.5}$ concentrations in the library were strongly correlated with the outdoor PM concentrations. These findings lead to the conclusion that most of the PM in the library originates from the outdoor air. High $PM_{2.5}/PM_{10}$ ratios in both the indoor and outdoor environments (0.66 and 0.67) point to the considerable influence of pollution sources of anthropogenic origin, such as fossil fuels combustion and traffic. The average I/O ratio for daily PM_{10} concentrations was 1.06, and 1.09 for daily $PM_{2.5}$ concentrations. This indicates the presence of indoor sources of PM, such as resuspension of particles caused by the activity of people

that passing through the library. The continuous measurements of PM concentrations with the OSIRIS monitor clearly show that the PM concentrations in the library rising at the beginning of the working hours and declining upon the library closure. Further studies in this area should include chemical analysis of collected samples in the aim to determine the origin of PM in the library.

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REFERENCES

1. Anderson, H.R., Bremner, S.A., Atkinson, R.W., Harrison, R.M., Walters S., 2001. Particulate matter and daily mortality and hospital admissions in the West Midlands conurbation of the United Kingdom: associations with fine and coarse particles, black smoke and sulphate, Occup. Environ. Med., 58, 504–510.
2. Atkinson, R.W., Fuller, G.W., Anderson, H.R., Harrison, R.M., Armstrong, B., 2010. Urban ambient particle metrics and health: a time series analysis, Epidemiology, 21, 501–511.
3. Franck, U., Herbath, O., Roder, S., Schlink, U., Bote, M., Diez, U., Kramer, U., Lehmann, I., 2011. Respiratory effects of indoor particles in young children are size dependent. Sci. Total Environ., 409, 1621-1631.
4. Pope, C.A., Burnett, R.T., Krewski, D., Jerrett, M., Shi, Y., Calle, E.E., et al, 2009. Cardiovascular mortality and exposure to airborne fine particulate matter and cigarette smoke. Shape of the exposure–response relationship, Circulation, 120, 941–948.
5. Pope, C.A., Burnett, R.T., Thun, M.J., Calle, E.E., Krewski, D., Kazuhiko, I., et al, 2002. Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air pollution, J. Am. Med. Assoc., 287, 1132–1141.
6. Pope, C.A., Dockery, D.W., 2006. Health effects of fine particulate air pollution: Lines that connect, Journal of the Air and Waste Management Association, 56, 709-742.
7. Ramachandran, G., Adgate, J.L., Pratt, G.C., Sexton, K., 2003. Characterizing indoor and outdoor 15-minute average PM2.5 concentrations in urban neighbourhoods, Aerosol Sci. Technol., 37, 33-45.
8. Tasić, V., Milošević, N., Kovačević, R., Jovašević-Stojanović, M., Dimitrijević, M., 2012. Indicative Levels of PM in The Ambient Air in The Surrounding Villages of the Copper Smelter Complex Bor, Serbia, Chemical Industry & Chemical Engineering Quarterly, 18, 643-652.
9. Tasić, V., Kovačević, R., Maluckov, B., 2013. Preliminary Measurements of PM10 in Apartments in Bor, Serbia, Proceedings from the 4th International WeBIOPATR Workshop&Conference Particulate Matter: Research and Management WeBIOPATR2013, 02.10.-04.10.2013, Belgrade, Serbia, pp. 117-120, ISBN: 978-86-83069-40-8
10. Tasić, V., Kovačević, R., Milošević, N., 2011. Particulate matter (PM) indoor – outdoor relationships in buildings in Bor, Serbia , CD Proceedings of 6th International Conference on Sustainable Development of Energy, Water and Environment Systems, 25. - 29.9.2011., Dubrovnik, Croatia, ISBN 978-953-7738-13-6
11. Tasić, V., Milošević, N., Kovačević, R., Petrović N. ,2010. The analysis of air pollution caused by particle matter emission from the copper smelter complex Bor (Serbia), Chemical Industry & Chemical Engineering Quarterly, 16, 219−228.

6. SCHOOLS AND KINDERGARTENS

6.1 PARTICULATE MATTER IN SCHOOL ENVIRONMENTS: CHARACTERIZATION, EXPOSURE LEVELS AND HEALTH IMPACTS ON SCHOOLCHILDREN

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ABSTRACT

In today's world, education has become a crucial component of the child's social development. Children spend a considerable period of their time at schools, both indoors and outdoors. Thus, indoor air quality, and specifically particulate matter levels and composition, found in these environments may significantly impact on the respective health outcomes of this susceptible group, and requires particular attention. In this study, the available PM data at school microenvironments, and levels of particle- bound polycyclic aromatic hydrocarbons are reviewed. The health impacts on schoolchildren are also discussed. There is a clear need to establish international guidelines or references for exposure limits in schools microenvironments.

INTRODUCTION

The education is nowadays a fundamental component of the child's social development, with an increased length and time permanence of children at schools. Children may spend at schools up to 10 h per day. Children are a sensitive population because their respiratory, immune, reproductive, central nervous and digestive systems are not fully developed. Due to their size, physiology and activity level, children inhalation rates are higher than adults exhibiting also higher oxygen consumption and resting metabolic rate per unit of body weight. Therefore, indoor air quality found in school microenvironments may significantly impact on the respective health outcomes and requires particular attention (Oliveira et al, 2014, 2015a,b). In that regard, there is no doubt that particulate matter (PM) is a health-relevant pollutant. Epidemiological studies demonstrated an association between increase morbidity and mortality rates due to respiratory and cardiovascular diseases and elevated levels of ambient PM (Brunekreef et al, 2009; Krewski et al, 2009; Turner et al, 2011; Slezakova et al, 2014). As evidence has been overwhelming, International Agency for Research on Cancer (IARC) in October 2013 classified PM from outdoor pollution as carcinogenic to humans (i.e., Group 1; IARC, 2013). Indoors, PM has been much less characterized in schools than in other buildings (i.e., offices and other working places) (Annesi-Maesano et al, 2013). Furthermore, the presence of some toxic compounds, such as polycyclic aromatic hydrocarbons (PAHs), in PM (in particular in the smaller fraction) is highly health-relevant because, although the precise mechanisms are not completely understood, synergic interactions between these components can cause eventually more adverse health effects. Data concerning PAHs in educational environments have been slowly emerging but the information is far from comprehensive. In this study, the available PM data at school microenvironments and levels of particle-bound polycyclic aromatic hydrocarbons are reviewed. The health impacts on schoolchildren are also discussed.

METHODOLOGY

The available scientific literature between 2003 and 2014 was searched in the Thomson Reuters ISI Web of Knowledge database by combining the following keywords: PM; PAHs; indoor air quality; school; health effects; children. The biological contaminants were not considered.

RESULTS AND DISCUSSION

Particulate Matter

Concerning school environments, the contribution from outdoor air, school activities, cleaning activities and the emissions from printers and photocopy machines are the most important PM sources (Slezakova et al, 2012). Adverse health effects of PM depend on particle size, surface, number, and chemical composition (Fonseca et al, 2014). The most commonly studied fractions of particles in school microenvironments are PM_{10} and $PM_{2.5,}$ while works concerning PM_1 and ultrafine particles (UFP; i.e. those with particle size less than 100 nm) are scarce

(Fonseca et al, 2014). In the last years, the scientific attention has focused on the smallest fractions because the epidemiological evidence indicates that these may have a greater potency to cause adverse health effects than large particles (Wang et al, 2011). The size of particles determines the place where particle deposition occurs in the respiratory system; the smaller the particles deeply they can penetrate.

The majority of the studies in schools were conducted, by decreasing order, in Europe, Asia, North America, South America, Africa and Oceania. Reported indoor PM_{10} and $PM_{2.5}$ concentrations ranged from 2 $\mu g/m^3$ (Austria; Wallner et al, 2012) to 5858.5 $\mu g/m^3$ (in Iran; Mohammadyan and Shabankhani, 2013) and from 1 (Austria; Wallner et al, 2012) to 1210 $\mu g/m^3$ (Portugal; Madureira et al, 2012), respectively. Regarding PM_1, levels varied from 0.7 $\mu g/m^3$ (in Greece; Dorizas et al, 2013) to 1180 $\mu g/m^3$ (Portugal; Madureira et al, 2012) for schools indoor air. WHO and USEPA do not provide any guidelines concerning the indoor PM levels. Even among the developed countries, the existence of some national indoor air quality guidelines is rare. Among the few countries with established indoor air legislation is Portugal which government updated in 2013 its existent guidelines for the indoor air in public buildings (Portuguese Regulation, 2013). The PM limits were re-defined with values of 25 and 50 $\mu g/m^3$ for $PM_{2.5}$ and PM_{10}, respectively (8-h mean). In more than 90% of the European studies, PM concentrations surpassed these limits, as well as levels reported from Asian countries (namely Korea, India, Pakistan or Iran). In that regard, it is necessary to point out that studies from Asian schools (as well as from Africa and South America) are predominantly focused on analyzing the PM levels in outdoor air of school microenvironments (such as playgrounds, school vicinity and surroundings), which do not consider the many indoor sources that may be present in the indoor areas. Recently, Amato et al (2014) analysed the outdoor and indoor sources of $PM_{2.5}$ measured at 39 schools in Barcelona (Spain); authors found that 47% of indoor $PM_{2.5}$ concentrations were generated indoors mainly due to continuous re-suspension of soil particles (13%) and a mixed source (34%) comprising organic (skin flakes, cloth fibers, possible condensation of VOCs) and calcium-rich particles (from chalk and building deterioration).

Particle-bound Polycyclic Aromatic Hydrocarbons

PM chemical composition in ambient air depends on the contribution made by both anthropogenic and natural sources. Still, even particles from the same type of source may vary in their chemical (and physical) compositions due to different conditions, such as different source location, different time or emission rates. To understand the relationship between PM composition and health, it is important to study indoor pollutants that have the most hazardous effects on human health. In that regard, PAHs are among the most health–relevant pollutants (IARC 2010). PAHs are a class of organic chemical compounds with two or more aromatic rings which are formed during pyrolysis or incomplete combustion of organic matter. They are ubiquitous environmental pollutants. PAHs represent the largest known group of carcinogens due to their cytotoxic and mutagenic properties. Out of sixteen PAHs recommended by US EPA as priority pollutants, benzo[a]pyrene is classified by the International Agency for Research on Cancer (IARC) as human carcinogen (IARC, 2010). Other PAHs have been considered as probable (benz[a]anthracene, dibenz[a,h]anthracene and dibenzo[a,l]pyrene) and possible (naphthalene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene and indeno[1,2,3-c,d]pyrene) human carcinogens (IARC, 2010). The re-emission and sorption of gaseous PAHs from indoor surfaces, infiltration of outdoor emissions (both gaseous and particulate), use of heating systems, re-suspension of indoor dust, emissions from cooking activities (in canteens), and some electronic equipment (such as printers, computers) are the main indoor sources of PAHs in schools (Heinrich, 2011).

Only 13 studies regarding the PAH levels in school indoor and outdoor areas were found during the time period covered by the literature search, being 54% conducted in European countries. One study reported data for USA (Wilson et al, 2003) and five studies were conducted with regard to Asian (Thai and Indian) schoolchildren (Jyethi et al, 2014; Ruchirawat et al, 2006; Tuntawiroon et al, 2007). Overall, total PAH levels ranged from 0.28 (Chonburi, Thailand; Ruchirawat et al, 2006) to 619.0 ng/m^3 (North Carolina, USA; Wilson et al, 2003) for indoor air and from 0.28 (Chonburi, Thailand; Ruchirawat et al, 2006) to 217.3 ng/m^3 (Delhi, India; Jyethi et al, 2014) for outdoors. WHO Air Quality Guidelines for Europe specify a unit risk of 8.7×10^{-5} $(ng/m)^{-1}$ for PAHs (i.e. benzo[a]pyrene) (WHO, 2010), which corresponds to 1 additional cancer case in 100 000 exposed individuals, as a consequence of a lifetime exposure to 0.12 ng/m^3 of benzo[a]pyrene. Indoor environment is protected from PAHs atmospheric degradation (by reaction with other pollutants, such as ozone, nitrogen oxides, and sulfur dioxide), and the particulate-bound PAHs may persist for longer periods. Outdoor air is usually the dominant contributor to indoor PAH levels at urban schools (Oliveira et al, 2014, 2015a,b). Diffusion of pollutants from outdoor air to indoor air is influenced by several factors such as geographic location, concentration of pollutants in outdoor air, type of building and type of ventilation.

Due to its carcinogenic potency, benzo[*a*]pyrene has been defined as an indicator of human PAHs exposure. Regarding background atmospheric values, over the last two decades, concentrations of BaP in urban regions ranged from 0.3 to 0.6 ng/m^3 in Houston, USA and London, UK, and from to 9.3 to 11 ng/m^3 in Santiago, Chile, Lahore, and Pakistan (Kim et al, 2013). The highest outdoor values are generally found when industrial, rather than traffic or residential, contributions are dominant. Benzo[*a*]pyrene levels were reported to account for as much as 25% (0.12 ng/m^3) of the total carcinogenic PAHs in outdoor air of an Italian school during the Spring season (Romagnoli et al, 2014), for about 13% (13.1 ng/m^3) of the total PAHs content in the outdoor air of a school located in close proximity of an industrial area with high traffic roads in Delhi, India (Jyethi et al, 2014), and *ca*. 10% (4 ng/m^3) of the total carcinogenic PAHs in outdoor air of a school in Bangkok (Ruchirawat et al, 2006). Overall, the reported levels of benzo[a]pyrene in the outdoor areas of schools were higher than the recommended guideline established by the European Union (1 ng/m^3 as annual mean of total content in PM_{10} fraction). Some of the few studies available in the literature for school environments also reported the levels of naphthalene which is the only PAHs that has a limit value established for indoors by WHO (10 μg/m^3 as annual mean). Overall, the reported levels concerning school indoor environments were lower than the guideline value set by WHO. This organization (WHO, 2010) also stated that no threshold could be defined for PAHs, pointing out that all indoor exposures are considered relevant to human health.

Health Effects

Particulate indoor air pollution has been linked to both acute and chronic health effects, including asthma, as well as impaired lung function, leading to a greater use of rescue medication and hospital admissions (Maynard, 2015). Sarnat et al (2012) found positive associations between traffic- and non–traffic-related PM and airway inflammation among asthmatic schoolchildren along the USA-Mexico border. Annesi-Maesano et al (2007) investigated the relation between asthma and allergy of 10 year-old children and traffic air pollution. They associated the exposure to PM (and particle-bound PAHs) in school environments with the increase in the risk of suffering from exercise-induced bronchoconstriction, hyper-reactivity, flexural dermatitis, positive skin-prick tests to indoor allergens and history of atopic asthma. High emphasis has been placed on the formation of oxidative free radicals in the lung as a result of interactions between particles and lung lining fluid or/and lung cells, which play an important role in subsequent oxidative stress and inflammatory response (Maynard, 2015). The smaller the particle size, the higher the toxicity through mechanisms of oxidative stress and inflammation (Chen et al, 2011). Furthermore, children can have a lesser nasal contribution to breathing, making less efficient particle uptake in the nasal airways, and deposition in the lower respiratory tract thus may be greater. Bae et al (2010) found evidence of effect of exposure to high levels of PM, PAHs and oxidative stress in schoolchildren. The formation of DNA adducts is believed to be the first step in the initiation of carcinogenesis of PAHs (Ruchirawat et al, 2006). Tuntawiroon et al (2007) reported that bulky carcinogen-DNA adduct levels in peripheral lymphocytes were significantly higher in Bangkok schoolchildren than in those from provincial areas. Furthermore, DNA strand breaks were significantly higher, while the DNA repair capacity was lower in schoolchildren from Bangkok (Ruchirawat et al, 2006; Tuntawiroon et al, 2007). These studies demonstrated that urban schoolchildren may present more problems in the repair of DNA damage, leading to more aberrations and deletions than for the rural schoolchildren.

CONCLUSIONS

More information regarding PM characterization in school microenvironments, in particular indoors and about the smaller fractions, are necessary in order to better understand the respective exposure and health impacts on children. Still, available data frequently show problems related with indoor air quality due to poor building construction, cleaning, and poor ventilation, and also highlight the importance of urban planning in order to reduce children's exposure to PM at schools. The installation of effective air filtration devices inside classrooms might help to reduce the exposure of schoolchildren to indoor pollutants of outdoor origin, especially at schools located near highly trafficked freeways, refineries and other important sources of PM and PAHs (and other air pollutants). Globally, PM is described as the primary pollutant responsible for the lung function deficit. There is a clear need to establish international guidelines or references for exposure limits in schools microenvironments.

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REFERENCES

1. Amato, F., Rivas, I., Viana, M., Moreno, T., Bouso, L., Reche, C., Álvarez-Pedrerol, M., Alastuey, A., Sunyer, J., Querol, X. 2014. Sources of indoor and outdoor $PM_{2.5}$ concentrations in primary schools. Sci Total Environ 490, 757-765.
2. Annesi-Maesano, I., Moreau, D., Caillaud, D., Lavaud, F., Le Moullec, Y., Taytard, A., Pauli, G., Charpin, D. 2007. Residential proximity fine particles related to allergic sensitisation and asthma in primary school children. Resp Med 101, 1721-1729.
3. Annesi-Maesano, I., Baiz, N., Banerjee, S., Rudnai, P., Rive, S., on behalf of the SINPHONIE Group, 2013. Indoor air quality and sources in schools and related health effects. J Toxicol Env Heal B: Critical Reviews. 16, 8, 491-550.
4. Bae, S., Pan, X-C., Kim, S-Y., Park, K., Kim, Y-H., Kim, H., Hong, Y-C. 2010. Exposures to particulate matter and polycyclic aromatic hydrocarbons and oxidative stress in schoolchildren. Environ Health Persp 118, 579-583.
5. Brunekreef, B., Beelen, R., Hoek, G., Schouten, L., Bausch-Goldbohm, S., Fischer, P., Armstrong, B., Hughes, E., Jerrett, M., van den Brandt, P. 2009. Effects of long-term exposure to traffic-related air pollution on respiratory and cardiovascular mortality in the Netherlands: the NLCS-AIR study. Res. Rep. Health Effects Inst. 139, 5–71.
6. Chen, B-Y., Chao, H. J., Chan, C-C., Lee, C-T, Wu, H-P., Cheng, T-J., Chen, C-C., Guo, Y. L. 2011. Effects of ambient particulate matter and fungal spores on lung function in schoolchildren. Pediatrics 127, e690-e698.
7. Dorizas, P. V., Kapsanaki-Gotsi, E., Assimakopoulos, M. N., Santamouris, M. 2013. Correlation of particulate matter with airborne fungi in schools in Greece. International Journal of Ventilation 12,1-15.
8. Fonseca, J., Slezakova, K., Morais, S., Pereira, M. C. 2014. Assessment of ultrafine particles in Portuguese pre-schools: levels and exposure doses. Indoor Air, 24, 618–628.
9. Heinrich, J. 2011. Influence of indoor factors in dwellings on the development of childhood asthma. Int J Hyg Envir Heal 214, 1-25.
10. International Agency for Research on Cancer (IARC). 2010. Some non-heterocyclic polycyclic aromatic hydrocarbons and some related exposures, Monographs on the Evaluation of Carcinogenic Risks to Humans 92, 773.
11. International Agency for Research on Cancer (IARC). 2013. The carcinogenicity of outdoor air pollution. Lancet Oncol. doi:10.1016/S1470-2045(13)70487.
12. Jyethi, D. S., Khillare, P. S., Sarkar, S. 2014. Risk assessment of inhalation exposure to polycyclic aromatic hydrocarbons in school children. Environ Sci Pollut Res 21, 366-378.
13. Kim, K-H., Jahan, S. A., Kabir, E., Brown, R. J. C. 2013. A review of airborne polycyclic aromatic hydrocarbons (PAHs) and their human health effects. Environment International 60, 71–80.
14. Krewski, D., Jerrett, M., Burnett, R. T., Ma, R., Hughes, E., Shi, Y., Turner, M. C., Pope 3rd., C. A., Thurston, G., Calle, E. E., Thun, M. J., Beckerman, B., DeLuca, P., Finkelstein, N., Ito, K., Moore, D. K., Newbold, K. B., Ramsay, T., Ross, Z., Shin, H., Tempalski, B. 2009. Extended follow-up and spatial analysis of the American Cancer Society study linking particulate air pollution and mortality. Res. Rep. Health Effects Inst. 140, 5–114.
15. Madureira, J., Paciência, I., Fernandes, E. O. 2012. Levels of indoor – outdoor relationships of size-specific particulate matter in naturally ventilated Portuguese schools. J Toxicol Env Heal A 75, 1423-1436.
16. Maynard, R. L. 2015. The effects on health of ambient particles: time for an agonizing reappraisal?. Cell Biol Toxicol 31,131-147.
17. Mohammadyan, M., Shabankhani, B. 2013. Particulate matter in Iranian primary schools. Arh Hig Rada Toksikol 64:371-377.
18. Oliveira, M., Slezakova, K., Delerue-Matos, C., Pereira, M. C., Morais, S. 2015a. Exposure to polycyclic aromatic hydrocarbons and assessment of potential risks in preschool children. Environ. Sci. Pollut. Res. 22, 13892–13902.
19. Oliveira, M., Slezakova, K., Delerue-Matos, C., Pereira, M. C., Morais, S. 2015b. Polycyclic aromatic hydrocarbons: levels and phase distributions in preschool microenvironment. Indoor Air, 25, 557-568.
20. Portuguese Regulation. 2013. Decreto Lei 118/2013, Sistema de Certificação Energética dos Edifícios, o Regulamento de Desempenho Energético dos Edifícios de Habitação e o Regulamento de Desempenho Energético dos Edifícios de Comércio e Serviços. Diário da Republica 1 série–A 235:6644(2)-6644(9).
21. Romagnoli, P., Balducci, C., Perilli, M., Gherardi, M., Gordiani, A., Gariazzo, C., Gatto, M..P., Cecinato, A. 2014. Indoor PAHs at schools, homes and offices in Rome, Italy. Atmos Environ 92, 51-59.
22. Ruchirawat, M., Navasumrit, P., Settachan, D., Autrup, H. 2006. Environmental impacts on children's health in Southeast Asia: genotoxic compounds in urban air. Ann N Y Acad Sci 1076:678-690.
23. Sarnat, S. E., Raysoni, A. U., Li, W-W., Holguin, F., Johnson, B. A., Luevano, S. F., Garcia, J. H., Sarnat, J. A. 2012. Air pollution and acute respiratory response in a panel of asthamatic children along the U.S.-Mexico border. Environ Health Perspect 120, 437-444.

24. Slezakova, K., Morais, S., Pereira, M. C. 2012. Indoor air pollutants: Relevant aspects and health impacts. In: Oosthuizen J (ed) Environmental Health – Emerging Issues and Practice, InTech-Rijeka, Croatia, pp 126-146.
25. Slezakova, K., Fonseca, J., Morais, S., Pereira, M. C. 2014. Ultrafine particles in ambient air of an urban area: dose implications for elderly. J Toxicol Env Heal A, 77, 827-836.
26. Tuntawiroon, J., Mahidol, C., Navasumrit, P., Autrup, H., Ruchirawat, M. 2007. Increased health risk in Bangkok children exposed to polycyclic aromatic hydrocarbons from traffic-related sources. Carcinogenesis 28, 816-822.
27. Turner, M. C., Krewski, D., Pope, C. A. III, Chen, Y., Gapstur, S. M., Thun, M. J. 2011. Long-term ambient fine particulate matter air pollution and lung cancer in a large cohort of never-smokers. Am. J. Respir. Crit. Care Med. 184, 1374–1381.
28. Wallner, P., Kundi, M., Moshammer, H., Piegler, K., Hohenblum, P., Scharf, S., Fröhlich, M., Damberger, B., Tappler, P., Hutter, H-P. 2012. Indoor air in schools and lung function of Austrian school children. J Environ Monitor 14, 1976-1982.
29. Wang, Y., Hopke, P. K., Chalupa, D. C., Utell, M. J. 2011. Long-term study of urban ultrafine particles and other pollutants. Atmos. Environ., 45,7672–7680.
30. Warneck, P., Williams, J. 2012. Chapter 5. The atmospheric aerosol. Atmospheric chemist's companion. Springer; p. 127–87.
31. WHO. 2010. Guidelines for indoor air quality: selected pollutants, World Health Organization, Regional Office for Europe, Copenhagen, Denmark, ISBN 978-92-890-0213-4.
32. Wilson, N. K., Chuang, J. C., Lyu, C., Menton, R., Morgan, M. K. 2003. Aggregate exposures of nine preschool children to persistent organic pollutants at day care and at home. J Expo Anal Env Epid 13, 187-202.

6.2 ULTRAFINE PARTICLE LEVELS IN URBAN AND RURAL SCHOOL ENVIRONMENTS IN PORTUGAL

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Indoor and outdoor ultrafine particles (UFPs) (aerodynamic diameter <0.1µm) number concentrations were measured in six urban schools (US) located in areas with different characteristics of urbanization and traffic density, and two rural schools (RS) situated in the north of Portugal during winter period of 2014.

The purpose of this study was to assess and determine the sources of indoor UFP number concentrations in urban and rural Portuguese primary schools with classrooms naturally ventilated.

The mean number concentrations of indoor UFPs were significantly higher in urban schools than in rural ones (10.4×10^3 pt/cc and 5.7×10^3 pt/cc, respectively; p=0.01). Higher indoor UFP levels were associated with higher squared meters per student, floor levels closer to the ground, chalk boards, furniture or floor covering materials made of wood and windows with double-glazing. In addition, indoor number concentrations of UFP were inversely correlated with indoor carbon dioxide (CO_2) levels.

The highest outdoor concentrations were measured at two schools, both affected by heavy traffic. Moreover, a wide variability of indoor/outdoor (I/O) ratios was detected among schools which seems to be associated namely to indoor sources, although further research is required. However, the obtained concentrations data give an insight on the important role of different traffic emission exposures, as UFP pollution is presented in augmented concentrations in urban schools when compared to rural ones highlighting thus the increased exposure of children due to urban planning decisions and pointing at school's location as a key variable in terms of UFP load.

The obtained concentration data may be also very useful in epidemiological studies, in order to estimate children total personal exposure though the calculation of exposures received in different environments. This kind of studies may contribute to the design of effective policies and mitigation measures for the protection of public health.

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6.3 INDOOR AND OUTDOOR LEVELS OF O3, NO2, CO2 AND PM FRACTIONS IN DIFFERENT URBAN SCHOOL ENVIRONMENT

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ABSTRACT

This study investigated pollutant concentrations in indoor and outdoor school buildings at different urban locations in Serbia during heating and non-heating seasons. Gaseous pollutants (NO_2 and O_3), comfort parameters (temperature, relative humidity and CO_2) and particulate matter fractions (PM_{10} and $PM_{2.5}$) were measured in three schools (industrial, traffic and residential locations) between January to July 2012. Significant seasonal variations of NO_2 and particulate matter fractions were observed with higher levels during the heating season, while concentrations of O_3 were higher indoors during non-heating season. Indoor and outdoor concentrations of NO_2 and O_3 were below the annual and hourly WHO guideline values. During the heating period, daily outdoor and indoor concentrations of PM_{10} and outdoor and indoor concentrations of $PM_{2.5}$ exceeded the 24-hour WHO guideline values in 73%, 71%, 93% and 86% of days, respectively.

INTRODUCTION

Children have greater susceptibility to air pollutants than adults, because they breathe higher volumes of air relative to their body weights and their tissue and organs are actively growing. Children spend 4-6 hours per day in schools. During their stay in school, children can be exposed to harmful indoor air pollutants and poor indoor air quality (IAQ) can affect school performance and attendance. The school environment is a major contributor to children`s exposure to air pollutants (Kulkarni and Grigg, 2008; Mejia et al, 2011). This is a primary reason why school environments need to be studied. The primary purpose of school buildings and facilities is to provide children with ideal places for their learning and development. Many aspects are unique to schools: classrooms have about four times as many occupants as office buildings for the same floor area; in general, maintenance suffers from financial cuts; the presence of a wide variety of emission sources, including art and science supplies, and gyms; highly variable heating and ventilation systems and sometimes portable classrooms or buildings that were not originally designed to meet the educational requirements are used (EPA, 2005).

Traffic is one of the most important sources of indoor and outdoor air pollution in schools. NO_2 is generally considered a marker for traffic (Mejia et al, 2011; Pegas et al, 2012). In contrast to NO_2, O_3 typically arises from indoor sources. Ozone can be released into the air from some office equipment such as laser printers and copiers (WHO, 2010). On the other hand, particulate matter (PMs) are associated with a broader range of sources including traffic, road dust and industry (Russell et al, 2009). Each of these contaminants is associated with adverse health effects. PMs are associated with cardiovascular and respiratory morbidity and mortality (Russell et al, 2009). Ozone can cause a variety of symptoms (reduced lung function, shortness of breath and irritation of eye, nose and throat), and NO_2 can cause adverse respiratory effects including airway inflammation in healthy people and increased respiratory symptoms in people with asthma (WHO, 2010). During the heating season in naturally ventilated classrooms, ventilation is usually limited, and that can be considered as one of the main causes of high concentrations of CO_2, as well as other air pollutants. Adequate ventilation significantly reduces indoor concentrations of pollutants (Heudorf et al, 2009).

The aim of this study was to measure and compare pollutant concentrations (NO_2, O_3, PMs and CO_2) in the indoor and outdoor air of three naturally ventilated schools at different urban locations in Serbia during the heating and non-heating period.

METHODOLOGY

The following pollutants were measured indoors and outdoors: nitrogen dioxide (NO_2), ozone (O_3), particulate matter (PM_{10} and $PM_{2.5}$), as well as comfort parameters (carbon dioxide (CO_2), temperature and relative

humidity). The measurements were performed simultaneously in three indoor locations and one outdoor location within each school, for five working days during heating and non-heating periods between January and July 2012. The main parameters of the selected schools are given in Table. 1. Selected classrooms had one external wall, one side in contact with a corridor and the other two sides in contact with the adjacent classrooms.

NO_2 and O_3 were passively monitored using diffusive passive samplers (Radiello). The diffusive sampler for NO_2 with steel grids impregnated with triethanolamine, chemiadsorb NO_2 as nitrite ion, which was quantified by visible spectrophotometry. The diffusive sampler for O_3 consists polyethylene tube filled with silica gel coated with 4,4'-dipyridylethylene. Upon exposure, acid-catalysed ozonolysis of 4,4'-dipyridylethylene leads to 4-pyridylaldehyde. In the laboratory, 4-pyridylaldheyde is condensed with 3-methyl-2-benzothiazolinone hydrazone to yield the yellow colored azide, which was also quantified by visible spectrophotometry. The diffusive samplers were positioned in the classrooms 1.5 m above the floor at least 1 m far from any windows or doors. Outdoor samplers were installed in the shelters, protected from rain, direct sunshine and wind. At each sampling location, two replicate samples were collected.

Table 1. *Details of selected schools and classrooms*

Parameter	School S1	School S2	School S3
Classrooms monitored	A1, A2, A3	B1, B2, B3	C1, C2, C3
Area (m^2)	56, 63, 60	72, 68, 72	60, 60, 60
Room volume (m^3)	182, 205, 195	288, 272, 288	210, 210, 210
Average occupation	29, 18, 31	24, 28, 21	20, 28, 16
Location	Urban, traffic	Urban, residential	Urban, industry
School working hours	non-heating (8–20) heating (8–20)	non-heating (8–19) heating (8–19)	non-heating (8–19) heating (8–16)
Type of window	Wood-double glazing	Aluminium-double glazing	Aluminium-double glazing
Window area (m^2)	15, 10, 10	22, 18, 22	14, 14, 14

In each school, daily sampling of PM_{10} and $PM_{2.5}$ was performed, simultaneously indoors and outdoors, using a low volume sampler (Sven Lackel). The PM samples were collected onto pre-baked quartz filters. Filters were weighed before and after sampling and PM mass concentrations were quantified following the SRPS EN 12341 method. Continuous measurements of comfort parameters were performed with Testo logger every 10 minutes. CO_2 concentration levels were measured every 10 minutes using the Testo 435 devices with IAQ probe, with the precision of ± 50 ppm and range 0-5000 ppm. The equipment was calibrated at the beginning of each measuring campaign

RESULTS AND DISCUSSION

Table 2 presents weekly mean and standard deviation ranges for PMs indoors and outdoors, as well as different seasons. Concentrations of PMs were higher in heating periods compared with non-heating periods, where the concentration of PMs is higher due to the influence of traffic and different combustion sources for heating. This may be explained by lower ventilation rates and the fact that children spend more time indoors. The indoor PM levels were higher than those outdoors during the non-heating season, suggesting that the physical activity of the children leads to resuspension of particles and greatly contributes to enhance PM coarse fraction ($PM_{2.5-10}$) in classrooms. The highest indoor levels of PMs were found in city school S2, for both seasons. These high indoor levels might have been cause by higher occupancy in the classrooms in the school S2 compare to other schools, which contributes to a higher level of PMs. During the heating season, in most cases, higher outdoor levels of PMs were observed, suggesting that indoor particles are affected by outdoors. Daily $PM_{2.5}$ concentrations during the non-heating period exceeded the 24-hour WHO guideline value (25 μg/m^3) during 38% of days outdoors and 12% of days indoors. During the heating period, daily outdoor and indoor concentrations of PM_{10}, as well as outdoor and indoor concentrations of $PM_{2.5}$ exceeded the 24-hour WHO guideline values in 73%, 71%, 93% and 86% of days, respectively. Daily outdoor PM_{10} concentrations during the non-heating period did not exceed the 24-hour WHO guideline value (50 μg/m^3), but daily indoor PM_{10} concentrations were exceeding the guideline values for 47% of days.

NO_2 and O_3 are the most commonly measured gaseous pollutants in school, together with CO and SO_2 (Mejia et al, 2011), and Table 3 shows the weekly concentrations of these pollutants in indoor and outdoor spaces. The I/O ratios were less than 1 in the most cases, which suggested that traffic is major source of these pollutants during both seasons. Indoor and outdoor NO_2 concentrations, for both periods, were below the annual and hourly guideline values of 40 μg/m^3 and 200 μg/m^3 (WHO, 2010). At the other hand, indoor and outdoor concentrations of O_3 ranged 0.49-1.80 μg/m^3 and 2.79-35.81 μg/m^3 during the heating period, respectively, and do not exceed the 8h guideline value of 100 μg/m^3 (daily maximum) (WHO, 2010). During the non-heating period, indoor and outdoor O_3 concentrations were up to five times higher than in the heating period, but the concentrations found here are much lower than the guideline values.

Table 2. *Concentrations of PM_{10} and $PM_{2.5}$ in schools*

School	Sampling site	PM_{10} (μg/m^3)		$PM_{2.5}$ (μg/m^3)	
		Heating	**Non-heating**	**Heating**	**Non-heating**
S1	Indoor	45.32±8.60	43.09±5.30	25.72±7.93	13.29±4.76
	Outdoor	56.62±11.79	16.61±6.37	46.50±10.23	10.55±5.33
S2	Indoor	80.38±14.86	78.59±35.64	36.42±15.46	24.01±7.01
	Outdoor	49.62±18.55	21.22±2.83	38.42±14.97	7.99±4.59
S3	Indoor	72.70±24.97	60.72±22.57	59.09±21.09	14.40±6.52
	Outdoor	90.67±35.43	40.21±7.40	95.68±32.94	6.39±1.60

Table 3. *Concentrations of NO_2 and O_3 in schools*

School	Sampling site	NO_2 (μg/m^3)		O_3 (μg/m^3)	
		Heating	**Non-heating**	**Heating**	**Non-heating**
S1	A1	12.16	9.91	1.36	6.00
	A2	12.60	7.15	0.93	3.38
	A3	12.99	9.48	1.21	1.35
	Outdoor	6.49	3.70	39.81	22.62
S2	B1	16.02	7.42	0.91	6.40
	B2	10.70	5.68	1.07	4.08
	B3	14.98	5.76	0.68	9.22
	Outdoor	25.19	6.72	10.53	21.83
S3	C1	24.27	7.34	0.98	4.61
	C2	29.88	14.60	0.49	3.82
	C3	27.06	18.50	1.80	4.04
	Outdoor	48.60	18.10	2.79	12.85

Table 4. presents average values of CO_2, T, and RH for all schools, for all periods and occupied periods only. CO_2 concentration during the heating period is significantly above a concentration of 1000 ppm during occupied periods, for 64-81 % of cases, for different schools. In the non-heating period in one school, for the occupied period, CO_2 concentration exceeds 1000 ppm during classes in 58% of cases, while in the other two, this is for less than 20% of cases. The temperature was in the recommended range, except for the heating period in one school when the outdoor temperature values were extremely low. During the study period (for the school S1) outdoor temperature was low (about -14°C), so lessons were shortened from 45 to 30 min. This shortening could contribute to overall lowering of indoor temperature for this school.

CO_2 concentrations are often used as a surrogate of the rate of outside supply air per occupant. Indoor CO_2 concentrations above approximately 1000 ppm are generally regarded as indicative of ventilation rates that are unacceptable with respect to body odours. The indoor concentrations of CO_2 showed inadequate classroom air exchange rates. Figure 1 depicts the variation of indoor CO_2 concentrations in heating and non-heating period at the three schools. A strong correlation of the CO_2 levels with occupancy has been observed. Lower ventilation rates can be associated with increased prevalence of asthma and allergic symptoms in children.

Table 4. *Average values of CO_2, T, and RH in schools for occupied and all period of measurements*

Psihical parameters	Period	Winter			Summer		
		S1	S2	S3	S1	S2	S3
Temperature [˚C]	All	14.64	21.22	21.23	19.7	23.1	25.2
	Occupied	16.25	21.83	21.13	20.4	23.4	25.6
Relative humidity [%]	All	27.03	32.58	33.45	54.8	57.5	45.0
	Occupied	29.55	34.14	35.29	56.1	55.8	44.3
CO_2 [ppm]	All	772	817	930	775	654	648
	Occupied	1120	1126	1333	1100	747	792
<1000 ppm [%]	Occupied	30	36	19	42	82	87
1000-1500ppm [%]	Occupied	59	52	46	46	17	13
>1500ppm [%]	Occupied	11	12	35	12	1	0

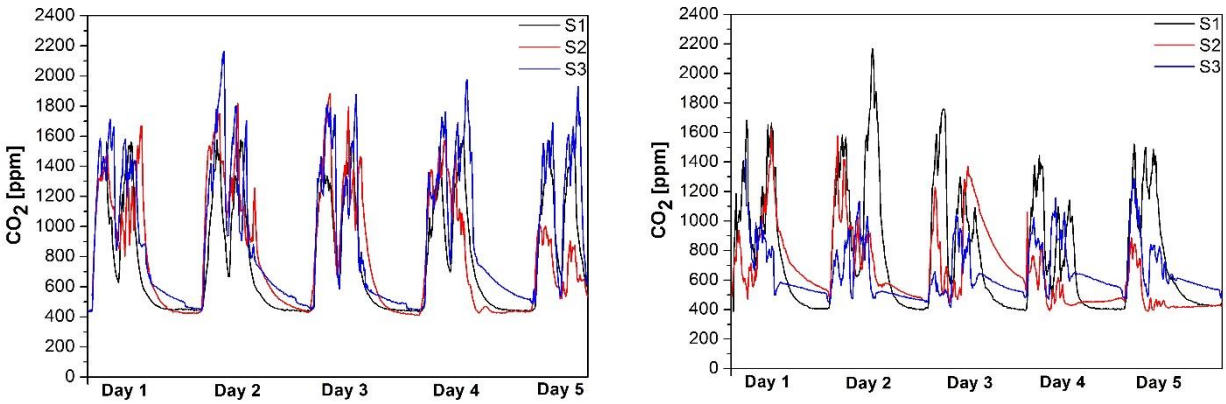

Figure 1. *CO_2 concentrations during winter (left) and summer (right) period in S1, S2 and S3 school*

CONCLUSIONS

This paper provides new data concerning the indoor and outdoor concentrations of NO_2, O_3, CO_2 and PMs in Serbian schools. The I/O ratios for NO_2 and O_3 during both seasons, and I/O ratios for PMs during heating season, were less than one, suggesting that outdoor sources (traffic exhaust, industrial pollution and combustion) contributed more than indoor sources in the classrooms. During the heating period, daily outdoor and indoor concentrations of PM_{10}, as well as outdoor and indoor concentrations of $PM_{2.5}$ exceeded the 24-hour WHO guideline values between 71-93% of days in each of the schools. During the non-heating season, exceedance of daily outdoor limit value of PM_{10} was not detected, while there were 38% exceedance of daily guide level for $PM_{2.5}$. However, daily indoor PM_{10} and $PM_{2.5}$ concentrations exceeded the guideline value during 47% and 12% of all monitor days during the non-heating period in three schools, respectively. The daily profiles of CO_2 during the heating season suggest that the classrooms are inadequately ventilated, which likely favours accumulation of air pollutants in the classrooms.

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REFERENCES

1. EPA-Environmental Protection Agency, 2005. IAQ Reference Guide. Tools for Schools, EPA 402-K-95001, Third Edition, Washington D.C.
2. U. Heudorf U., V. Neitzert V., J. Spark J., 2009. Particulate matter and carbon dioxide in classrooms – The impact of cleaning and ventilation, Int. J. Hyg. Environ. Health 212, 45–55
3. Kulkarni, N., Grigg, J., 2008. Effect of air pollution on children, Paediatrics and Child Health, 18, (2008), 238-243.
4. Mejia, J.F., Low ChoyC., S., Mengersen, K., Morawska, L., 2011. Methodology for assessing exposure and impacts of air pollutants in school children: Data collection, analysis and health effects – A literature review, Atmospheric Environment, 45, 813-823.
5. Pegas, P.N., Nunes, T., Alves, C.A., Silva, J.R., Vieira, S.L.A., Caseiro, A., Pio, C.A., 2012. Indoor and outdoor characterisation of organic and inorganic compounds in city centre and suburban elementary schools of Alveiro, Portugal, Atmospheric Environment, 55, 80-89.
6. Russell, A.G., Brunekreef, B., 2009. A focus on particulate matter and health, Environmental Science and Technology, 43, 4620-4625.
7. World Health Organization (WHO), 2010. Selected pollutants, Copenhagen, Denmark, 2010. http://www.euro.who.int/__data/assets/pdf_file/0009/128169/e94535.pdf, accessed October 2015.

6.4 CORRELATING SCHOOL INDOOR THERMAL COMFORT PARAMETERS AND PM10 CONCENTRATION WITH RESPIRATORY SYMPTOMS OF SCHOOL CHILDREN

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ABSTRACT

Key objective was to correlate elements of indoor thermal comfort, PM10 concentration and ventilation rate (VR) with respiratory symptoms in children from ten Belgrade primary schools. We monitored indoor air pollutants and measured physical parameters. A standardized questionnaire on the respiratory health of children was given to the caregivers. 735 children in 44 classrooms participated in the research, chosen by random sampling. Five-day measurements of carbon dioxide, indoor air temperature, relative humidity and PM_{10} were undertaken in classrooms, during school hours. Significant correlation exists for "cough ever" and "day/night cough in autumn/winter seasons" and high indoor PM_{10}, meaning cough is more frequent when IAQ PM_{10} exceeds outdoor concentration. Higher indoor air temperature correlates "cough ever" with statistical significance. "Cough with phlegm" correlates with high indoor temperature, relative humidity, PM10, and with low ventilation rate. Statistically significant correlation exists for "wheezing ever" vs. elevated indoor air temperature and PM_{10} concentration. "Wheezing after exercise" is strongly correlated to PM_{10} concentration 50-80 $\mu g/m^3$, while "dry cough in last 12 months" is significantly correlating with elevated PM_{10}.

Keywords: indoor air quality, classroom, particulate matter, primary school, respiratory symptoms, thermal comfort

INTRODUCTION

The quality of indoor air of homes, offices, or other public or private dwellings could be accounted as one of essential determinants of a healthy life and wellbeing of each individual (WHO, 2010). School indoor air quality (IAQ) is expected to have a key role in the assessment of children's personal exposure to air pollution, concerning the fact that they spend at least a third of their time inside school buildings, approximately 7 hours a day (Almeida et al, 2010; Bako-Biro et al, 2004, 2011; Pegas et al, 2010). In a school they have much less floor space, than adults working in a typical office. The typical classroom has on average four times as many occupants per square meter as the typical office building. According to Eurostat, the average primary class size in European countries and the US was 21 pupils corresponding to a density ranging from 2 to 3.1 m^2 per person (Eurostat, 2011). The high occupancy densities in school classrooms result in high internal heat gains, high carbon dioxide (CO_2) levels, emissions of body odors together with various indoor pollutants (physical, chemical and microbial) (Chatzidiakou et al, 2014). School buildings are complex spaces to design as they need to perform well in all aspects of environmental conditions, including air quality, while needing to accommodate periods with very high occupant densities (Wall et al, 2008).

Children are particularly vulnerable to all types of pollutants, because their breathing and metabolic rates are high. Their breathing zone tends to be closer to pollutants sources, such as new carpet, and less likely to be well ventilated as it is bellow window level. The immune system of young children is yet, immature, and exposure to pollutants can mean allergic reactions or ill health. Therefore, it is of utmost importance to provide good IAQ in classrooms, to help minimize these effects (Annesi-Maesano et al, 2012).

Former meta-analytic reviews (Chatzidiakou et al, 2012; Mendell and Heath, 2005; Daisey et al, 2003) offer a comprehensive picture of air quality and thermal conditions in school settings, emphasizing that reduced ventilation rates and elevated indoor temperatures in schools are common, frequently much worse than in office buildings (Wargoski and Wyon, 2013). Children are more vulnerable to airborne pollutants than adults because their developing lungs breathe more air compared to the relative size of their bodies, and they have an underdeveloped ability to communicate concerns in response to pollutant levels. Children spend most of their time indoors while at school (Eurostat, 2011). School authorities have a particular duty of care for their pupils in ensuring that appropriate conditions in the indoor environment are maintained. In this context, thermal comfort levels and Indoor Air Quality (IAQ) have a crucial role to play in producing an environment that supports optimal educational and health outcomes.

METHODOLOGY

Key objective of this paper was to correlate elements of indoor thermal comfort, PM_{10} concentration and ventilation rate (VR) with respiratory symptoms in children from ten Belgrade primary schools. We monitored indoor air pollutants and measured physical parameters of indoor environment in the classrooms. A standardized questionnaire on the respiratory health of children was given to the caregivers. 735 children attending 44 classrooms participated in the research, chosen by using random sampling. A standardized questionnaire on the respiratory health of children was given to the caregivers. Five-day measurements of carbon dioxide, indoor air temperature, relative humidity and PM_{10} were undertaken in classrooms, during school hours. The paper deals with the quantitative indicators of the thermal comfort zone, as given by the ASHRAE Standards (ASHRAE 62-2007, 2007), such as: ventilation rate, optimum indoor air temeperature (18-23 C^o), relative air humidity (40-75%), space occupancy (< $2m^2$ of indoor space per child, not suitable), correlating it to the measure values of indoor PM_{10}. Ventilation surrogates the IAQ level, minimizing the concentration of harmful pollutants. Higher ventilation rates are associated with improved health (Salleh et al, 2011). In the EU, current regulatory framework focuses on CO_2 levels as a proxy for air quality (ASHRAE 62.1-2010, 2010; EN ISO15251, 2007) as it is a useful tool for the estimation of ventilation rates and the dilution of pollutants with indoor sources and the improvement of perceived IAQ. For both indoor and ambient air PM_{10} sampling, a portable HAZ-DUST EPAM-5000 particulate monitor was used. It uses light scattering to measure particle concentration and provide real-time determinations and data recordings of airborne particle concentration in mg/m^3. For indoor air monitoring it was positioned in classrooms, at 1.5m height, away from the walls, to prevent influence of chipping. Monitor was positioned outside of the school building, in front of the indicated classroom, for ambient air PM10 sampling. Monitoring lasted for one whole working week, in both school shifts, while the children were present indoors, only.

Primary schools were grouped by their location, i.e. by the level of their exposure to potential sources of air pollution in their vicinity (be it traffic or industrial facility), as suburb schools ("Aca Milosavljević", "Kosta Abrašević", "Stevan Sremac"), schools in broader urban area ("Nikola Tesla", "I.G.Kovačić", "Ivan Gundulić"), and downtown ones ("Petar Petrović Njegoš", "Skadarlija", "Radojka Lakić", "Drinka Pavlović"). As for the vicinity of busy traffic, it can be easily comprehended by consulting the GIS map of them, together with traffic characterization (Figure 1). Schools' traffic characterization is given in the following list. Their given registered number is according to the order of the sampling process schedule:

1. "Aca Milosavljević"- suburb Rusanj village, valley downhill the regional highway;
2. "Kosta Abrašević" - suburb Resnik, residential area, trees in between street and school;
3. "Nikola Tesla" - Rakovica, suburban municipality, ex-industrial zone, ordinary urban traffic mode;
4. "I.G.Kovačić" - Broad city centre, isolated from dense traffic, residential area;
5. "Skadarlija" - downtown, high density traffic, backyard towards pedestrian zone, bus stop in front;
6. "Stevan Sremac" - Borča III, urbanized suburb, with no heavy traffic;
7. "Drinka Pavlović" - downtown, close to two monitoring stations with continuously high values of traffic-induced pollutants;
8. "Petar Petrović Njegoš" - downtown, high traffic density;
9. "Radojka Lakić"- Squeezed between two streets with high density traffic (lots of heavy traffic), downtown, next to Central Rail Station;
10. "Ivan Gundulić" - New Belgrade, broader urban zone, frequent traffic.

Statistical methodology

Simple descriptive statistics, such as mean ± standard deviation, was used for continuous variables, IAQ and OAQ PM_{10}, number and % of IAQ interval distributions, by schools and schools' position, while numbers (percentages) were used for categorical variables. The Kolmogorov–Smirnov test was used to check if IAQ and OAQ PM_{10} had a normal distribution. Quantitative variables with normal distribution were compared using ANOVA F test, and categorical variables were compared using contingency tables and Chi-Square or non-parametric Kruskal Wallis test. Chi-square test was used to compare IAQ PM10 between groups - schools or schools' position. For correlations between variables we used Spearman's Correlation for the linear relationship between two variables, by schools.

RESULTS AND DISCUSSION

This case study involved 735 students from 10 Belgrade primary schools, of which 364 (49.5%) girls and 371(50.5%) boys (p=ns). Mean age of children participating in the study ranged from 8,85±0.50 years in School N^{o} 2 to 9.88 ± 0.79 years in School N^{o} 10. Total mean value for the age of children is 9.34±0.7 years. A statistically significant difference exist for the mean age of children attending all 10 schools (F=18.985, p<0.000). Simple distribution of children, according to the respiratory symptoms reported by the parent/caregiver, who filled in the questionnaire, is given in Table 1.

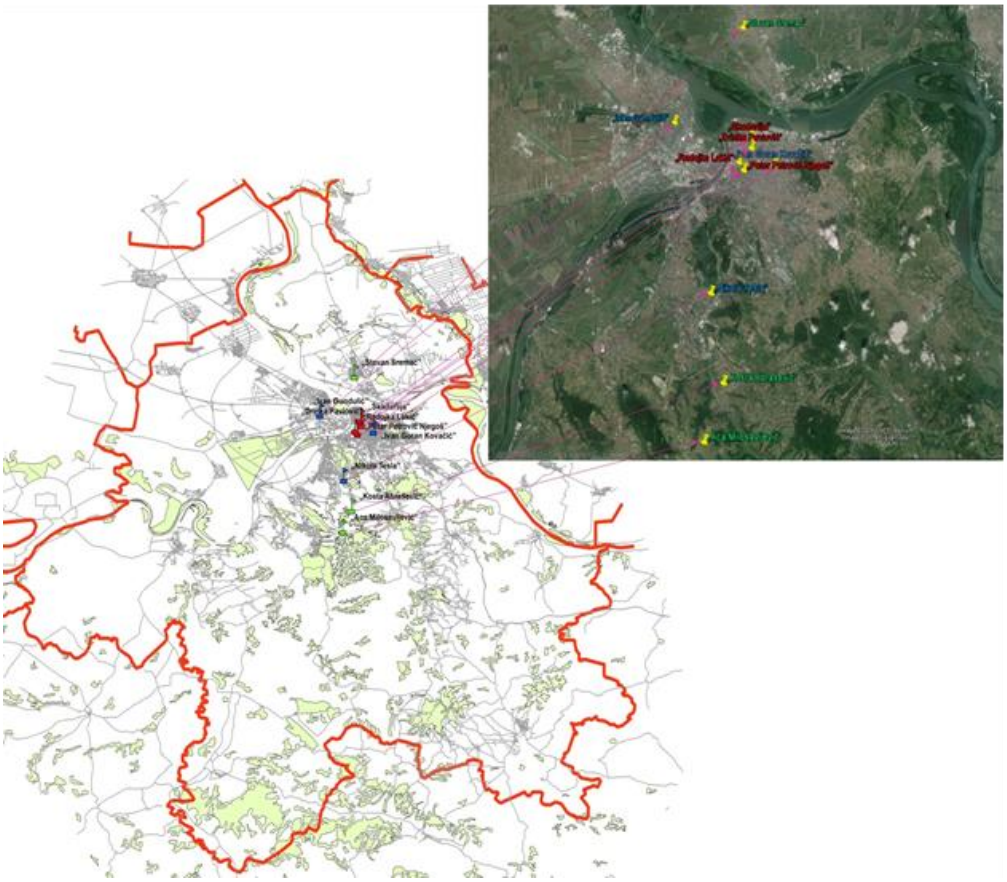

Figure 1. *Spatial distribution of surveyed schools by using GIS methodology*

Table 1. *Distribution of the involved children by the respiratory health status*

Respiratory symptoms	Total	No		Yes		χ2 test	sig
		Number	%	Number	%		
Cough ever	717	559	78.0	158	22.0%	224.26	0.000
Morning cough	716	639	89.2	77	10.8%	441.12	0.000
Day/night cough	719	646	89.8	73	10.2%	456.64	0.000
Continuous cough > 3 months	711	688	96.8	23	3.2%	621.97	0.000
Cough with phlegm	717	648	90.4	69	9.6%	467.56	0.000
Wheeze ever	719	564	78.4	155	21.6%	232.65	0.000
Wheeze in last 12 m	716	647	90.4	69	9.6%	466.59	0.000
Wheeze after exercise	722	685	94.9	37	5.1%	581.58	0.000
Dry cough at night in last 12 months	724	622	85.9%	102	14.1%	373.48	0.000
Woken by wheeze in last 12 months	720	676	93.9	44	6.1%	554.75	0.000

The most frequent among all reported symptoms for all participating children was “cough ever” (22%), followed by “wheeze ever” (21,6%), while, “dry cough at night in last 12 months was positioned third (14.1%). The least reported respiratory symptom pattern is “continuous cough for more than 3 months” (3.2%) together with the “wheeze after exercise” (5.1%), while “awaken by wheeze in last 12 months” is positioned third (6.1%).

Table 2 shows distribution of the involved children by the respiratory health status, by each school.

Cough was reported mostly in School No.1 (39.8%), while in School N^{o} 7 it was the least reported symptom (12%). A statistically significant difference is noted for the cough symptom among the students of all 10 schools involved in the research (p<0.0001).

Morning cough (in autumn/winter) was most often present among pupils in School N^{o} 6 (16.2%), while in School N^{o} 4 it was the least reported symptom (5.1%). There was no proven statistically significant difference for this symptom among the students of all 10 schools involved in the research (p=0.551).

Table 2. *Distribution of the involved children by the respiratory health status related by schools*

School N^{o}		**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**Sign.**
Cough ever	N^{o}	39	13	23	8	18	20	6	13	8	10	p<0.000
	%	39.8	19.4	32.4	13.1	23.4	26.7	12.0	17.6	12.9	12.2	0
Morning Cough (aut/win)	N^{o}	11	9	11	3	6	12	5	7	7	6	p=0.551
	%	11.6	13.4	14.5	5.1	7.8	16.2	10.0	9.5	11.3	7.3	ns
Day/night Cough (aut/win)	N^{o}	11	7	16	4	2	8	2	10	5	8	p<0.025
	%	11.6	10.4	21.1	6.8	2.6	10.8	4.0	13.3	7.9	9.8	
Continuous Cough > 3 months	N^{o}	5	3	3	2	3	2	1	2	0	2	p=0.852
	%	5.3	4.5	4.5	3.3	3.9	2.7	2.0	2.6	0.0	2.4	ns
Cough with phlegm	N^{o}	26	3	6	6	14	7	2	1	1	3	p<0.000
	%	26.5	4.5	8.3	9.8	18.4	9.5	4.0	1.3	1.6	3.7	0
Wheeze ever	N^{o}	25	11	22	13	14	17	11	10	11	21	p=0.345
	%	26.3	16.4	**28.9**	21.3	18.4	23.0	21.6	13.3	17.2	26.3	ns
Wheeze in last 12 m.	N^{o}	10	5	11	7	9	11	5	2	5	4	p=0.215
	%	10.2	7.5	**15.1**	11.5	11.8	14.9	9.6	2.7	7.9	5.1	ns
Wheeze after exercise	N^{o}	9	4	5	6	1	4	3	0	3	2	p=0.117
	%	9.2	6.0	6.7	**9.8**	1.3	5.4	5.8	0.0	4.8	2.5	ns
Dry night cough last 12 m.	N^{o}	21	5	12	5	16	10	8	12	4	9	p=0.056
	%	22.1	7.5	16.0	8.2	20.8	13.2	15.4	16.0	6.3	11.0	ns
Woken by wheeze in last 12 m.	N^{o}	10	2	10	8	2	5	1	1	1	4	p<0.002
	%	10.5	3.0	13.7	13.1	2.6	6.6	1.9	1.3	1.6	4.9	

Day and night cough (in autumn/winter) was most often present among pupils in School N^{o} 3 (21.1%), while in School No 5 it was the least reported symptom (2.1%). A statistically significant difference is noted for this pattern of symptoms among the students of all 10 schools involved in the research (p<0.025).

Continuous Cough for more than 3 months was reported mostly in School No.1 (5.3%), while in School N^{o} 7 it was the least reported symptom (1%). There was no proven statistically significant difference for this symptom among the students of all 10 schools involved in the research (p=0.852/ns).

Cough with phlegm was reported mostly in School No.1 (26.5%), while in School N^{o} 8 (1.3%). A statistically significant difference is noted for this symptom among the students of all 10 schools involved in the research (p<0.0001).

Wheeze ever was most often present among pupils in School N^o 3 (28.9%). The same position repeats for this school when reporting on symptom patterns such as *wheeze in last 12 months* (15.1%), and *been awaken by wheeze in last 12 months* (13.7%).

Dry night cough in last 12 months is most often reported by children from School N^{o}4.

From the list of reported symptoms, it shows that School N^o 8 was the one whose pupils reported the least cases of the following symptoms: wheeze ever, wheeze in last 12 months, wheeze after exercise, dry cough, and being awaken by wheeze in last 12 months, among all 10 schools involved in the study. Concerning the number of children, from all 10 schools, exposed to particular indoor air pollutants and thermal comfort parameters, Table 3 shows that in most cases, majority of pupils are exposed to values that do not comply with the given standards for IAQ. Statistical insignificance was calculated only in the case when exposure to all parameters of thermal comfort were correlated together to the number of exposed/non exposed children (51.3% vs. 48.7%), with p= 0.483.

Table 3 presents the overall number of children exposed to potentially unsuitable indoor environmental quality parameters, such as: carbon-dioxide concentration, indoor temperature (C°), relative humidity (%), occupancy rate, ventilation rate (L/s/ per person), PM_{10} indoor concentration, together with the PM_{10} indoor/outdoor ratio. A statistically significant difference exists in distribution of children exposed to mean indoor CO_2 meaning that 64.6% children attend classrooms with mean CO_2 above 1000 ppm, while only 35.4% spend time in classrooms with values of CO_2 below 1000ppm (p<0.0001).

Statistically significant number of children is exposed to unsuitable mean indoor air temperature (74.7%), while 25.3% attends classrooms in which air temperature mean value is within the given thermal comfort zone (p<0,0001). Concerning indoor relative air humidity (in %), there is high statistical difference between number of students exposed to higher mean humidity values and those attending classrooms with lower percentage of relative humidity (p<0.007). There is no statistically significant difference in the distribution of students towards the interval distribution of the overall indicators of the thermal comfort zone (p=ns). On the other hand, statistically significant difference shows for the value of mean RH within indoor thermal comfort vs. mean RH values, beyond the given standards (p<0.0001). Higher statistical significance shows for the number of pupils exposed to mean PM_{10} >50µg/m^3 (76.2%) from the number of children (23.8%) exposed to mean PM_{10} below 50 µg/m^3 (p<0.0001). High statistical significance is proven for the number of children attending classrooms with low values of ventilation rates 3-8 l/s per person (59.5%) compared to the number of children spending time in classrooms with the ventilation rates values complied to the given standard value of ≥8 l/s/person (p<0.0001).

Table 3. *Distribution of the involved children by indoor air IAQ parameters, mean±SD and medians*

		Total	%	**χ2**, sign	Mea n± SD	95 % CI Lower -Upper	Median
CO_2 IAQ (ppm)	CO_2<1000	260	35.4	p<0.0001	820.4±98.2	808.4-832.4	834.0
	CO_2>=1000	475	64.6		2020.1±3160.4	1735.2-2305.1	1441.0
Total		735	100.0		1595.7±2604.4	1407.1-1784.3	1122.0
C°	Within range	186	25.3	p<0.0001	25.06±1.07	24.90-25.21	25.00
	Beyond range	549	74.7		22.14±0.95	22.06-22.22	22.00
Total		735	100.0		22.88±1.60	22.76-23.00	23.00
RH(%) ≤40>	Within range	331	45.0	p<0.007	31.11±8.10	30.23-31.98	34.00
	Beyond range	404	55.0		46.39±5.21	45.88-46.90	44.00
Total		735	100.0		39.51±10.11	38.77-40.24	41.00
Comfort zone (C° 18-23, RH 30-75% & >2.2m^2/st.)	Comfort zone	358	48.7	p=0.483/ ns	C° / 22.0±1.1,	RH /41.9±8.3,	m^2/2.8±0.5
	Beyond comfort zone	377	51.3		C° /23.7±1.6 ,	RH /37.2±11.1,	m^2/2.2±1.1
Total		735	100.0				
PM_{10} I/O RATIO	< 1	442	60.1	p<0.0001	0.73±0.18	0.71-0.75	0.80
	=1	27	3.7		1.00±0.00	1.00-1.00	1.00
	> 1	266	36.2		1.30±0.23	1.27-1.32	1.23
Total		735	100.0		0.94±0.33	0.92-0.97	0.92

PM_{10} IAQ < 50µg/m^3>	PM_{10}< 50	175	23.8		39.71±5.10	38.95-40.47	41.00
	PM_{10} > 50	560	76.2	p<0.0001	95.53±40.15	92.20-98.86	91.00
Total		735	100.0		82.24±42.43	79.17-85.31	70.00
Ventilation rate	3- 8 L/s person	437	59.5		5.21±1.71	5.05-5.37	4.80
	8 + L/s person	298	40.5	p<0.0001	12.79±3.92	12.34-13.23	12.14
Total		735	100.0		8.28±4.67	7.94-8.62	7.10

Table 4 represents distribution of values (Mean ± SD) of carbon monoxide, carbon dioxide, indoor air temperature, relative humidity, ventilation rate, PM10 concentrations and PM10 Indoor/Outdoor ratio by schools. In cases when PM_{10} Indoor/Outdoor ratio exceeds 1.0, it means that predominant source of particulate pollution is indoors, or it is due to the resuspension of particles, depending on children's activities and occupancy rates (Alves et al, 2013). Statistically significant difference exists between schools for PM_{10} Indoor/Outdoor ratio (p<0.0001), as well as for the indoor PM_{10} concentration (p<0.0001), carbon monoxide (p<0.0001), carbon dioxide (p<0.0001), indoor air temperature (p<0.0001), relative humidity (p<0.0001), and ventilation rate (given as % of children exposed to a certain value), (p<0.0001).

Table 4. *Distribution of values (Mean ± SD) of CO, CO_2, indoor air temperature, relative humidity, PM_{10}, ventilation rate and PM_{10} Indoor/Outdoor ratio by schools*

School N^o	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Total	77	68	77	45	78	77	53	76	64	82
PM_{10} **µg/m^3**	109.16 ±18.44	**162.12 ±41.93**	99.7 ±45.62	44.72 ±12.48	58.24 ±18.28	62.47 ±23.59	65.68 ±26.9	103.87 ±8.52	52.31 ±11.22	50.4 ±6.22
PM_{10}	F=158.176, p<0.000									
I/O ratio	**1.06 ±0.15**	0.54 ±0.11	0.81 ±0.29	0.61 ±0.14	0.76 ±0.23	1.03 ±0.34	0.99 ±0.24	1.07 ±0.12	1.02 ±0.22	1.39 ±0.34
	KW=397.283, p<0.000									
CO mg/ m^3		**1.03 ±0.73**	0.84 ±0.65	0.57 ±0.5	0.14 ±0.35		1±0	0.61 ±0.78	0.14 ±0.35	
	KW=364.56, p<0.000									
CO_2	1470.14 ±181.71	1537.75 ±101.32	1180.69 ±320.02	**6177.41 ±7650.61**	1113.83 ±278.35	822.34 ±90.67	958.19 ±77.05	1395.95 ±176.82	1191.94 ±331.08	873.98 ±137.54
	KW=361.477, p<0.000									
T(C°)	**24.27 ±0.97**	21.74 ±2.01	23.1 ±0.84	23.48 ±1.51	22.01 ±0.63	23.39 ±1.51	22.77 ±0.8	22.89 ±0.76	21.64 ±1.19	22.87 ±2.42
	F=27.876, p<0.000									
RH(%)	46.61 ±3.38	26.18 ±12.96	28.77 ±6.85	32.87 ±7.39	42.95 ±3.24	35.81 ±2.81	35.96 ±5.01	41.13 ±2.04	**52.25 ±2.74**	48.05 ±7.45
l/s/person	F=141.776, p<0.000									
VR	4.90 ±1.09	4.55 ±0.35	7.94 ±3.34	8.08 ±6.10	9.88 ±7.84	12.65 ±3.08	9.70 ±1.61	5.29 ±0.99	**8.43 ±2.94**	12.03 ±3.35
	K-W=341.21, p<0.000									

Table 5 presents distribution of children exposed to indoor air PM_{10}, CO_2, relative humidity, temperature, ventilation rate by school. Analyzing distribution of the children exposed to $CO_2 \geq 1000$ ppm, statistically significant difference is proven among schools, meaning that the least number of pupils exposed to CO2 above 1000 ppm attends School No. 6 (0%), and School N^o 10 (24.4%), (p<0.0001). Attending classrooms with inappropriate indicators of the thermal comfort zone (T C° 18-23, RH 30-75 % and occupancy rate >2.2m^2/pupil) is with the lowest statistical significance for Schools No. 6, 7,9,10 (p<0.0001). The least number of pupils exposed to RH above 40% attends Schools N^o 5&9, and Schools N^o 8 and 10 (p<0.0001). Children attending School N^o 1 are mostly exposed to indoor air temperature that is not in compliance with the thermal comfort standards (63.6%), with high statistical significance(p<0.0001). Among schools, a statistically significant

difference is proved for the distribution of children exposed to IAQ PM_{10} concentration ($p<0.0001$). School 4 has significantly higher frequency of measured values IAQ PM_{10} below 50 μg/m^3. On the other hand, children mostly exposed to PM_{10} mean values above 50 μg/m^3 attend Schools No. 1,2,3 and 8 ($p<0.0001$).

Table 5. *Distribution of children exposed to IAQ PM_{10}, PM10 I/O Ratio, CO_2 concentration, relative humidity, indoor air temperature, ventilation rate by school*

School No.	1	2	3	4	5	6	7	8	9	l0
Carbon dioxide (ppm)										
CO_2≥1000	99	68	54	30	62	0	22	76	44	20
%	100.0	100.0	70.1	49.2	79.5	0.0	41.5	100.0	68.8	24.4
sign	$\chi2=359.539$, $p<0.0001$									
Comfort zone (C° 18-23, RH 30-75% & occupancy > 2.2m^2/pupil)										
Beyond comfort Zone	99	35	77	25	62	18	12	36	0	13
%	100.0	51.5	100.0	41.0	79.5	23.4	22.6	47.4	0.0	15.9
sign	$\chi2=345.06$, $p<0.0001$									
Relative humidity										
RH<40%	0	68	77	41	0	77	41	14	0	13
%	0.0	100.0	100.0	67.2	0.0	100.0	77.4	18.4	0.0	15.9
$\chi2=552.86$, $p<0.0001$										
Indoor air temperature										
T(C°) <18-23>	63	16	31	15	0	18	12	18	0	13
%	63.6	23.5	40.3	24.6	0.0	23.4	22.6	23.7	0.0	15.9
$\chi2=138.63$, $p<0.0001$										
Indoor IAQ PM10 > 50 μg/m^3										
PM_{10} >50	99	68	77	20	47	59	36	76	27	51
%	100.0	100.0	100.0	32.8	60.3	76.6	67.9	100.0	42.2	62.2
sign	$\chi2=225.91$, $p<0.0001$									
Ventilation rate (L/s per person)										
	99	68	54	30	62	0	10	76	18	20
%	100.0	100.0	70.1	49.2	79.5	0.0	18.9	100.0	28.1	24.4
sign	$\chi2=402.26$, $p<0.0001$									
PM_{10} Indoor /Outdoor RATIO > 1										
	61	0	23	0	16	24	12	44	18	68
%	61.6	0.0	29.9	0.0	20.5	31.2	22.6	57.9	28.1	82.9
sign	$\chi2=356.71$, $p<0.0001$									

All pupils attending Schools No. 1,2 and 8 were exposed to ventilation rate below 8l /s per person. The least number of students (<30%) exposed to badly ventilated classrooms attended Schools N° 6,7,9 and 10, with high

statistical significance ($p<0.0001$). PM_{10} I/O Ratio >1 is a sign of predominant indoor source of particulate matter. Majority of involved students in Schools N° 1and 8. were exposed to PM_{10} from an indoor source, rather than from the influx of outdoor air, although both schools are surrounded with bussy streets.

As Table 6 shows (Spearman's nonparametric correlations), statistically significant correlation exists between "cough ever" and "day/night cough in autumn/winter seasons" and high indoor PM_{10}, and PM_{10} Indoor/Outdoor ratio, meaning that "cough ever" is more frequent when IAQ PM_{10} exceeds the outdoor concentration ($p<0.001$), and with PM_{10} Indoor/Outdoor ratio >1.0 ($p<0.017$). The following correlations are also explained in Table 6: "Day/night cough in autumn/winter seasons" significantly correlates with PM_{10} Indoor/Outdoor ratio ($p<0.012$), and also, "Day/night cough in autumn/winter seasons" correlates with ventilation rate ($p<0.035$). Higher classroom indoor air temperature correlates "cough ever" with high statistical significance ($p<0.01$). "Cough with

phlegm" correlates strongly with high levels of classroom indoor air temperature ($p<0.038$), relative humidity ($p<0.025$), PM_{10} ($p<0.001$), as well as with low ventilation rate ($p<0.050$). There is no statistical significance in correlating "morning cough in autumn/winter" with measured values of classroom indoor air temperature, relative humidity, ventilation rate and indoor PM_{10}. Statistically significant correlation exists between "wheezing ever" and elevated classroom indoor air temperature ($p<0.026$), and PM_{10} concentration ($p<0.017$). "Wheezing after exercise" is strongly correlated to PM_{10} concentration 50-80 $\mu g/m^3$ ($p<0.042$), while "dry cough in last 12 months" is in statistically significant correlation with elevated values of PM_{10} ($p<0.012$), taken as a continuous feature. "Wheeze in last 12 months" correlates with higher values of PM_{10} concentration ($p<0.019$).

Table 6. *Spearman's nonparametric correlations*

IAQ		C°	RH	PM_{10} continuous	I/O RATIO	PM_{10} interval	VR	VR interval <8l/s>
Cough ever	R	0.096**	-0.003	0.144**	0.089*	-0.035	0.037	-0.049
	Sig.p	0.01	0.93	0.001	0.017	0.346	0.323	0.194
	N	717	717	717	717	717	717	717
Morning cough	R	0.039	-0.049	-0.004	0.047	-0.011	0.011	0.019
	Sig.p	0.299	0.193	0.91	0.207	0.771	0.762	0.614
	N	716	716	716	716	716	716	716
Day/night cough	R	0.033	-0.058	0.034	0.094*	-0.022	0.079*	-0.042
	Sig.p	0.378	0.118	0.356	0.012	0.555	0.035	0.259
	N	719	719	719	719	719	719	719
Cough with phlegm	R	0.078*	0.084*	0.149**	0.057	-0.001	0.016	-0.073*
	Sig.p	0.038	0.025	0.001	0.124	0.98	0.666	0.050
	N	717	717	717	717	717	717	717
Wheeze ever	R	0.083*	-0.035	.089*	-0.021	-0.003	-0.035	0.046
	Sig.p	0.026	0.348	0.017	0.582	0.945	0.354	0.22
	N	719	719	719	719	719	719	719
Wheeze after exercise	R	0.051	-0.043	0.026	-0.019	-0.076*	-0.018	-0.022
	Sig.p	0.172	0.25	0.492	0.619	0.042	0.624	0.563
	N	722	722	722	722	722	722	722
Wheeze in last 12 mon.	R	0.050	0.063	0.087*	0.016	0.05	0.003	-0.052
	Sig.p	0.183	0.089	0.019	0.674	0.175	0.926	0.164
	N	724	724	724	724	724	724	724
Woken by wheeze in last 12 m	R	0.049	-0.026	0.066	0.005	-0.018	0.007	-0.013
	Sig.p	0.191	0.480	0.077	0.896	0.633	0.852	0.719
	N	720	720	720	720	720	720	720
Continuous Cough > 3 months	R	0.050	0.063	0.016	0.017	0.003	-0.036	-0.037
	Sig.p	0.183	0.089	0.674	0.640	0.926	0.336	0.324
	N	724	724	724	724	724	711	711
Dry cough at night in last12 m	R	0.030	0.003	0.112*	-0.044	-0.045	-0.052	-0.068
	Sig.p	0.425	0.946	0.012	0.246	0.228	0.164	0.057
	N	711	711	711	711	711	724	724

CONCLUSIONS

From the above developed analyses of measured indoor air quality indicators and parameters of indoor thermal comfort, we can conlude the folowing:

1. High indoor temperature correlates with „cough / wheezing ever", as well as with „cough with phlegm".
2. Higher PM_{10} concentration also correlates with „cough /wheezing ever", as well as with „cough with phlegm".

3. PM_{10} Indoor/Outdoor ratio >1 correlates with „cough ever“, as well as with „cough day and night in automn/winter season“.
4. Unsuitable thermal comfort parameters correlate with „cough ever“.
5. Low ventilation rate values correlate with „day and night cough in automn/winter“ and with „cough with phlegm“
6. High relative humidity (%) correlates with „cough with phlegm“.

REFERENCES

1. Almeida, S.M., Canha, N., Silva, A., Freitas, M.C., Pegas, P., Alves, C., Evtyugina, M.,Pio,C.A., 2010. Children exposure to air particulate matter in indoor of Lisbon primary schools. Atmospheric Environment, 45, 7594-7599.
2. Alves C., Nunes T., Silva J., Duarte M., 2013. Comfort Parameters and Particulate Matter (PM_{10} and $PM_{2.5}$) in School Classrooms and Outdoor Air, Aerosol and Air Quality Research, 13, 1521–1535.
3. Annesi-Maesano, I., Hulin, M., Lavaud, F., Raherison,C., Kopferschmitt, C., de Blay F., Charpin,D.A., Caillaud, D., 2012. Poor air quality in classrooms related to asthma and rhinitis in primary schoolchildren of the French 6 Cities Study; Thorax, 67, 682-688.
4. ASHRAE 62-2007, 2007. “Ventilation for acceptable indoor air quality”, Definitions
5. ASHRAE 62.1-2010, 2010. Ventilation for Acceptable Indoor Air Quality
6. Bako-Biro, Z., Clements-Croome, D.J., Kochhar, N., Awbi, H.B. and Williams, M.J. (2011); Ventilation rates in schools and pupils’ performance. Building and Environment, 48, 215-223.
7. Bako-Biro, Z., Wargocki, P., Weschler, C.J., and, Fanger, P.O. 2004, Effects of pollution from personal computers on perceived air quality, SBS symptoms and productivity in offices; Indoor Air, 14, 178-187.
8. Chatzidiakou, L., Mumovic, D., Dockrell, J.; The Effects of Thermal Conditions and Indoor Air Quality on Health, Comfort and Cognitive Performance of Students; Publ. The Bartlett, UCL Faculty of the Built Environment, London, 2014. ISBN 978-0-9930137
9. Chatzidiakou, L., Mumovic, D., Summerfield, A.J. 2012. What do we know about Indoor Air Quality in School Classrooms? A critical review of the literature, Intelligent Buildings International, 4(4), 228-259.
10. Daisey J.M., Angell W.J., and Apte M.G., 2003. “Indoor air quality, ventilation and health symptoms in schools: an analysis of existing information”, Indoor Air, 13, 53–64.
11. EN ISO 15251:2007; Indoor environmental input parameters for design and assessment of energy performance of buildings- addressing indoor air quality, thermal environment, lighting and acoustics
12. Eurostat, “School enrolment and levels of education,” 2011.
13. Mendell M.J. and Heath G.A., 2005. “Do indoor pollutants and thermal conditions in schools influence student performance? A critical review of the literature,” Indoor Air, 15, 27–52.
14. Pegas, P.N, Evtyugina, M.G., Alves, C.A., Nunes,T., Cerqueira,M., Franchi, M., et al, 2010. Outdoor/Indoor air quality in primary schools in Lisbon: a preliminary study. Quı´mica Nova, 33, 1145–1149.
15. Salleh N.M., Kamaruzzaman S.N., Mahbob N. S., 2011. Indoor Air Quality at School: Ventilation Rates and its impact towards Children – A Review. 2011. 2nd International Conference on Environmental Science and Technology, IPCBEE Vol. 6, 2011. IACSIT Press, Singapore, 2011.
16. Wall, K., Dockrell, J., and Peacey, N. 2008. Primary Schools: The Built Environment. Research Briefing 6-1, Technical Report, 2008.
17. Wargocki P., and Wyon, D.P., 2013. Providing better thermal and air quality conditions in school classrooms would be cost-effective, Building and Environment, 59, 581–589.
18. World Health Organization (WHO), 2010. Guidelines for indoor air quality – selected pollutants. Denmark, ISBN 978 92 890 0213 4.

7. OCCUPATIONAL EXPOSURE

7.1 SELECTION OF RESPIRATORY PROTECTION FOR BIOAEROSOLS - APPLICATION OF CONTROL BANDING

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ABSTRACT

The Canadian Standards Association (CSA) undertakes creation and maintenance of a standard for "Selection, Use and Care" of Respirators first issued in 1982, last updated in 2011, which provides a best practice in its subject area for use in Canada. While following conventional guidance for respirator selection for materials with identified exposure limits, the 2011 edition was the first standard in the world to propose a control banding method for selecting respirators for protection from bioaerosols. This augments existing methods of advice on respirator selection based on expert opinion or calculation.

The method is used after completion of a comprehensive risk assessment by a qualified individual, and employs control banding to recommend a level of respiratory protection based on semi-quantitative input information about the nature of the hazard, the process generating the aerosol and the control measures in place. Separate criteria for healthcare facilities and general workplaces addressed, and the hazard, generation rate and control measure inputs are each assessed on a four-level scale. The inputs are combined through a simple algorithm to provide a recommended level of respiratory protection on a five-point scale, which covers a range of respirator types. A simple protocol and diagrammatic method for executing the method have been created. The rating criteria and process have been designed to match existing guidance as far as possible and also gaps in current guidance are filled.

Selection of respiratory protection for airborne chemical hazards follows well-established methods that rely on measuring airborne concentrations in the exposure environment (usually a workplace): these data are combined with established exposure limits for respective chemicals to determine a hazard ratio. Combination of this information with set respiratory protective equipment protection factors drives selection of the appropriate respirator systems for individual protection.

For airborne biological materials, there are in general no exposure limits and exposure measurement is not straightforward, so this direct method is normally not applied. The risk posed by infectious pathogens where very small numbers of particles may cause disease also means that there may not be a linear exposure/response relationship for individuals.

This means that historically often "expert opinion" provides guidelines to determine the need for and selection of respiratory protection equipment for bioaerosols. Organisations with expertise and authority in workplace environments and regulation issue guidance on protective equipment based on expert input. Advantages are that sources are authoritative and well recognised, but disadvantages are limitation to specific circumstances, and sometimes there are delays for emerging threats, differences between sources or inconsistencies with occupational hygiene principles.

As an alternative, a fully quantitative assessment of exposure situations and protection options potentially has broad application: for an infectious pathogen this method determines a "probability of infection". It supports wide range of scenarios and can be justified by measurable inputs. However, the concept of "probability of infection" can raise social issues, and the measured data needed as inputs may be difficult to obtain or initially unavailable in the case of an emerging disease.

As a new approach, use of semi-quantitative assessment of the factors involved in bioaerosol exposure and their combination through an algorithm to recommend an appropriate protection level has been explored, and a form of this technique is adopted into the current (2011) version of the Canadian Standard for "Selection, Use and Care of Respirators" (CSA Z94.4-11, available from Canadian Standards Association). This is a version of "control banding" which is currently applied for assessing chemical exposure in some circumstances. In the standard, this method is provided for use by qualified individuals in the absence of established guidance: advantages are that it is relatively simple, but recognised disadvantages are that it relies on judgement to asses some inputs and may lead to over-simplification or wrong assumptions.

The method requires a risk assessment by a qualified person and then a semi-quantitative assessment of three factors in the exposure environment which can contribute to exposure resulting in a physiological response from an exposed individual. Each is assessed on a four-level scale. For each level on the scale, a numerical value is assigned for use in calculation. The values used were determined so that the output for multiple example cases matched existing guidance.

The factors used in the assessment are:

- Hazard posed by the bioaerosol – the scale applied in the standard is the US National Institutes of Health "Guidelines for Research Involving Recombinant DNA Molecules" (2013), with assessment as appropriate whether the bioaerosol could be infectious by the airborne route;
- Controls in place – effective ventilation levels: there are two scales for this: one for healthcare facilities, one for general workplaces reflecting the general higher level of ventilation control in healthcare facilities;
- Generation rate of the bioaerosol – gauged according to workplace activities and tasks; in healthcare this includes patient actions such as coughing and sneezing.

A seven-step process (Table 1) described in the standard (CSA Z94.4-11, 2011) gives guidance in a series of necessary assessments to provide a recommendation on protection levels and associated respiratory protective equipment – according to the nature of the bioaerosol and the exposure environment.

Table 1. *Steps in the Selection Guidance*

Step	Activity
1	Identify the bioaerosol (known or suspected)
2	Confirm that a risk of transmission of disease, infection, or adverse health effects is produced from inhalation of the bioaerosol
3	Select applicable control banding wheel: health care facilities or general workplace environments
4	Determine the bioaerosol risk group (R1, R2, R3, or R4) using Table 2 below
5	Determine the generation rate (G1, G2, G3, or G4) using Table 3 below
6	Determine the control level (C1, C2, C3, or C4 using Table 4 below
7	Using the calculation and Table 5 or the selection wheel, identify the number and colour of the segment selected at the intersection of the items identified in Steps 4 to 6 This corresponds to the range of options in the hierarchy of respiratory protection. The respirator shall be selected based on the level of protection identified.

Table 2. *Identification of Risk Group (R1 to R4)*

Rank	**Effect**	(R)
R1	Agents that are not associated with disease or serious adverse health effects in healthy adult humans	1
R2	Agents that are associated with human disease or adverse health effect which is rarely serious and for which preventive or therapeutic interventions are often available	2
R3	Agents that are associated with serious or lethal human disease or adverse health effect for which preventive or therapeutic interventions may be available (high individual risk but low community risk)	3
R4	Agents that are likely to cause serious or lethal human disease or adverse health effect for which preventive or therapeutic interventions are not usually available (high individual risk and high community risk)	4

US National Institutes of Health "Guidelines for Research Involving Recombinant DNA Molecules" (March 2013)

Table 3. *Identification of Generation Rates (G1 to G4)*

Rank	**Qualitative Example**	**Factor Used (G)**
Healthcare		
G1	Patient not coughing or sneezing	1

G2	Patient coughing or sneezing with mouth covered	3
G3	Patient coughing or sneezing with mouth uncovered	5
G4	Aerosol generating procedure	12
General Workplace		
G1	Low - Vacuuming with a HEPA filter	1
G2	Medium - Soaking then shovelling pigeon droppings	2
G3	High – Misting then shovelling pigeon droppings	3
G4	Very High – Dry Sweeping pigeon droppings	6

Table 4. *Identification of Control Rankings*

Level	ACH	Qualitative Example	Factor Used (C)	Guidance
Healthcare				
C1	<3	Storage Area	3	Adapted from Canadian Standard Z317.2
C2	3-6	Patient Room/Corridor	6	
C3	6-12	Autopsy	12	
C4	12-25	Surgery	25	
General Workplace				
C1	<1	Indoor/Poor Ventilation	1	Quebec Occupational Health and Safety Regulation 2011
C2	1-4	Indoor Natural Ventilation	2.5	
C3	4-6	Indoor Mechanical Ventilation/Outdoor low wind	4	
C4	>6	Outdoor moderate wind	6	

The algorithm applied calculates a sum which is then translated into a protection level in Table 5:

Sum = R + G/C

Table 5. *Calculation Sums, Protection Levels and Respiratory Protection Options*

Sum	Protection Level	Minimum Air Purifying Options	Minimum Atmosphere-Supplying Options
Sum <1.5	0	No Respiratory Protection Required	
1.5 ≤ Sum < 4.5	1	Negative Pressure Air-Purifying, half mask or filtering face-piece	No Atmosphere-Supplying options
4.5 ≤ Sum < 5.5	2	Loose-fitting PAPR or Tight-Fitting PAPR without SWPF study	Loose-fitting Air-Line or Tight-Fitting Air-Line without SWPF study
5.5 ≤ Sum < 6.5	3	Half-Facepiece PAPR Full-Facepiece Negative Pressure	Half-Facepiece Air-Line Pressure Demand or Continuous Flow
Sum ≥6.5	4	Loose-fitting PAPR or Tight-Fitting PAPR with SWPF study	Loose-fitting Air-Line or Tight-Fitting Air-Line with SWPF study

PAPR = Powered air-purifying respirator; SWPF = Simulated workplace protection factor

For user purposes, the diagrammatic layout in Figures 1 and 2 provide a straightforward method for executing the assessment, and these are represented in the standard (CSA Z94.4-11, 2011).

As an example of use of the model following the steps above:

"A registered nurse is attending a patient diagnosed with pulmonary *Mycobacterium Tuberculosis*. The patient has a productive cough and is currently in airborne isolation in a negative pressure room. The nurse is changing the patient's abdominal dressing".

1 Identify bioaerosol: *Mycobacterium Tuberculosis*

2 Confirm transmission: Confirmed (Tuberculosis)

3	Select Control Banding wheel:	Healthcare
4	Risk group:	R3: Tuberculosis (Factor = 3)
5	Generation Rate:	G3: Patient coughing or sneezing with mouth uncovered (5)
6	Control level:	C3: 6-12 ACH (negative pressure room) (Factor = 12)
7	Identify segment:	R3 G3 C3 = Green 1 (Sum = 3+5/12 = 3.4, so 1.5≤Sum< 4.5)

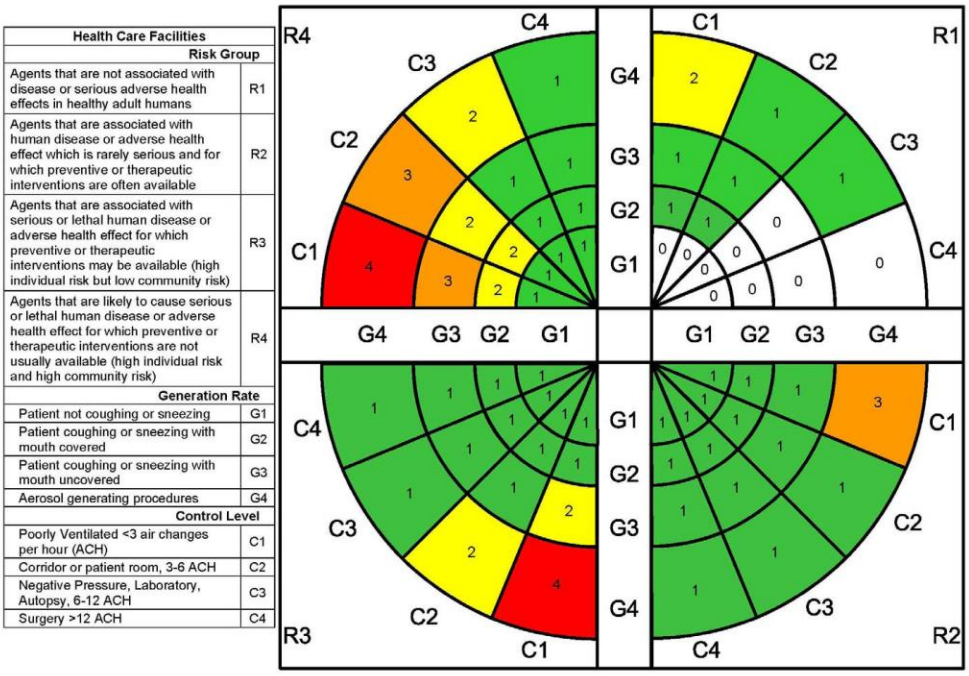

Figure 1. *Control Banding Wheel for Healthcare facilities.*

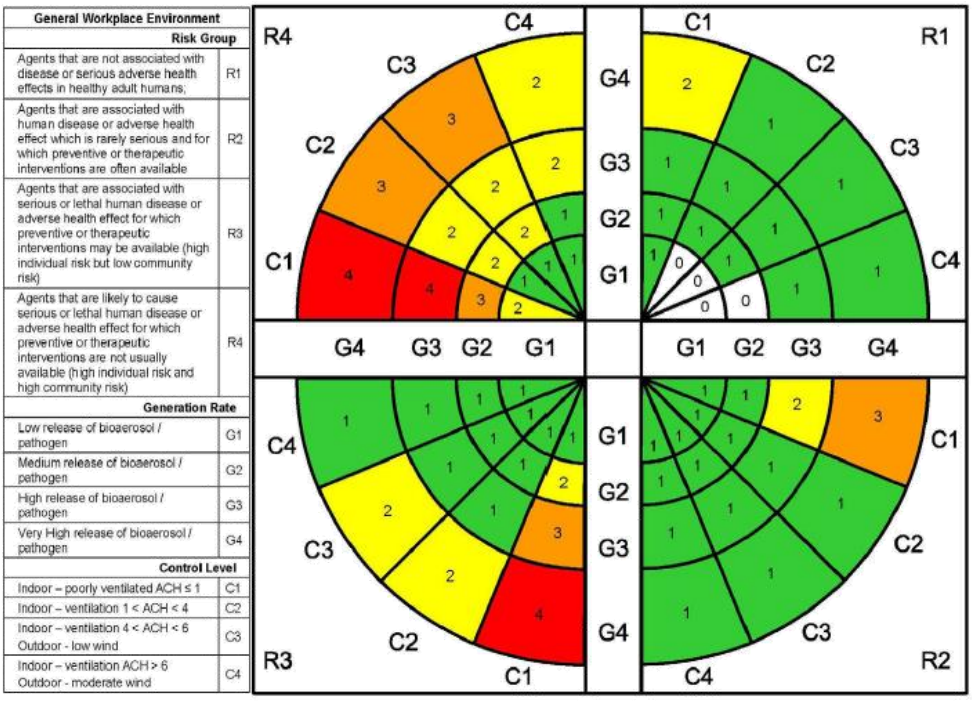

Figure 2. *Control Banding Wheel for General Workplaces*

Minimum option is a Negative Pressure Air-Purifying, half mask or filtering face-piece.

Guidance from the United States Occupational Health and Safety Agency recommends a N95-type filtering facepiece respirator for tuberculosis in healthcare environments, with the option for higher level protection if warranted. This is matches the output of this control banding method, and it is noted that a change in generation rate would correspond with a higher level of protection.

REFERENCES

1. Canadian Standards Association-CSA , 2011. Selection, Use and Care of Respirators, Canadian Standard Z94.4-11.
2. McCullough, N., Brosseau L., 1999., Selecting Respirators for Control of Worker Exposure to Infectious Aerosols, Infection Control and Hospital Epidemiology, 20, 136-144.
3. Nelson D, Chiusano S, Bracker A, et al, 2007. Guidance for conducting control banding analyses. AIHA Guideline 9—2007, AEAG07–726. Fairfax, VA: American Industrial Hygiene Association
4. US National Institutes of Health, 2013. Guidelines for Research Involving Recombinant DNA Molecules

7.2 DUST LEVELS AND LUNG FUNCTION DECLINE IN THE COTTON INDUSTRY IN PAKISTAN

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ABSTRACT

We report about a cross-sectional study in the cotton industry of Faisalabad, Pakistan. We selected 47 cotton mills based on a stratified sampling strategy to cover all types and sizes: 5 spinning and 16 large compact mills and 26 small/medium weaving plants (power looms). Occupational safety and hygiene measures were documented via a pre-checked observational survey questionnaire. Suspended dust and ultrafine particles were measured. Suspended dust was collected on filters to analyze respiratory exposure to endotoxin and several pesticides. Dust exposures were generally high and highest in power looms, while endotoxin was highest in the spinning mills. Poor working conditions were documented throughout the sector.

Symptoms (800 workers) and poor lung function (ca. 150 investigated) were most pronounced among power loom workers. These also displayed signs of cytotoxicity in buccal cells (100 slides) and with increasing years of occupation also a higher frequency of mutagenic damage of buccal cells.

INTRODUCTION

Un-hygienic conditions and lack of protective measures (masks, ear plugs, first aid box etc.) contribute to eye-problems, cough, headache and other health problems in weaving industries. Various mechanical and chemical processes are employed in textile industries, resulting in different acute and chronic environmental and health problems (Forstater, 2009; Watto and Mugera, 2014). For nearly 300 years, work in textile industry has been recognized as hazardous (Oldenburg et al, 2007; Shackter, 2011; Schilling, 1950; Kennedy et al, 1987; Rylander et al, 1985). Continuous exposure to cotton dust is associated with progressive impairment of pulmonary function and with respiratory tract symptoms. By far the most important respiratory disease in that industry is byssinosis (Basinas et al, 2012; Lai and Christiani, 2013; Nafees et al, 2013; Memon et al, 2008).

We therefore initiated a cross-sectional study in the cotton industry of Faisalabad, Pakistan. Here we report about the dust levels observed in various types of cotton factories and about the respiratory health of the workers. The cotton mills were selected based on a stratified sampling strategy with the aim to cover all types and sizes. In the end we accessed 47 cotton mills: 5 spinning and 16 large compact mills and 26 small/medium weaving plants (power looms). Ethical Approval was provided by the Ethical Review Committee, HSA, Ministry of National Health Services, Regulation & Coordination, Islamabad, Pakistan. Factory owners approved of the visits and the examined workers gave their informed consent. The examinations were carried out in February to April 2014.

METHODS

Eight-hundred male workers were approached at random and were asked to fill a short questionnaire containing questions on occupational history and current symptoms. A sub-sample of these workers (in total 109 cotton workers, 51 from power looms, 58 from large factories) were investigated by spirometry (EasyOne spirometer, NDD) in a cross-sectional study. In addition 52 workers not occupied in the cotton industry were also examined as controls.

Suspended fine dust was measured in a representative sample of factories with two instruments. The Grimm Portable Aerosol Spectrometer 1108 (Grimm Aerosol Technik, Germany) counts airborne particles in 16 size channels using laser scatter technology. From the size-dependent particle number the particle mass in standardised size ranges (environmental standards: PM2.5 and PM10, occupational standards: inhalable, thoracic and alveolic) are calculated. The MiniDiSC (matter aerosol, Switzerland) is a diffusion size classifier that can determine 3 quantities simultaneously with a high time resolution (1 second): particle number concentration, average particle diameter and lung-deposited surface area. The instrument is based on charging and current detection. Endotoxin levels were measured in suspended dust (Paba et al, 2013; Duquenne et al, 2013). Suspended dust was collected with an Aircheck Sampler Model 224-52 (SKC Inc., USA) with an SKC IOM

sampler head and a flow rate of 2 litres/minute. Dust was collected on glass-fibre filters (25 mm diameter, pore size 1 µm). Endotoxin on filters were determined according to the European Guideline EN 14031 using the chromogen-kinetic LAL (Limulus Amoebocyte Lysate) assay (Iwanaga, 2007).

Symptom rates were compared by factory type and factory size by chi² test. Logistic regression was used to estimate the odds ratios of developing symptoms by years of occupation in large factories or in power looms. Lung function values were modeled by general linear regression models controlling for age, weight and height. The main independent variables of interest were smoking and exposure defined either as type of factory or duration of occupation. As an alternative approach "poor lung-function" (obstructive and restrictive lung disease respectively) defined according to GLI equations was examined by logistic regression. Data were entered into an excel sheet and statistical analysis was performed using STATA SE Vers. 13.1 (StataCorp, 4905 Lakeway Drive, College Station, Texas 77845 USA).

RESULTS

Dust levels were especially high in small weaving factories (so-called power looms) where mainly unskilled workers (starting to work at an early age) are employed for long (12 hour) working shifts (Table 1).

Table 1. *Dust levels in the various types of factories*

Type (1)	Size fraction (2)	Mean	Std.Dev.	Min	Max
Processing (11; 4.4)					
	Inhalable	907.46	706.45	188.89	2108.27
	Thoracic	678.25	588.10	129.41	1699.03
	Alveolic	287.68	237.71	63.38	724.85
Spinning (11; 6.5)					
	Inhalable	2076.18	1500.29	582.20	5049.84
	Thoracic	1382.57	1098.65	427.19	4971.54
	Alveolic	653.57	806.32	227.31	3855.89
Weaving (29; 18.75)					
	Inhalable	4621.37	2468.76	307.28	9428.27
	Thoracic	4147.22	2421.90	183.90	8717.48
	Alveolic	2612.70	1792.06	91.61	6049.57

(1) Type of factory (number of plants; total hours of monitoring)

(2) Values in µg/m³

Numbers of ultrafine particles, on the other hand, were highest in large compact factories that comprise all production steps (mean ± standard dev.: 82,000±48,000/cm³), followed by weaving (54,000±21,000) and spinning factories (18,000±12,000). Nevertheless the highest endotoxin concentrations were found in the spinning sections (mean: 1500 EU/m³). The latter is not surprising because the spinning is among the first steps of the production process with the still rather fresh cotton entering the production line. High humidity in the working areas is maintained to keep the cotton threads flexible and easy to handle.

Reported respiratory symptoms were most frequent among weavers (table 2). After controlling for smoking, work duration in years was associated with declines in all spirometric indices studied (FVC, FEV1, FEV1/FVC%, PEF, MMEF; table 3). The declines were significant for most indices among power-loom workers even after controlling for age but not among workers in large compact factories. Risk of obstructive lung disease increased by 8% per year of occupational exposure in power-looms (table 4) when the Global Lungs Initiative (GLI) equations were applied. Workers from power looms performed worse than workers in larger factories but the study lacked the power to disentangle the effects of duration and intensity of exposure.

In addition to the findings reported here we also found generally poor working conditions in all visited factories but the poorest conditions again in power-looms (Khan et al, 2015a; Khan et al, 2015b; Khan et al, 2015c). Compared to manual workers without cotton dust exposure and matched for age and socio-economic status, workers from power-looms displayed significantly more signs of cytotoxicity in buccal cells. With increasing duration of occupational exposure also signs of mutagenic damage increased.

Table 2. *Symptoms frequencies according to questionnaire responses.*

	Small weaving	**Medium weaving**	**Big weaving**	**Spinning**	**Compact**	**Total** **p-value**
Worker	289	125	110	80	196	800
Symptoms%						
Fever	22.5	24.8	11.8	12.5	6.1	p (chi²)<0.001
Shortness of breath	28.7	22.4	10.9	17.5	5.6	p (chi²)<0.001
Chest tightness	41.5	36.8	32.7	31.2	10.7	p (chi²)<0.001
Dry cough	30.1	36	26.4	31.3	12.2	p (chi²)<0.001
Mucous cough	6.9	4	5.5	8.8	0.5	p (chi²)<0.001

Table 3*. Results of linear regression analysis of lung function parameters: regression coefficient (p-value) after controlling for age, height, weight and weight². Bold: p<0.05*

Factor	**Duration in large factory (yr)**	**Duration in power loom (yr)**	**Cigarettes per day**	**Adjusted R²**
FVC (L)	-0.025 (0.070)	-0.008 (0.326)	**-0.038 (<0.001)**	0.285
FEV1 (L)	-0.022 (0.125)	**-0.017 (0.033)**	**-0.044 (<0.001)**	0.327
FEV1/FVC%	0.000 (0.919)	**-0.003 (0.033)**	**-0.005 (0.003)**	0.165
PEF (L/s)	-0.053 (0.242)	**-0.053 (0.039)**	**-0.127 (<0.001)**	0.186
FEF25 (L/s)	-0.062 (0.183)	-0.048 (0.070)	**-0.119 (<0.001)**	0.16
MMEF (L/s)	-0.033 (0.263)	**-0.036 (0.029)**	**-0.063 (0.004)**	0.172
FEF50 (L/s)	-0.020 (0.576)	-0.028 (0.186)	**-0.082 (0.003)**	0.107
FEF75 (L/s)	-0.017 (0.299)	**-0.022 (0.017)**	**-0.026 (0.029)**	0.206

Table 4. *Results of logistic regression models of GLI (Global Lungs Initiative) assignment to possible pathological categories obstruction and restriction: Odds ratio (95% confidence interval).* ***Bold****: p<0.05*

Factor	Obstruction	Restriction
Duration in large factory (yr)	1.068 (0.909 to 1.253)	**1.110 (1.001 to 1.230)**
Duration in power loom (yr)	**1.086 (1.000 to 1.180)**	1.062 (0.999 to 1.129)
Cigarettes per day	1.097 (0.995 to 1.211)	1.064 (0.987 to 1.146)
Nagelkerke's R²	0.208	0.146

CONCLUSION

Occupational health and safety are still burning issues in developing countries. Poor industrial hygiene and poor health could be documented in the cotton industry, which is an important sector of the Pakistani economy. While consumer awareness campaigns like the "Clean Clothes" Campaign have helped to improve the working conditions in many large plants that directly produce for the Western markets no such improvements are visible

in small family-size factories like so-called power-looms. These power-looms employ poorly educated workers that start work early and without any formal education. They work 12-hour shifts (day- and night shifts) often (depending on production volume) 7 days a week. Poor working conditions increase the risks of injuries, noise-induced hearing loss, and last, but not least, respiratory disease.

It is difficult to conceive a strategy to improve the working conditions in these very small enterprises. They are the back-bone of the local industry and due to their shear number give work to the majority of the local people. The financial resources of these enterprises are low and their profits are marginal. Expensive technical fixes are therefore not feasible. Educating the workers about personal protection and also generally raising their education seems the only reasonable approach though promising success in the long term only.

We want to express our thanks to the workers participating in the study and the factory owners that enabled us to approach the workers.

REFERENCES

1. Basinas I., Schlunssen V., Heederik D., Sigsgaard T., Smit L.A., Samadi S., et al, 2012. Sensitisation to common allergens and respiratory symptoms in endotoxin exposed workers: a pooled analysis. Occup Environ Med 69 (2), 99-106.
2. Duquenne P., Marchand G., Duchaine C., 2013. Measurement of endotoxins in bioaerosols at workplace: a critical review of literature and a standardization issue. Ann Occup Hyg 57, 137-72.
3. Forstater M., 2009. Implications of the global financial and economic crisis on the textile and clothing sector. International Labour Organization. International Labour Office, Geneva.
4. Iwanaga S., 2007. Biochemical principle of Limulus test for detecting bacterial endotoxins. Proc Jpn Acad Ser B Phys Biol Sci 83 (4), 110–9.
5. Kennedy S.M., Christiani D.C., Eisen E.A., Wegman D.H., Greaves I.A., 1987. Olenchock SA, et al. Cotton dust and endotoxin exposure-response relationships in cotton textile workers. Am Rev Respir Dis135 (1), 194-200.
6. Khan A.W., Kundi M., Moshammer H., 2015. Diminished pulmonary function in long-term workers exposed to cotton dust determined in a cross-sectional study in small Pakistani enterprises. Occup Environ Med. 2015 Aug 11. pii: oemed-2015-102902. [Epub ahead of print]
7. Khan A.W., Nersesyan A., Knasmüller S., Moshammer H., Kundi M., 2015. Nuclear anomalies in exfoliated buccal cells in Pakistani cotton weavers. Mutagenesis. 30 (5) 613-9.
8. Khan, A.W., Moshammer, H.M., Kundi, M., 2015. Industrial hygiene, occupational safety and respiratory symptoms in the Pakistani cotton industry. BMJ Open 5 (4), e007266
9. Lai P.S., Christiani D.C., 2013. Long-term respiratory health effects in textile workers. Curr Opin Pulm Med 19 (2),152-7.
10. Memon I., Panhwar A., Rohra D.K., Azam S.I., Khan N., 2008. Prevalence of byssinosis in spinning and textile workers of Karachi, Pakistan. Arch Environ Occup Health 63 (3),137-42.
11. Nafees A.A., Fatmi Z., Kadir M.M., Sathiakumar N., 2013. Pattern and predictors for respiratory illnesses and symptoms and lung function among textile workers in Karachi, Pakistan. Occup Environ Med. 70 (2), 99-107.
12. Oldenburg M., Latza U., Baur X., 2007. Exposure-response relationship between endotoxin exposure and lung function impairment in cotton textile workers. Int Arch Occup Environ Health 80 (5), 388-395.
13. Paba E., Tranfo G., Corsetti F., Marcelloni A.M., Iavicoli S., 2013. Indoor exposure to airborne endotoxin: a review of the literature on sampling and analysis methods. Ind Health 51 (3), 237-55.
14. Rylander R., Haglind P., Lundholm M., 1985. Endotoxin in cotton dust and respiratory function decrement among cotton workers in an experimental cardroom. Am Rev Respir Dis 131 (2), 209-13.
15. Schilling R.S., 1950. Byssinosis in the British cotton textile industry. British Medical Bulletin 7 (1-2), 52-56.
16. Shackter E.N., 2011. Respiratory effects and other disease patterns in the textile industry - Part XIV. International Labor Organization; Geneva, available from: http://www.ilo.org/oshenc/part-xiv/textile-goods-industry/item/891-respiratory-effects-and-other-disease-patterns-in-the-textile-industry.
17. Watto M.A., Mugera A., 2014. Measuring efficiency of cotton cultivation in Pakistan: a restricted production frontier study. J Sci Food Agric. 94 (14) 3038-3045.

7.3 DUST AND COBALT LEVELS IN THE TUNGSTEN INDUSTRY

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ABSTRACT

To better evaluate cancer risk in the tungsten industry a multi-national cohort study was set up. The Austrian part of that cohort consists of approximately 2000 workers having been first employed at or after 1950 in one of the leading European plants of the tungsten industries. In a first step we set out to evaluate the data describing the exposure of the Austrian workers. Industrial hygiene data both from area and personal air sampling for dust, tungsten, and cobalt were examined. These three measures (dating back since 1985) are highly correlated and the ratio of the dust components does not vary by job classification. Concentrations fell over the years and differed by department. Since 2008 highly exposed workers provide urine samples that are analyzed for cobalt. Cobalt in urine is well predicted by concentration in the air.

INTRODUCTION

Cobalt is classified as carcinogenic since the 1970s (IARC, 2006). French (Lasfargues et al, 2004; Moulin et al, 1998; Wild at al, 2000) and Swedish (Hogstedt and Alexandersson, 1987) occupational cohort studies suggest that cobalt increased the risk of lung cancer particularly strongly in combination with tungsten carbide in the hard metal industry. This suspicion will be investigated in an international multicenter cohort study. An Austrian plant participates in the study. The scientific coordination of the Austrian part is done at the Institute of Environmental Health.

Also according to Austrian law (Grenzwerteverordnung, 2011) cobalt is classified as carcinogenic. As a consequence, no health based limit value ("MAK"), but a technical reference concentration (TRK) is specified. The TRK value (as a shift average) is set at 0.5 mg / m³ in the respirable dust in the carbide industry (and in some other unnamed industry sectors). At all other locations a more stringent limit of 0.1 mg / m³ applies. A particular danger of skin absorption and the risk of sensitization are also pointed out in that legal document.

According to the Regulation on health surveillance in the workplace (Gesundheitsüberwachung am Arbeitsplatz, 2014) exposed workers must be tested annually for exposure to cobalt. For the urine test, a limit of 10 µg/l cobalt is defined. In case of its exceedance a closer monitoring (6 months) is mandatory, but no further consequences are stipulated.

In principle, the employer must ensure that the air at the workplace is free of hazardous substances or, if that is not achievable, that the concentrations are kept as low as possible. This should also ensure that the internal exposure of workers, such as indicated by the excretion of harmful substances or their metabolites in urine, remains low. The rationale for assessing the internal exposure is basically twofold: (a) In case of other important exposure pathways (e.g. skin or oral absorption) biomonitoring is the method of choice to control for these. (b) In case of difficulties in monitoring the breathing air (e.g. in case of high spatial and temporal variability of the concentration, limited room for the apparatus to collect air samples) to ensure that the limit has not been exceeded. In both cases, it makes no sense to stipulate a limit in urine that is exceeded when the limit value in the air is kept and no other exposure occurred. If on the other hand stricter limit values for the urine are feasible this would indicate that the limit values in the air (that in the case of carcinogenic substances are based on technical feasibility only) are too high.

With carcinogenic substances an experimental approach with targeted exposure of subjects is ethically problematic. Therefore, to estimate the association between cobalt in the air of the workplace and in post-shift urine samples it is necessary to study routine data, albeit they are not primarily collected for answering research questions, but to verify compliance with legal limits. The data from a large Austrian plant, which have been collected as part of the preparatory work for an international retrospective cohort study, lends itself to this investigation.

METHODS

In a first step, the work histories were collected from all workers who were hired by the plant since 1.1.1950. In addition, the industrial hygiene data of measurements of dust, tungsten, and cobalt were collected. In addition, biomonitoring data of cobalt in urine from exposed workers were obtained from the occupational health department. The following questions had to be answered: (1) Are the routine industrial health (IH) data sufficient to estimate at least the ranking of cumulative exposures among the cohort members? (2) Can the validity of the IH data be supported by the biomonitoring data? (3) What is the relation between cobalt in the air and in urine? (4) Can we estimate temporal trends in exposure so that gaps in IH measurements especially in earlier years can be closed?

The following data were available: Air measurements to dust (n = 130), tungsten (n = 141) and cobalt (n = 147) for the years 1985 to 2012 and urine tests of 253 people (a total of 1166 records) from the years 2008 to 2014.

The evaluation of cobalt measurements in filter samples of the workplace air is hampered by differences in methodology and purpose of measurements. Of the 147 measurements on cobalt 45 were personal and 102 area-related. Two of the measurements were carried out during the night shift, where only maintenance work and no full-scale operations were carried out. Only 134 measurements were carried out over the entire shift, while the rest were significantly shorter (e.g. 1 hour). The shorter measurements took place in the first study years mainly. For 10 measurements the dust fraction is specified as “less than 5 microns”. For the remainder information is missing in this regard. Numerous different reference methods are mentioned. The limit of quantification declined over the years from 0.01 to 0.002 mg / m³. A total of 17 samples were below the respective detection limit.

Values below the detection limit were recoded as "half detection limit". IH data exhibited a markedly skewed distribution and were therefore log-transformed and entered into multiple logistic regression models as dependent variables. Log-Levels of dust, cobalt and tungsten were explained by a linear time trend, by analytical method, and department. “Analytical method” in that case stands for a set of parameters including personal or area-related measurement, type of pump and filters used, analytical instruments to measure the load on the filters, duration of sampling, and night versus day shift. This regression model allowed predicting exposures at other times at each department as well. The point estimates (for the year and department) were then converted back to the linear baseline.

Predicted exposures of cobalt were entered as the explanatory variable for the urine values in a second regression model. This model also included current smoking status and the examination date to control for residual confounding by time trend. It was expected that the regression line should go through the zero point because without external (inhalative) exposure we would not expect any excretion.

In addition, we analyzed the correlation between the 3 IH markers dust, cobalt, and tungsten. We performed linear regressions to see how well cobalt and tungsten exposure is explained by the overall dust exposure and if this association differs between departments.

RESULTS

Under the simplifying assumption of a "steady state", which is valid in case of a constant exposure over a sufficiently long period, the uptake is equal to the excretion. When only inhalation is considered the uptake depends on the concentration in the air, the breathing volume per minute, the duration of working shift (8 hours usually), and the percent retention of the dust in the airways. The dust particles contained in the air we breathe are partially deposited in the airways, partially exhaled, the respective percentage depends on the particle size distribution. The particles deposited in the respiratory tract are transported partly via the mucociliary clearance to the pharynx and swallowed and afterwards partly absorbed in the intestine, but also excreted in the stool. Assuming a concentration of 0.5 mg cobalt/m³ and a ventilation of 10 l/min (typical for light work) a dose of 2400 µg cobalt is inhaled over 8 hours, of which about half, i.e. 1200 µg is absorbed. About half of this is excreted via the bile and to a lesser extent, through the sweat, the remainder via the kidneys. Assuming a daily urine volume of 2 liters leads to a urine concentration of 300 µg/l. The same air-urine association is reported by the German MAK Commission (MAK-Werte Kommission, 1986; MAK-Werte Kommission, 2006). It follows that the Austrian TRK-value is by more than an order of magnitude too high if compliance with the BAT value (in urine) is sought.

Cobalt and tungsten were each highly and significantly correlated with dust. Per mg/m³ of dust cobalt concentration (air) increased by 0.11 mg/m³ (95% CI: 0.1-0.11). The corresponding values for tungsten were 0.21 (0.15-0.27). This ratio did not vary significantly between the departments although for some departments there were not enough data-points for reasonable estimates. Assuming the same dust levels tungsten levels declined over time by 0.06 mg/m³ (0.02-0.11) annually. This was not seen with cobalt. Assuming the same dust levels tungsten values were lower in personal compared to area level samples (0.02 mg/m³ per mg/m³ compared to 0.24; p for interaction = 0.015). Contrary to that cobalt levels were higher in personal samples (0.19 compared to 0.1; p < 0.001).

The logarithmic values of all IH parameters (dust, cobalt, and tungsten) significantly declined over time and differed by department. Table 1 describes the findings for cobalt after controlling for details of analytical procedures. Results for dust and tungsten were similar (data not shown).

Also cobalt concentration in urine declined over time. Cobalt in the air (estimated from the regression model described in table 1 after back-transformation from logarithmic values) was associated with cobalt values in urine. The constant value in that regression model was practically zero and dropping the constant did not virtually alter the other point estimates (table 2).

Table 1. *Results of linear regression: Time trend and differences per department in log(cobalt) concentration levels after controlling for various analytical details. Note that for some departments there are only very few data points rendering the point estimates imprecise.*

Factor		Point estimate	P-value
Trend per year		**-0.046**	**0.023**
Personal sampling		0	(Comparison)
Area level		-0.498	0.225
Department	(Number of measurements)		
Extrude	(19)	0	(Comparison)
Drill, mill, bore 2	(1)	0.729	0.683
Furnace	(1)	-0.706	0.688
Graphite spray plant	(5)	**2.41**	**0.009**
Drill, mill, bore 1	(1)	**4.449**	**0.017**
Powder room	(25)	**1.464**	**0.006**
Press	(19)	0.297	0.595
Refractory metals	(2)	0.169	0.894
Shape	(74)	**1.129**	**0.028**
Constant		**-3.958**	**< 0,001**

Workers with missing information on smoking did not differ significantly from non-smokers in this model. Therefore it was assumed that most of these were non-smokers or at least light smokers only. In an additional regression model they were merged with the non-smokers. The significantly higher cobalt burden in smokers is plausible considering the additional oral exposure via the dust-hand cigarette-mouth path. In that case an interaction between smoking and cobalt in the air would be expected: The higher the occupational exposure the stronger the additional effect of smoking. Indeed in this interaction model no direct effect of smoking per se was found (-1 µg/l, p=0.366). The impact of cobalt in air (per mg/m³) was slightly attenuated in non-smokers (122.2 µg/l, p<0.001) while in smokers the urine concentration (per mg/m³ in the air) increased by an additional amount of 169.6 µg/l, p<0.001).

Even after controlling for cobalt concentrations in the air there were still some differences in urine concentrations between departments. This indicates that the IH data only insufficiently reflect the actual exposure of individual workers leading to residual confounding by workplace.

Table 2. *Results of linear regression: Association between cobalt in urine (µg/l) and in the air (mg/m³) and effect of (current) smoking.*

Factor	Point estimate	P-value
Cobalt in air (mg/m³)	200.08	< 0.001
Non-smoker	0	(Comparison)
Smoker	4.45	< 0.001
Missing information	0.28	0.806
Constant	-0.18	0.855
Cobalt in air (mg/m³)	199.14	< 0.001
Non-smoker	0	(Comparison)
Smoker	4.30	< 0.001
Missing information	0.13	0.869

CONCLUSION

Overall, work histories were collected from 1970 workers. Repeated urine tests were available from 253 of those workers from the years 2008-2014. Air measurements of dust (n = 130), tungsten (n = 141) and cobalt (n = 147) exist for the years 1985 to 2012. For all substances a significant decrease over the years is detectable. The air and urine values of cobalt correlate with each other: One mg/m³ cobalt in the air leads to an excretion of 200 µg/l cobalt in urine. This ratio differs by smoking status.

The available data allow the initial assessment of the inhalation exposure of these workers cohort. The Austrian occupational limit value for cobalt (0.5 mg/m³) is too lenient compared to the limit in urine (10 µg/l). The correlations between the different IH parameters (dust, cobalt, and tungsten) on the one hand are reassuring. On the other hand this finding prevents a separate analysis of the effects of cobalt alone compared to mixed exposures.

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REFERENCES

1. Gesundheitsüberwachung am Arbeitsplatz, 2014. BGBl. II Nr. 27/1997 zuletzt geändert durch BGBl. II Nr. 26/2014.
2. Grenzwerteverordnung, 2011. BGBl. II Nr. 253/2001 zuletzt geändert durch BGBl. II Nr. 429/2011. Anhang I: Stoffliste (MAK-Werte und TRK-Werte).
3. Hogstedt C., Alexandersson R., 1987. Mortality among hard-metal workers in Sweden. Scand J Work Environ Health 13, 177–178.
4. IARC, 2006. Monographs on the Evaluation of Carcinogenic Risks to Humans, Volume 86 Cobalt in Hard Metals and Cobalt Sulfate, Gallium Arsenide, Indium Phosphide and Vanadium Pentoxide. IARC, Lyon.
5. Lasfargues G., Wild P., Moulin J.J., Hammon B., Rosmorduc B., Rondeau du N.C., Lavandier M., Moline J., 1994. Lung cancer mortality in a French cohort of hard-metal workers. Am J Ind Med. 26 (5), 585-595.
6. MAK-Werte Kommission, 1986. Grenzwerte in biologischem Material. Cobalt und Cobaltverbindungen.
7. MAK-Werte Kommission, 2006. Grenzwerte in biologischem Material. Addendum zu Cobalt und Cobaltverbindungen.
8. Moulin J.J., Wild P., Romazini S., Lasfargues G., Peltier A., Bozec C., Deguerry P., Pellet F., Perdrix A. 1998, Lung Cancer Risk in Hard-Metal Workers. American Journal of Epidemiology 148 (3), 241-248.
9. Wild P., Perdrix A., Romazini S., Moulin J., Pellet F., 2000. Lung cancer mortality in a site producing hard metals. Occup Environ Med. 57 (8), 568–573.

8. HEALTH EFFECTS

8.1 BREAST CANCER AND AIR POLLUTION: REVIEW

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ABSTRACT

Breast cancer is the most common cancer type and leading cause of death among women worldwide. Still, only about one third of new cases are attributable to known risk factors, most of which are not easily modifiable for preventive purposes. Breast cancer incidence is higher in industrialized than in developing countries, and higher in urban than rural areas suggesting possible relevance of air pollution. Laboratory animal data and toxicological evidence for a link between number of carcinogens present in air pollution (most consistent for PAHs) and breast cancer is consistent, but lack of epidemiological data has precluded scientific consensus on the role of air pollution on breast cancer risk. In this paper an overview of current epidemiological evidence on the link of exposure to air pollution with breast cancer is given.

INTRODUCTION

Breast cancer is the most common cancer type among women worldwide (Brody et al, 2007). Established risk factors include genetic mutations, family history of breast cancer, late age at first birth, null parity, physical inactivity, high alcohol consumption, and hormone therapy use (Brody et al, 2007). Only about one-third of new cases are attributable to known risk factors, and most are not easily modifiable for prevention efforts (Brody et al, 2007). The relevance of environment was suggested by observations of higher breast cancer incidence in industrialized than in developing countries (Terzano et al, 2010). Furthermore, breast cancer incidence is higher in urban than rural areas (Akinyemiju et al, , 2015; Ranzi et al, 2011) and trends in breast cancer incidence over last 30 years in entire USA correlated well with trends in traffic density and nitrogen oxides (NO_x) emissions (Chen et al, 2012; Wei et al, 2012), all pointing at air pollution as a possible risk factor.

Air pollution is a risk factor for lung cancer (Raaschou-Nielsen et al) and possibly for bladder, liver and brain cancer (Raaschou-Nielsen et al, 2011), making it plausible that at least one of the many carcinogenic constituents in air pollution may affect breast cancer. Polycyclic aromatic hydrocarbons (PAHs), constituents of ambient particles, have been found to cause mammary tumors in laboratory animals (Brody et al, 2007; Mordukhovich et al, 2010), whereas ultrafine ambient particles, which contain PAHs, are able to translocate from the lung to circulatory system, adipose, mammary and other tissues (Secretan et al, 2009). However, many chemicals, such as endocrine disruptors, and mammary gland carcinogens (MGC) identified as potentially harmful in animal studies have not been yet studied in humans (Brody et al, 2007), mainly due to difficulties in assessing human exposure to these hazardous substances, calling for more epidemiological studies (Brody et al, 2007).

Tobacco smoke is the leading cause of lung and other cancers worldwide, containing over 4,000 known carcinogenic substances (International Agency for Research on Cancer, 2012), many of which, including PAHs, are also found in air pollution. Due to similar toxicological properties of tobacco smoke and air pollution, smoking related diseases are typically also linked to air pollution later, strengthening the support for causal relationship for both exposures, as with cardiovascular disease (Pope et al, 2009). The views on the role of tobacco smoke on breast cancer have fluctuated over the last 20 years, from early suggestions that antiestrogenic effects of smoking might protect against breast cancer, to the long lasting consensus that there was no association (International Agency for Research on Cancer, 2012). However, recent, large prospective cohorts studies with 302,865 Norwegian women (2 et al), 79,900 women from American Women's Health Initiative Study (Gaudet et al, 2013), and 73,388 women from American Cancer Society's Cancer Prevention Study II (Luo et al, 2011) and meta-analyses (Gaudet et al, 2013) published since 2011, with high quality data on smoking duration, intensity, windows of exposure (before and after first birth), all show increased risk of breast cancer in active smokers. Furthermore, enhanced risk of breast cancer was related to long duration and high intensity, with especially high risk of breast cancer related to smoking before first childbirth (Bjerkaas et al, 2013; Gaudet et al, 2013). These studies provided powerful evidence base for association between smoking and breast cancer, and strengthen the plausibility of a link between air pollution and breast cancer.

In this paper, a brief review of the current epidemiological evidence on the link between air pollution and breast cancer is given.

METHODOLOGY

The PubMed database was searched for articles in English published in peer-reviewed journals through December 4, 2015 for human studies of breast cancer and outdoor air pollution. Searches included term "breast cancer" in combination with "air pollution", "traffic", vehicle exhaust", "particles", "particulate matter". Reference lists of selected articles were examined for additional articles. We included individual level cohort, case-control studies, cross-sectional studies, on breast cancer incidence, mortality or survival.

RESULTS AND DISCUSSION

We have identified 13 epidemiological studies on air pollution and breast cancer (Bonner et al, 2005; Cambra et al, 2011; Crouse et al, 2010; Garcia et al, 2015; Hu et al, 2013; Huo et al, 2015; Hystad et al, 2015; Lewis-Michl et al, 1996; Liu et al, 2015; Nie et al, 2007; Raaschou-Nielsen et al, 2011; Ranzi et al, 2011; Reding et al, 2015), of which 9 examined association between air pollutants and breast cancer incidence, and of these four were cohort (Garcia et al, 2015; Liu et al, 2015; Raaschou-Nielsen et al, 2011; Reding et al, 2015) and five case-control studies (Bonner et al, 2005; Crouse et al, 2010; Hystad et al, 2015; Lewis-Michl et al, 1996; Nie et al, 2007). Furthermore, of 13 studies, one was cross-sectional ecological study on proximity to industrial facilities and breast cancer mortality (Cambra et al, 2011), and one longitudinal ecological study on proximity to incinerators and breast cancer mortality (Ranzi et al, 2011), and two studies on air pollution and survival after breast cancer (Hu et al, 2013; Huo et al, 2015).

Table 1. *Epidemiological studies on air pollution and breast cancer incidence.*

Author, year,	Design, n, year	Exposure	BC Type	Results/Effect Estimate
Lewis-Michl, 1996 NY, USA	Case-control	Traffic density, 20 years prior to BC	Postmeno (no effect in premeno)	Proximity chemical facilities OR: 1.61 (1.06-2.43). No association with traffic density.
Bonner, 2005 NY, USA	Case-control 1,166/2,105 (1959-1997)	Modeled TSP at birth, menarche, 1st childbirth, and later	Postmeno (no effect in premeno)	OR: 2.42 (0.97-6.09) high: >140 $\mu g/m^3$ vs. low: <84 $\mu g/m^3$ at own birth; none with menarche, 1st childbirth, or later.
Nie, 2007 NY, USA	Case-control 1,166/2,105 (1959-1997)	Modeled traffic emissions at own birth, 1st childbirth, menarche, or later	Postmen (no effect in premeno)	OR: 2.57 (1.16-5.69) high vs. low quartile at 1st birth; none at own birth, menarche, or later
Crouse, 2010 Montreal, Canada	Case-control 383/416 (1996-1997)	Modeled NO_2 in1996, 1985 or 2006	Postmeno women only in study	Modeled NO_2 at 1996 OR: 1.31 (1.00-1.71) per 5 ppb; none with NO_2 at 1985 or 2006.
Raaschou-Nielsen, 2011 Copenhagen & Aarhus, Denmark	Cohort, Diet Cancer & Health Cohort 1971-2010	Modeled NO_x 1971-2010	Pre- and postmeno combined	HR per 100 $\mu g/m^3$: HR: 1.16 (0.89-1.51)
Hystad, 2015 10 provinces, Canada	Case-control 1,569/1,872 (1994-1997)	Modeled NO_2 1975-1994	Pre- and postmeno combined	OR per 10 ppb: Premeno: 1.32 (1.05-1.67) Postmeno: 1.10 (0.88-1.36)
Reding, 2015 USA	Cohort, The Sister Study 47,591 (1,749 cases) (2003/09-2013)	$PM_{2.5}$, PM_{10}, NO_2 1-year mean baseline address	Pre- and postmeno combined. Receptor status.	Overall HR: $PM_{2.5}$: 1.03 (0.96-1.11) PM_{10}: 0.99 (0.98-1.00) NO_2: 1.02 (0.97-1.07) ER+/PR+: NO_2: 1.10 (1.02-1.19)
Liu, 2015 CA, USA	Cohort, The California Teachers Study, 133,479 (5,361	11 estrogen disruptors, modeled levels in 2002: diesel, styrene,	Pre- and postmeno Receptor status.	No assoc. overall; no difference in pre- and postmeno women; some assoc. with inorganic arsenic and breast cancer in non-smoking

	cases) (1995/96-2010)	inorganic arsenic, selenium, cadmium		non-movers, and cadmium with ER-/PR- breast cancer.
Garcia, 2015 CA, USA	Cohort, The California Teachers Study, 112,378 (5,676 cases) (1995/96-2012)	24 MGC modeled levels in 2002: benzene, styrene, acrylamide, benzidine, etc.	Pre- and postmeno Receptor status.	Assoc. with propylene oxide and vinyl chloride overall. In subset, ER+/PR+ assoc. with acylamide, benzidine, carbon tetrachloride, ethylidene dichloride, vinyl chloride; ER-/PR- with benzene.

OR odds ratio; HR Hazard ratio; TSP total suspended particles; NO_2 nitrogen dioxide; NO_x nitrogen oxides; CO carbon monoxide; PM_{10} particulate matter with diameter less than 10 µm; $PM_{2.5}$ particulate matter with diameter less than 2.5 µm; MGC mammary gland carcinogen.

Most of the evidence came from USA (Bonner et al, 2005; Garcia et al, 2015; Hu et al, 2013; Huo et al, 2015; Lewis-Michl et al, 1996; Liu et al, 2015; Nie et al, 2007; Reding et al, 2015), two studies from Canada (Crouse et al, 2015; Hystad et al, 2015), and a single study from Italy (Ranzi et al, 2015), Spain (Cambra et al, 2011), Denmark (Raaschou-Nielsen et al, 2011), and China (Wei et al, 2012). A variety of air pollutants were examined, with most studies including proxies of traffic related air pollution at individual residential address, in terms of modeled levels of nitrogen dioxide (NO_2) (Crouse et al, 2015; Hystad et al, 2015; Reding et al, 2015), nitrogen oxide (NO_x) (Raaschou-Nielsen et al, 2011), total suspended particles (TSP) (Bonner et al, 2005), modeled traffic emissions (Nie et al, 2007), traffic density (Lewis-Michl et al, 1996). Only two studies had data on $PM_{2.5}$ and PM_{10} (Nie et al, 2007; Reding et al, 2015). Furthermore, two studies used modeled concentrations of a number of selected estrogen disruptors (Liu et al, 2015) or mammary gland carcinogens (MGC) (Garcia et al, 2015), 11 and 24, respectively. Three studies used distance to industrial facilities with respect to breast cancer mortality (Cambra et al, 2011; Ranzi et al, 2011), and two ecological studies examined traffic density (Chen et al, 2012) and levels of nitrogen oxides (NO), carbon monoxide (CO), sulphur dioxide (SO_2) and volatile organic compounds (VOC) (Wei et al, 2012) in the entire USA over time.

As many factors may influence survival after breast cancer diagnosis and breast cancer mortality beyond air pollution, such as access to and quality of received health care, treatment, cancer stage, socio-economic status, etc., studies on breast cancer incidence are in this review ranked higher than studies on breast cancer mortality and survival, for the purpose of disentangling relevance of air pollution for breast cancer etiology. Thus, we describe briefly results of all 15 studies, but focus mainly on 9 studies on breast cancer incidence, which are described in Table 1.

Studies of Breast Cancer Incidence

An early case-control study from 1996 by Lewis-Michl et al, based in Nassau and Suffolk Counties on Long Island, NY, USA, found significantly increased risk of postmenopausal breast cancer in women living close to chemical facilities, but only slightly increased, statistically non-significant risk in women living close to busy roads for 20 years (Lewis-Michl et al, 1996) (Table 1). Bonner et al has in 2005, in a case control study (Western New York Exposures and Breast Cancer (WEB) Study) based in Erie and Niagara Countries in New York State, found association between postmenopausal breast cancer and TSP levels at birth address (odds ratio (OR) and 95% confidence interval: 2.42 (0.97-6.09) comparing high (>140 µg/m^3) to low (<84 µg/m^3) TSP), but none with exposure to TSP later in life, at menarche, 1st childbirth, 10 and 20 years prior to breast cancer (Bonner et al, 2005). Bonner et al used TSP as a proxy of exposure to PAHs (Bonner et al, 2005). Nie et al in 2007 used the WEB case-control study (Bonner et al, 2005) adding the data on traffic emissions throughout life and found significantly increased odds of postmenopausal breast cancer (2.57 (1.16-5.69) high vs. low quartile of modeled traffic emissions levels) at residence at 1st childbirth, but none with other exposure windows: menarche, 10 or 20 years prior to breast cancer diagnosis (Nie et al, 2007). All three studies found effects for postmenopausal breast cancer only, and none in premenopausal women (Bonner et al, 2005; Lewis-Michl et al, 1996; Nie et al, 2007). In the case-control from 2010 based in Montreal, Canada, Crouse et al has in study with 383 cases and 416 controls found borderline statistically significant association between NO_2 levels at residential address in 1996 and postmenopausal breast cancer (OR: 1.31 (1.00-1.71) per 5 ppb), but none with premenopausal cancer, or with NO_2 at 1985 or 2006 (Crouse et al, 2010). In a related study from the same group, Hystad et al has in 2015 expanded the study to 10 Canadian provinces including 1,569 breast cancer cases and 1,872 controls, and found statistically significant associations with NO_2 levels at residence from 1975-1994 (1.32 (1.05-1.67)) per 10 ppb, for postmenopausal, but none with premenopausal breast cancer (1.10 (0.88-1.36)) (15 et al). These two studies (Crouse et al, 2010; Hystad et al, 2015) provided the most convincing evidence to date for a causative relationship between air pollution and breast cancer risk. However, evidence from cohort studies (Raaschou-

Nielsen et al, 2011; Reding et al, 2015) is less convincing. A cohort study from Denmark has in 27,735 women (987 developed breast cancer) examined association between long-term exposure of over 30 years to NO_x at residence with all cancer types, and reported positive but statistically non-significant associations with breast cancer incidence (hazard ratio (HR) and 95% confidence interval; 1.16; 0.89-1.51 per 100 $\mu g/m^3$), but did not distinguish between pre- and postmenopausal breast cancer (Raaschou-Nielsen et al, 2011). Reding et al has in 47,591 women from the Sister Cohort Study in USA, of whom 1,749 developed breast cancer, failed to detect associations of PM_{10}, $PM_{2.5}$, or NO_2 with overall breast cancer incidence, but found association between NO_2 and ER+/PR+ breast cancer subtype (1.10; 1.02-1.19 per interquartile range increase of 5.8 ppb in NO_2) (Reding et al, 2015). Finally, Liu et al has in 2015, in 112,379 women from the California Teachers Study, of whom 5,361 developed breast cancer, failed to find association between any of 11 estrogen disruptors (modeled at residence) and breast cancer risk, but found some evidence of association between inorganic arsenic and breast cancer in non-smoking non-movers, and between cadmium with ER-/PR- breast cancer (Liu et al, 2015). Finally, in the same cohort of California Teachers, Garcia et al has in 2015 linked modeled levels of 24 MGCs at residential address and found association between propylene oxide and vinyl chloride with overall breast cancer risk, as well as acylamide, benzidine, carbon tetrachloride, ethylidene dichloride, and vinyl chloride with ER+/PR+ breast cancer, and benzene with ER-/PR- breast cancer.

Breast Cancer Mortality

A population based cohort study of people living close to incinerators in Forly, Italy, by Ranzi et al found increased risk of dying from breast cancer in women with high levels of exposure to heavy metals from incinerators (Ranzi et al, 2011). Similar ecological cross-sectional study from Basque County in Spain by Cambraa et al from 2011, found excess breast cancer mortality in women living close to industrial sites, specifically from mineral industry (Cambra et al, 2011). Hu et al studied survival after breast cancer diagnosis in 255,128 Californian and found that women living in areas with high levels of $PM_{2.5}$ and PM_{10} had significantly worse survival than women living in areas with low air pollution (Hu et al, 2013). Hue et al has in 2015 reported same findings in the Chinese women from northern Shandong Province, reporting poorer survival in women with high levels of PM_{10}, but only in ER+ breast cancer cases (Huo et al, 2015), suggesting that air pollution mainly contributes to development of ER+ breast cancer.

CONCLUSIONS

Epidemiological evidence on association between air pollution and breast cancer to date is limited, with variety of different study designs, proxies of exposure to air pollution, and different windows of exposure reported, precluding direct comparisons of effect estimates between studies. While several case-control studies report statistically borderline significant or significant positive associations with breast cancer and NO_2 (Crouse et al, 2010; Hystad et al, 2015; Nie et al, 2007), two large, well designed cohort studies failed to find associations of NO_2, $PM_{2.5,}$ or PM_{10} with breast cancer (Raaschou-Nielsen et al, 2011; Reding et al, 2015). Some consistency in current literature is noted. Studies which present data separately for pre- and postmenopausal breast cancer (Bonner et al, 2005 Crouse et al, 2015; Hystad et al, 2015; Lewis-Michl et al, 1996; Nie et al, 2007) report relevance of air pollution for postmenopausal breast cancer. Similarly, some of the most recent studies with data on subtype of breast cancer according to ER and PR receptor status, report significant associations mainly with ER+ breast cancer type, specifically ER+/PR+ breast cancer with NO_2 (Reding et al, 2015), or PM_{10} with ER+ breast cancer (Huo et al, 2015). Thus overall evidence is suggestive of possible association between air pollution and breast cancer, mainly for postmenopausal, and ER+ breast cancer. However, data are too sparse and results inconsistent precluding definite conclusions on associations between air pollution and breast cancer, and more studies are urgently needed. Current data on air pollution and breast cancer are limited to North America and North Europe, and data from other locations with higher air pollution levels are needed. A single study has reported that association with air pollutions was limited to life-time nonsmokers (Nie et al, 2007). In the light of emerging evidence that smoking is a risk factor for breast cancer, careful consideration of confounding and effect modification by smoking is needed in future studies of air pollution and breast cancer. There is a need for more large cohort studies on breast cancer incidence and/or mortality with good quality data on multiple pollutants, especially $PM_{2.5}$ and PM_{10}, different windows of exposure, preferably early life exposure, before first birth, which was found to be most relevant exposure for breast cancer risk in tobacco smoke studies, and data on breast cancer subtypes with respect to menopausal status and receptor status.

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REFERENCES

1. Akinyemiju, T.F., Genkinger, J.M., Farhat, M., Wilson, A., Gary-Webb, T.L., Tehranifar, P. 2015. Residential environment and breast cancer incidence and mortality: a systematic review and meta-analysis. BMC Cancer. 15, 191.
2. Bjerkaas, E., Parajuli, R., Weiderpass, E., Engeland, A., Maskarinec, G., Selmer, R., Gram, I.T. 2013. Smoking duration before first childbirth: an emerging risk factor for breast cancer? Results from 302,865 Norwegian women. Cancer Causes Control. 24, 1347-56.
3. Bonner, M.R., Han, D., Nie, J., Rogerson, P., Vena, J.E., Muti, P., et al. 2005. Breast cancer risk and exposure in early life to polycyclic aromatic hydrocarbons using total suspended particulates as a proxy measure. Cancer Epidemiol Biomarkers Prev. 14, 53-60.
4. Brody JG, Rudel RA, Michels KB, Moysich KB, Bernstein L, Attfield KR, Gray S. 2007. Environmental pollutants, diet, physical activity, body size, and breast cancer: where do we stand in research to identify opportunities for prevention? Cancer. 109,2627-2634.
5. Brody JG, Moysich KB, Humblet O, Attfield KR, Beehler GP, Rudel RA. 2007. Environmental pollutants and breast cancer: epidemiologic studies. Cancer. 109,2667-771.
6. Cambra K, Martínez-Rueda T, Alonso-Fustel E, Cirarda FB, Ibáñez B, Esnaola S, Calvo M, Aldasoro E, Montoya I. 2011. Mortality in small geographical areas and proximity to air polluting industries in the Basque Country (Spain). Occup Environ Med. 68,140-7.
7. Chen F, Bina WF. 2012. Correlation of white female breast cancer incidence trends with nitrogen dioxide emission levels and motor vehicle density patterns. Breast Cancer Res Treat. 132, 327-333.
8. Crouse DL, Goldberg MS, Ross NA, Chen H, Labrèche F. 2010. Postmenopausal Breast Cancer is Associated with Exposure to Traffic-related Air Pollution in Montreal, Canada: A Case-Control Study. Environ Health Perspect. 118,1578-83.
9. Garcia E, Hurley S, Nelson DO, Hertz A, Reynolds P. 2015. Hazardous air pollutants and breast cancer risk in California teachers: a cohort study. Environ Health. 14, 14.
10. Gaudet MM, Gapstur SM, Sun J, Diver WR, Hannan LM, Thun MJ. 2013. Active smoking and breast cancer risk: original cohort data and meta-analysis. J Natl Cancer Inst. 8,:515-25.
11. Hamajima N, Hirose K, Tajima K, Rohan T, Calle EE, Heath CW Jr, et al; Collaborative Group on Hormonal Factors in Breast Cancer. 2002 Alcohol, tobacco and breast cancer--collaborative reanalysis of individual data from 53 epidemiological studies, including 58,515 women with breast cancer and 95,067 women without the disease. Br J Cancer. 87, 1234-1245.
12. Hu H, Dailey AB, Kan H, Xu. 2013. The effect of atmospheric particulate matter on survival of breast cancer among US females. Breast Cancer Res Treat. 139,217-226.
13. Huo Q, Cai C, Yang Q. 2015. Atmospheric particulate matter and breast cancer survival: estrogen receptor triggered? Tumour Biol. 36, 3191-3.
14. Huynh S, von Euler-Chelpin M, Raaschou-Nielsen O, Hertel O, Tjønneland A, Lynge E, Vejborg I, Andersen ZJ. 2015. Long-term exposure to air pollution and mammographic density in the Danish Diet, Cancer and Health cohort. Environ Health. 1, 14:31.
15. Hystad P, Villeneuve PJ, Goldberg MS, Crouse DL, Johnson K; Canadian Cancer Registries Epidemiology Research Group. 2015. Exposure to traffic-related air pollution and the risk of developing breast cancer among women in eight Canadian provinces: a case-control study. Environ Int. 74, 240-8.
16. International Agency for Research on Cancer. 2012 Some Chemicals in Industrial and Consumer Products, Food Contaminants and Flavourings and Water Chlorination By-products: Volume 100E, Personal Habits and Indoor Combustions. Lyon (France).
17. Lewis-Michl EL, Melius JM, Kallenbach LR, Ju CL, Talbot TO, Orr MF, et al. 1996. Breast cancer risk and residence near industry or traffic in Nassau and Suffolk Counties, Long Island, New York. Arch Environ Health. 51,255-265.
18. Liu R, Nelson DO, Hurley S, Hertz A, Reynolds P. 2015. Residential exposure to estrogen disrupting hazardous air pollutants and breast cancer risk: the California Teachers Study. Epidemiology. 26, 365-73.
19. Luo J, Margolis KL, Wactawski-Wende J, Horn K, Messina C, Stefanick ML, Tindle HA, Tong E, Rohan TE. 2011. Association of active and passive smoking with risk of breast cancer among postmenopausal women: a prospective cohort study. BMJ. 342, d1016.
20. Mordukhovich I, Rossner P Jr, Terry MB, Santella R, Zhang YJ, Hibshoosh H, Memeo L, Mansukhani M, Long CM, Garbowski G, Agrawal M, Gaudet MM, Steck SE, Sagiv SK, Eng SM, Teitelbaum SL, Neugut AI, Conway-Dorsey K, Gammon MD. 2010. Associations between polycyclic aromatic hydrocarbon-related exposures and p53 mutations in breast tumors. Environ Health Perspect. 118,511-518.
21. Nie J, Beyea J, Bonner MR, Han D, Vena JE, Rogerson P, Vito D, Muti P, Trevisan M, Edge SB, Freudenheim JL. 2007. Exposure to traffic emissions throughout life and risk of breast cancer: the Western New York Exposures and Breast Cancer (WEB) study. Cancer Causes Control. 18,947-55.

22. Pope CA 3rd, Burnett RT, Krewski D, Jerrett M, Shi Y, Calle EE, Thun MJ. 2009. Cardiovascular mortality and exposure to airborne fine particulate matter and cigarette smoke: shape of the exposure-response relationship. Circulation. 120,941-8.
23. Raaschou-Nielsen O, Andersen ZJ, Hvidberg M, Jensen SS, Ketzel M, Sørensen M, Hansen J, Loft S, Overvad K, Tjønneland A. 2011. Air Pollution from Traffic and Cancer Incidence: a Danish cohort study. Environ Health. 10,67.
24. Raaschou-Nielsen O, Andersen ZJ, Beelen R, Samoli E, Stafoggia M, Weinmayr G, et al. 2013. Air pollution and lung cancer incidence in 17 European cohorts: prospective analyses from the European Study of Cohorts for Air Pollution Effects (ESCAPE). Lancet Oncology. 14; 813-22.
25. Ranzi A, Fano V, Erspamer L, Lauriola P, Perucci CA, Forastiere F. 2011. Mortality and morbidity among people living close to incinerators: a cohort study based on dispersion modeling for exposure assessment. Environ Health. 24,10:22..
26. Reding KW, Young MT, Szpiro AA, Han CJ, DeRoo LA, Weinberg C, Kaufman JD, Sandler DP. 2015. Breast Cancer Risk in Relation to Ambient Air Pollution Exposure at Residences in the Sister Study Cohort. Cancer Epidemiol Biomarkers Prev. 24, 1907-9.
27. Secretan B, Straif K, Baan R, Grosse Y, El Ghissassi F, Bouvard V, Benbrahim-Tallaa L, Guha N, Freeman C, Galichet L, Cogliano V; WHO International Agency for Research on Cancer Monograph Working Group. 2009 A review of human carcinogens--Part E: tobacco, areca nut, alcohol, coal smoke, and salted fish. Lancet Oncol. 10,1033-1034.
28. Terzano C, Di Stefano E, Conti V, Graziani E, Petroianni A. 2010. Air pollution ultrafine particles: toxicity beyond the lung. Eur Rev Med Pharmacol Sci. 14,809-821.
29. Wei Y, Davis J, Bina WF. 2012 Ambient air pollution is associated with the increased incidence of breast cancer in US. IntJEnvironHealthRes. 22;12-21.

8.2 THE ASSOCIATION BETWEEN SHORT-TERM PM10 EXPOSURE AND MORTALITY CAUSED BY RESPIRATORY SYSTEM DISEASES IN THE BELGRADE AREA

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ABSTRACT

In this study, we evaluated the association between the observed PM_{10} concentrations and mortality caused by respiratory diseases in the Belgrade area (Serbia). The estimated health-related risk for the two-year period (2010-2011) is expressed as % increase in respiratory system-related mortality per unit increase in daily PM_{10} levels. According to the results, a 30-day moving average is found to be a stronger predictor of death rate than a single day's exposure. The effects were mostly pronounced for the middle-aged population, whereas the lower estimated increase in respiratory system-related mortality of 3.13% for elderly males is more significant due to a higher number of observed cases. Better understanding of the relationship between air pollution and health outcomes provides a solid basis for the establishment of new environmental legal framework in developing countries which could significantly reduce exposure and related public health hazards.

INTRODUCTION

Considerable research attention has been devoted to the role of particulate matter (PM_{10}) in the impairment of the respiratory system function, aggravation of the pre-existing chronic obstructive pulmonary disease and increase of the respiratory-related death rate among the susceptible groups. According to Pope and Dockery (2006), the shape of the exposure-response function across the broad range of PM_{10} pollution is found to be linear with no safe threshold level, which indicates that further refinement of air quality standards would result in public health improvements. Therefore, numerous epidemiological studies conducted worldwide are aimed at evaluating the health effects of PM_{10} exposure and revealing the specific features of particles that pose the greatest risk (Gray et al, 2015). The present study was conducted in Belgrade, a city of 1 600 000 citizens, which experiences high levels of air pollution. As previously reported, high PM_{10} loadings in Belgrade pose a significant threat, partly due to long-range and regional pollutant transport, but mainly due to outdated technology, the use of sulfur-containing fuels, emission sources located in industrial suburban zones and considerable portion of old, poorly-maintained vehicles (Perišić et al, 2014). Hence, studies aimed at exploring the growing public health burden in Serbia would yield a solid basis for the new environmental policy design and human welfare improvement.

METHODOLOGY

Mortality statistics including total and respiratory system related mortality (J00-J99 according to the International Classification of Diseases, 10th Revision, ICD-10), were retrieved from the Institute of Public Health, Belgrade for the two-year period (2010-2011). The deaths attributed to injuries, poisoning and external causes were excluded from the overall death rate. Daily PM_{10} concentrations were provided by the automatic monitoring network comprising 7 stations. Meteorological data obtained from the Global Data Assimilation System with spatial resolution of 1 degree were averaged over a 24-hour periods to provide a mean, median, maximum, minimum and range for temperature, relative humidity and pressure. Daily counts of respiratory system-related mortality were modeled using quasi-Poisson regression, selected in order to compensate for overdispersion (*i.e.* residual deviance is larger than residual degrees of freedom). The confounding factors, including days of the week, seasonal trends and meteorological conditions, were selected on the basis of previous studies (Schwartz, 1995; Samet et al, 2000a; Samet et al, 2000b; Dominici et al, 2006; Bell et al, 2008; Peng and Dominici, 2008).

The model was specified as follows:

$$E(Y_t) = \exp\{\beta_1 PM\Delta3_t + \beta_2 PM\Delta7_t + \beta_3 PM30MA_t + \beta_4 PRSS_t + \beta_5 RH2M_t + S(time, \lambda_1) + S(temp, \lambda_2) + \alpha DOW_t\}$$

Y_t – the expected number of respiratory disease-related deaths on day t; $PM\Delta3_t$ – difference between 3-day simple moving average and 7-day simple moving average of mean concentration ($\mu g\ m^{-3}$) of PM_{10} ending on day t; $PM\Delta7_t$ – difference between 7-day simple moving average and 30-day simple moving average of mean

concentration (μg m^{-3}) of PM_{10} ending on day t; $PM30MA_t$ – 30-day simple moving average of mean concentration (μg m^{-3}) of PM_{10} ending on day t; $PRSS_t$ – daily range of pressure at surface (hPa) on day t; $RH2M_t$ – daily range of relative humidity at 2m AGL (%) on day t; S(.,λ) – natural cubic spline of time with λ degrees of freedom (five/year for time and three in total for temperature); DOW_t – day of the week on day *t*; β_n – regression coefficients relating covariate levels to number of deaths; and α – regression coefficient relating the day of the week to the number of deaths.

As presented in Dominici et al (2003), the smooth function S(.,λ) was applied to adjust fluctuations in mortality over time so that only short-term variations in mortality and pollutant concentrations are used to estimate β.

RESULTS AND DISCUSSION

During the study period 37,540 deaths occurred, out which 1,342 cases were attributed to respiratory failure. The daily mean concentrations of PM_{10} were in the range from 10.36 to 276.43 μg m^{-3}, with 229 days exceeding the 50 μg m^{-3} level threshold. The pollutant levels exhibited seasonal variations with the lowest values recorded during the spring and summer months (Figure 1). The number of death cases caused by respiratory diseases is ranked third in Serbia, immediately after circulatory and malignant-related mortality. The majority of deaths are detected among the population aged 65 and older. According to the data obtained from the Statistical Office of the Republic of Serbia (2015), the death rate in Belgrade area ranged between 28 and 60 per 100 000 inhabitants over the period 2000-2014, which is comparable to the levels registered in the surrounding countries, namely in Bulgaria (54.0), Hungary (62.5), and Croatia (44.3) available at The European Detailed Mortality Database (WHO, 2014).

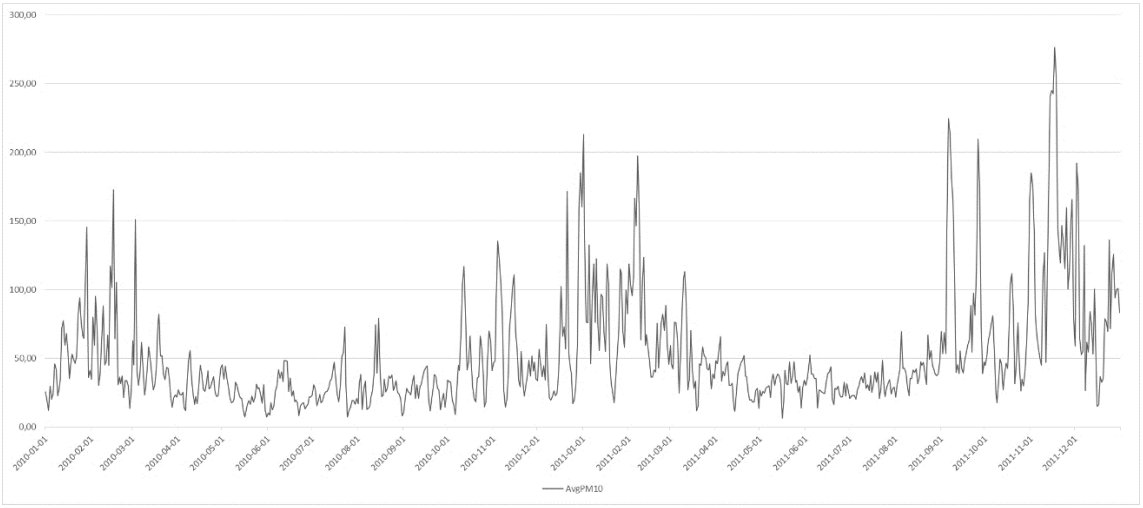

Figure 1. *Seasonal variations of PM_{10} concentrations during the study period.*

The model estimates of the association between PM_{10} concentrations and respiratory system-related mortality are shown in Table 1. As can be seen, the statistical significance of the estimated association between PM_{10} concentrations and respiratory-related mortality is not high probably due to the limited number of observations (1,342) over the specified two-year period. Accordingly, the effects on young population (<30) and people of non-identified age are not presented and discussed in this paper.

Relative risks calculated for 10-μg m^{-3} increase in PM_{10} concentrations are shown in Table 2. It can be seen that an increase of 10 μg m^{-3} of PM_{10} levels was related to a significant rise in the number of daily deaths, particularly after a cumulative exposure over the last 30 days. The effects were mostly pronounced for the middle-aged population, which could be explained by the fact that younger people have higher minute ventilation, intense physical activity and spend more time outdoors. During the exposition, the coarse particles deposited in the upper airways or larger lower airways may cause the disruption of lung endothelial barrier integrity via oxidative stress which further leads to their transfer from lungs to blood (Wang et al, 2010). Unlike the middle-aged group, the estimated change in mortality of 3.13% for elderly males associated with 30-day average concentrations is lower, but still more significant due to a higher number of the observed cases.

Table 1. *Model estimate of the association between PM_{10} and respiratory system-related mortality.*

	Total	Middle-aged males	Middle-aged females	Elderly males	Elderly females
PM_{10} 3 days delta	-0.001	-0.003	0.0004	0.001	-0.004
	(-0.004, 0.002)	(-0.012, 0.005)	(-0.011, 0.012)	(-0.004, 0.006)	(-0.010, 0.001)
PM_{10} 7 days delta	0.001	0.004	0.012**	-0.0004	-0.001
	(-0.002, 0.004)	(-0.004, 0.011)	(0.002, 0.022)	(-0.004, 0.004)	(-0.006, 0.004)
PM_{10} 30 days MA	0.003	0.01	0.015	0.003	-0.001
	(-0.002, 0.008)	(-0.004, 0.024)	(-0.005, 0.036)	(-0.004, 0.010)	(-0.009, 0.007)
PRSS range	-0.008	-0.024	0.071	-0.013	-0.013
	(-0.032, 0.016)	(-0.096, 0.049)	(-0.020, 0.162)	(-0.050, 0.024)	(-0.054, 0.029)
RH2M range	-0.002	0.003	-0.017	0.001	-0.004
	(-0.008, 0.004)	(-0.017, 0.022)	(-0.043, 0.008)	(-0.009, 0.010)	(-0.015, 0.007)
Tuesday	-0.112	-0.105	0.017	-0.062	-0.228
	(-0.318, 0.093)	(-0.725, 0.514)	(-0.843, 0.876)	(-0.366, 0.242)	(-0.588, 0.132)
Wednesday	-0.097	0.096	-0.301	-0.122	-0.119
	(-0.302, 0.109)	(-0.496, 0.689)	(-1.236, 0.634)	(-0.431, 0.186)	(-0.470, 0.232)
Thursday	-0.067	-0.182	0.357	-0.216	0.07
	(-0.271, 0.136)	(-0.820, 0.456)	(-0.445, 1.159)	(-0.531, 0.100)	(-0.264, 0.404)
Friday	-0.063	0.072	-0.09	-0.043	-0.119
	(-0.266, 0.141)	(-0.527, 0.671)	(-0.974, 0.794)	(-0.344, 0.259)	(-0.469, 0.231)
Saturday	-0.087	0.069	-0.274	-0.08	-0.122
	(-0.292, 0.117)	(-0.532, 0.669)	(-1.186, 0.637)	(-0.385, 0.226)	(-0.472, 0.229)
Sunday	0.039	-0.03	0.346	-0.005	0.095
	(-0.160, 0.237)	(-0.641, 0.581)	(-0.442, 1.134)	(-0.305, 0.296)	(-0.236, 0.426)
nsTime1	-0.056	-1.651	3.657*	0.282	-0.577
	(-1.088, 0.977)	(-4.417, 1.115)	(-0.518, 7.832)	(-1.337, 1.901)	(-2.346, 1.191)
nsTime2	-0.2	-3.515*	4.003	0.165	-0.433
	(-1.511, 1.111)	(-7.172, 0.143)	(-1.515, 9.522)	(-1.872, 2.202)	(-2.664, 1.797)
nsTime3	0.151	-1.32	1.355	0.695	-0.121
	(-0.989, 1.290)	(-4.365, 1.725)	(-3.441, 6.150)	(-1.090, 2.480)	(-2.063, 1.820)
nsTime4	-0.123	-2.602*	2.009	0.323	-0.44
	(-1.178, 0.933)	(-5.401, 0.197)	(-2.435, 6.453)	(-1.336, 1.982)	(-2.249, 1.369)
nsTime5	0.797	-0.99	1.572	1.088	0.847
	(-0.270, 1.863)	(-3.811, 1.831)	(-2.927, 6.071)	(-0.589, 2.765)	(-0.972, 2.665)
nsTime6	-0.002	-2.725	4.942*	0.402	-0.35
	(-1.215, 1.212)	(-6.040, 0.590)	(-0.134, 10.017)	(-1.490, 2.293)	(-2.416, 1.716)
nsTime7	-0.423	-2.299	1.02	0.018	-0.729
	(-1.647, 0.800)	(-5.619, 1.021)	(-4.310, 6.350)	(-1.889, 1.924)	(-2.807, 1.350)
nsTime8	-0.143	-1.691	1.074	0.062	-0.148
	(-0.926, 0.639)	(-3.860, 0.477)	(-2.382, 4.529)	(-1.154, 1.278)	(-1.478, 1.181)
nsTime9	0.473	-5.486*	3.242	1.81	0.069
	(-1.768, 2.715)	(-11.732, 0.761)	(-6.289, 12.774)	(-1.665, 5.285)	(-3.769, 3.906)
nsTime10	0.587**	-0.285	0.128	0.774**	0.634
	(0.130, 1.044)	(-1.776, 1.206)	(-2.062, 2.318)	(0.101, 1.446)	(-0.162, 1.431)
nsTemp1	0.196	0.071	-0.651	0.195	0.338
	(-0.309, 0.700)	(-1.389, 1.530)	(-2.691, 1.390)	(-0.568, 0.958)	(-0.539, 1.214)
nsTemp2	0.717	-0.699	-0.534	0.424	1.692*
	(-0.333, 1.767)	(-3.419, 2.022)	(-4.438, 3.370)	(-1.185, 2.033)	(-0.231, 3.615)
nsTemp3	0.837***	0.529	-0.888	0.885**	1.180***
	(0.316, 1.359)	(-1.098, 2.156)	(-3.104, 1.328)	(0.101, 1.669)	(0.303, 2.058)
Constant	0.266	0.506	-4.995**	-0.839	-0.728
	(-0.850, 1.383)	(-2.412, 3.425)	(-9.714, -0.276)	(-2.583, 0.905)	(-2.659, 1.202)

Note: *p<0.1; **p<0.05; ***p<0.01. Middle-aged – 30-65 years; Elderly - >65 years; PRSS – pressure at surface; RH2M – relative humidity at 2 m AGL.

Similar effect estimates for PM_{10} exposure were reported by Hoek et al (2013), who found a 4.5% increase in respiratory system-related mortality for a 10 μg m^{-3} increase in PM_{10} concentrations. The gender-differences can be explained by a smaller diameter of upper airways in females due to which particles are deposited in the trachea and bronchioles and later on swallowed or expelled by coughing (Gehr and Heyder, 2000).

The majority of previous studies have estimated the PM_{10} effects at multiple lag days (0-day to 3-day lags were mostly examined) and according to their findings, the relative risk estimates are shown to be highest over 3 days of exposure (Anderson et al, 2012). However, our results indicate that the period longer than just a few days might play an important role in the aggravation of the pre-existing respiratory conditions and related mortality. This is in compliance with the study of Zanobetti et al (2003), who reported that, during the first 40 days after exposure, the effect size estimate becomes five times higher. According to their findings, a 10 μg m^{-3} increase in PM_{10} concentrations was associated with a 4.2% increase in respiratory mortality, whereas the effects of pollutant exposure observed for the same day and the day preceding the fatal outcome were considerably lower (0.74%).

Dockery and Pope (1994) summarized the results of several studies with the conclusion that the PM_{10} exposure was followed by an increase in mortality attributed to respiratory diseases ranging from 1.5% to 3.7%. It is worth noting that some of these studies, particularly those with lower estimated effect size, were conducted in the regions where PM_{10} concentrations were considerably lower compared to those registered in Belgrade area.

Table 2. *The percent changes in respiratory system-related mortality with a 10-μg m^{-3} increase in pollutant concentrations.*

Model 1	Total	Middle-aged males	Middle-aged females	Elderly males	Elderly females
PM10 3 days delta	-1.24%	-3.47%	0.38%	0.91%	-4.31%
PM10 7 days delta	1.01%	3.51%	11.92%	-0.39%	-0.86%
PM10 30 days MA	3.16%	10.13%	15.50%	3.13%	-0.83%
PRSS range	-0.81%	-2.33%	7.36%	-1.33%	-1.25%
RH2M range	-0.19%	0.26%	-1.73%	0.09%	-0.38%

Note: Middle-aged – 30-65 years; Elderly - >65 years; PRSS – pressure at surface; RH2M – relative humidity at 2 m AGL.

One of the major limitations of the retrospective epidemiological studies is associated with the possibility of misinterpretation of the health outcomes due to neglecting the underlying causes of death. For instance, the respiratory-related death rate might even be higher when taking into account that patients with chronic obstructive pulmonary disease are often removed by cardiovascular failure (Pope et al, 2004). Furthermore, it has been argued that true pollutant effects might remain underestimated since the information obtained from the ambient monitoring networks is not always correlated with the personal exposure levels on the days preceding the fatal outcome (Tellez-Rojo et al, 2001). Nevertheless, despite the potential uncertainties mentioned in the literature, the evidence derived from the retrospective epidemiological studies is still a useful indicator of public health burden.

CONCLUSIONS

This study is focused on the quantification of health risks associated with PM_{10} exposure in the Belgrade area, Serbia. Unlike previous studies that estimated PM_{10} effects at multiple lag days, this study focuses on cumulative pollutant exposure during the 3, 7 or 30 days preceding the death. The presented findings confirm that high pollutant loadings, which are nowadays common in many urban areas, pose a significant risk factor for mortality caused by respiratory diseases. Due to the fact that the problem of air pollution in Serbia is severe, the introduction of clean technologies in the industry, energy production and transportation sectors, as well as the development of new environmental regulations, shall remain a key target for the future public-health action. Further studies in the region are also needed to gain better insight into the effects of real life exposure and to help policy makers to determine acceptable risk levels.

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REFERENCES

1. Anderson, J. O., Thundiyil, J. G., Stolbach, A., 2012. Clearing the air: a review of the effects of particulate matter air pollution on human health. *Journal of Medical Toxicology*, *8*(2), 166-175.
2. Bell, M. L., Ebisu, K., Peng, R. D., Walker, J., Samet, J. M., Zeger, S. L., & Dominici, F., 2008. Seasonal and regional short-term effects of fine particles on hospital admissions in 202 US counties, 1999–2005. *American Journal of Epidemiology*, *168*(11), 1301-1310.
3. Dockery, D. W., & Pope, C. A., 1994. Acute respiratory effects of particulate air pollution. *Annual Review of Public Health*, *15*(1), 107-132.
4. Dominici, F., Peng, R. D., Bell, M. L., Pham, L., McDermott, A., Zeger, S. L., & Samet, J. M.,(2006. Fine particulate air pollution and hospital admission for cardiovascular and respiratory diseases. *Jama*, *295*(10), 1127-1134.
5. Dominici, F., Sheppard, L., & Clyde, M., 2003. Health effects of air pollution: a statistical review. *International Statistical Review*, *71*(2), 243-276.
6. Gehr, P., & Heyder, J. (Eds.)., 2000. *Particle-lung interactions*. CRC Press.
7. Gray, D. L., Wallace, L. A., Brinkman, M. C., Buehler, S. S., & La Londe, C., 2015. Respiratory and Cardiovascular Effects of Metals in Ambient Particulate Matter: A Critical Review. In *Reviews of Environmental Contamination and Toxicology* (pp. 135-203). Springer International Publishing.
8. Hoek, G., Krishnan, R. M., Beelen, R., Peters, A., Ostro, B., Brunekreef, B., & Kaufman, J. D., 2013. Long-term air pollution exposure and cardio-respiratory mortality: a review. *Environmental Health*, *12*(1), 43.
9. Peng, R. D., Dominici, F., 2008. Statistical methods for environmental epidemiology with R. In *R: A Case Study in Air Pollution and Health*. Springer Publishing Company New York, NY.
10. Perišić, M., Stojić, A., Stojić, S. S., Šoštarić, A., Mijić, Z., & Rajšić, S. (2014). Estimation of required PM10 emission source reduction on the basis of a 10-year period data. *Air Quality, Atmosphere & Health*, 1-11.
11. Pope III, C. A., & Dockery, D. W. (2006). Health effects of fine particulate air pollution: lines that connect. *Journal of the Air & Waste Management Association*, *56*(6), 709-742.
12. Pope, C. A., Burnett, R. T., Thurston, G. D., Thun, M. J., Calle, E. E., Krewski, D., Godleski, J. J., 2004. Cardiovascular mortality and long-term exposure to particulate air pollution epidemiological evidence of general pathophysiological pathways of disease. *Circulation*, *109*(1), 71-77.
13. Samet, J. M., Dominici, F., Zeger, S. L., Schwartz, J., Dockery, D. W. ,2000a. The National Morbidity, Mortality, and Air Pollution Study. Part I: Methods and methodologic issues. *Research Report (Health Effects Institute)*, (94 Pt 1), 5-14.
14. Samet, J. M., Zeger, S. L., Dominici, F., Curriero, F., Coursac, I., Dockery, D., ... & Zanobetti, A., 2000b. The National Morbidity, Mortality, and Air Pollution Study (HEI project no. 96-7): morbidity and mortality from air pollution in the United States. *Cambridge, MA: Health Effects Institute*. Available at: http://www.ncbi.nlm.nih.gov/pubmed/11354823
15. Schwartz, J., 1995. Short term fluctuations in air pollution and hospital admissions of the elderly for respiratory disease. *Thorax*, *50*(5), 531-538.
16. Statistical Office of the Republic of Serbia, 2015. The additionally processed mortality data, Vital statistics
17. Tellez-Rojo, M. M., Romieu, I., Ruiz-Velasco, S., Lezana, M. A., & Hernandez-Avila, M. M., 2001. Daily respiratory mortality and PM10 pollution in Mexico City. *European Respiratory Journal*, *18*(6), 1076-1076.
18. Wang, T., Chiang, E. T., Moreno-Vinasco, L., Lang, G. D., Pendyala, S., Samet, J. M., ... & Garcia, J. G., 2010. Particulate Matter Disrupts Human Lung Endothelial Barrier Integrity via ROS-and p38 MAPK–Dependent Pathways. *American Journal of Respiratory Cell and Molecular Biology*, 42(4), 442-449.
19. World Health Organization, Regional Office for Europe, 2014. Detailed Mortality Database, Division of Information, Evidence, Research and Innovation, Copenhagen, available at: http://data.euro.who.int/dmdb/ (last change July 2016.)
20. Zanobetti, A., Schwartz, J., Samoli, E., Gryparis, A., Touloumi, G., Peacock, J., ... & Katsouyanni, K. , 2003. The temporal pattern of respiratory and heart disease mortality in response to air pollution. *Environmental Health Perspectives*, *111*(9), 1188.

8.3 WHO AIRQ+ TOOL: METHODOLOGIES TO CALCULATE THE IMPACTS OF AIR POLLUTION ON HEALTH

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ABSTRACT

Various tools to assess the burden of air pollution on mortality and morbidity have been disseminated over the last fifteen years. In 2001, the World Health Organization (WHO) developed the AirQ software to support the collection and analysis of air pollution data. WHO is currently working on developing a new version of the original AirQ software for estimating the burden of disease from ambient and household air pollution for one or several cities in a country or for a region. The work is carried out based on the recent developments in the field and the recommendations by the HRAPIE project and the most recent available meta-analyses. 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.

Keywords: Air Pollution – Quantification of Health Impacts, Air Pollution Long-term Exposure, Air Pollution Short-Term Exposure, Concentration–Response Functions

INTRODUCTION

Exposure to air pollution accounted for 7 million deaths worldwide in 2012, including almost 600,000 in the WHO European Region. Specifically, 482,000 deaths are attributable to ambient air pollution and 117,200 deaths to household air pollution, associated with the inefficient combustion of solid fuels, in the WHO European Region. While deaths from ambient air pollution occur in all European countries regardless of their income, those from household air pollution are over five times greater in low- and middle-income countries than wealthier ones (WHO, 2014)[8]. WHO European Centre for Environment and Health prepared air quality guidelines, published by the WHO Regional Office for Europe (2006). They are currently under revision to produce a new update.

Various tools for assessing the burden of air pollution on mortality and morbidity have been developed and circulated over the last fifteen years (WHO Regional Office for Europe, 2014). In 2001, WHO Regional Office for Europe developed the AirQ software to stimulate the collection and analysis of air pollution data. The software was used in various assessments including European cities, Asian megacities, industrialized areas and transport policies (see for example: Boldo et al, 2006; Fattore et al, 2011; Hosking et al, 2011; Tonne et al, 2008; Yorifuji et al, 2005). Unfortunately, AirQ is not fully compatible with contemporary operating systems. In addition, air quality data is today widely available. Large databases on air pollution are maintained by agencies such as the European Environment Agency (EEA). Therefore, the stimulation of data collection is no longer a priority for tools like AirQ, at least in Europe. The focus has shifted to support easy, standardized data analysis and documentation of the origin of data used in specific analyses. Like the previous version of AirQ, the new version will include modules for calculating short-term/long-term impacts and estimates of years of life lost based on life table calculations. The new version is named AirQ+. The development of the software has been planned in seven phases:

1. Assessment of potential technological platforms.
2. Discussions of the functional requirements for the development of AirQ+ with a variety of experts.
3. Software specifications.
4. Invitation to bid and selection of developer.
5. Implementation of the software; internal evaluation.
6. Pilot testing of AirQ+ based on real and simulated datasets.

[8] The leading environmental risk factor for death and disability worldwide is household air pollution. Household air pollution is responsible globally for 4.3 million deaths, which is 7.7% of total mortality in 2012. In the same year, ambient air pollution has contributed to 6.7% of all deaths and 3.7 million deaths globally were attributable to ambient air pollution in 2012 (WHO, 2014).

7. Production of documents on algorithms and methods.

The development of AirQ+ is currently in phase five, entering into the final phases in December 2015 and January-February 2016.

AIRQ+: PRINCIPLES OF DESIGN

Some points were discussed and they represent the orientation to develop the software:

- Being transparent in methodologies and algorithms.
- Presenting a user-friendly interface.
- Including both calculations for ambient and household air pollution.
- Considering effects attributable to short-term and long-term exposure.
- Guiding the user in assessing impacts for the most important and best recognized effects of air pollution.
- Estimating the impacts due to current and changing levels of pollution.
- Utilizing concentration–response functions (CRFs) based on HRAPIE recommendations or from the most recent scientific studies (WHO Regional Office for Europe, 2013; Burnett et al, 2014)).
- Using, whenever possible, data from WHO databases but also providing options for the user to input their own data.
- Producing results such as attributable fractions (AF), mortality and morbidity impacts, and years of life lost (YLL).
- Providing additional documents on algorithms, methods and examples used.

AIRQ+: DETAILS ON SOME FEATURES

After a focused expert consultation, it was decided to realize the software using the Java programming language. This allows easy installation, provides good operating system independence and a rather long lifetime of the application. Some data will be available with the software, for example health statistics from WHO databases or conversion factors at the national level for the estimation of $PM_{2.5}$ levels based on PM_{10} measurements. However, no automatic download from websites will be allowed. Air pollution data have to be imported by the user. AirQ+ includes a description of the procedures for data collection, such as only using stations with valid data available for at least 75% of days (see European Union (EU) directive 2001/752/EC on air pollution).

The work on ambient air pollution is based on the recent WHO recommendations for concentration–response functions compiled by the HRAPIE project (WHO Regional Office for Europe, 2013). The selection of pollutants that the user can model includes particulate matter ($PM_{2.5}$ and PM_{10}), nitrogen dioxide (NO_2), and ozone (O_3). Moreover, black carbon (BC) is also considered for inclusion in AirQ+ (Janssen et al, 2012).

Quantification of the health impacts (selected outcomes) for the exposure to the selected air pollutant is based on the population attributable risk proportion concept (Prüss-Ustün, et al. 2003). The attributable proportion for a certain time period is the fraction of the health outcome which can be attributed to the exposure in a given population, assuming there is a causal association between the exposure and the health outcome and no major confounding effects on this association. (Krzyzanowski, 1997). For mortality due to long-term exposure to PM2.5, the user can use either relative risks based on the so-called integrated exposure risk functions (IER) (Burnett et al, 2014) or relative risks from standard meta-analyses. The IER methodology is related to four adult mortality causes: ischemic heart disease (IHD), cerebrovascular disease (stroke), chronic obstructive pulmonary disease (COPD), and lung cancer (LC). While PM, NO_2 and BC share similar procedures in assessing impacts, ozone presents some peculiarities; calculations are based on SOMO35[9] and valid days of measurement values, or maximum daily 8h mean values. AirQ+ calculates impacts with a SOMO35 intrinsic counterfactual equal to 70 $\mu g/m^3$ (Miller, Hurley and Shafrir, 2011). Hints on potential double counting due to effects of simultaneously present pollutants will be raised, for example impacts on mortality through combined effects of PM and NO_2 (WHO Regional Office for Europe, 2013). However, the first version of AirQ+ will not provide specific calculations for effects of multiple pollutants or for combined ambient and household air pollution.

Calculations for household air pollution are based on the burden of disease methodology for 2012 and include relative risks for five mortality causes: acute lower respiratory disease (ALRI) for children, chronic obstructive

[9] 35 parts per billion (ppb) is equal to 70 $\mu g/m^3$.

pulmonary disease (COPD), lung cancer (LC), ischemic heart disease (IHD) and stroke for adults (Smith et al, 2014; Burnett et al, 2014). Controlling exposure to household air pollution could reduce the risk of multiple child and adult health outcomes (Bruce et al, 2015). AirQ+ includes a table available from the Global Health Observatory Data Repository with the estimation of the yearly use of solid fuels by country. This table facilitates users that have no input data available or are in need of national reference values.

AirQ+ can save various different analyses and filter them by time, pollutant or location. The scheme for AirQ+ is to allow users to either use default pollutants and risk values provided by WHO or allow the definition of individual parameter values, for example for relative risk coefficients. AirQ+ also facilitates importing data for air pollution measurements using files in comma separated values (CSV) format. AirQ+ will not present geographical information system (GIS) capabilities such as grid computing. Users are expected to use other specialized software for this kind of analysis.

AIRQ+ EVALUATION AND TESTING

The testing was performed in the AirQ+ prototype version 0.3. The accuracy of calculations and limits of input values were primary objectives.

AirQ+ can process air quality data in comma separated value files only. Nevertheless, other formats were tested as well, for example Microsoft® Excel formats, in order to evaluate the respond of the software to unspecified data formats. AirQ+ only accepts four columns of data, which is in line with the specifications. If there was a value missing in the first column of import data ("concentration low"), AirQ+ would only import the rows up to the one with missing. Both simulated and real data sets were used for the testing. Simulated data especially tested the limit values of input values and whether out of range data was handled correctly, such as negative pollutant levels which are unphysical. The real data sets were both data related to air pollution and data entirely unrelated to air pollution. Indeed, the version tested allowed for zero or negative concentrations or relative risks, which lead to computational errors and unreliable results. This was corrected in version 0.4. In addition, the range for years was extended to 1700 to 2500 and the population count type was changed to double in order to allow estimated population sizes. It was decided that AirQ+ would display four decimals but export the full values, which is similar for how many databases deal with data in order to allow for validation of results, which is difficult if only rounded "statistically significant" values were stored.

Overall the AirQ+ prototype version 0.3 was very robust. It correctly identified input fields containing letters and symbols (beyond denoting negative values) as incorrect and provided a warning message that the user should check their data. It managed to calculate when only daily means were available in the data. A real world data example regarding air pollution in El Paso, Texas produced consistent results.

CONCLUSIONS

The user-friendly AirQ+ contributes to the aim of WHO to promote and support the quantitative assessment of air pollution impacts on health, foster the implementation of established methodologies and stimulate policies aiming at improving air quality in the WHO European Region. The combined use of AirQ+ with other tools, for example one which simulates air pollution levels due to changes in mobility patterns, can assist in decision-making processes to select strategies for beneficial health effects. The output of AirQ+ can also help estimate economic costs of air pollution, evaluate the evolution of air pollution in cities and countries, model different scenarios with various proportions of sources to air pollution, and compare measurements of air quality obtained methodologies and means.

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REFERENCES

1. Boldo, E., Medina, S., Le Tertre, A., Hurley, F., Mücke, H. G., Ballester, F., & Aguilera, I. 2006. Apheis: Health impact assessment of long-term exposure to PM2. 5 in 23 European cities. *European journal of epidemiology*, 21(6), 449-458.
2. Bruce, N., Pope, D., Rehfuess, E., Balakrishnan, K., Adair-Rohani, H., & Dora, C. 2015. WHO indoor air quality guidelines on household fuel combustion: Strategy implications of new evidence on interventions and exposure–risk functions. *Atmospheric Environment*, 106, 451-457.
3. Burnett, R. T., Pope III C. A., Ezzati M., et al. 2014. An Integrated Risk Function for Estimating the Global Burden of Disease Attributable to Ambient Fine Particulate Matter Exposure. *Environmental Health Perspectives*, 122(4): 397-403.
4. Fattore, E., Paiano, V., Borgini, A., Tittarelli, A., Bertoldi, M., Crosignani, P., & Fanelli, R. 2011. Human health risk in relation to air quality in two municipalities in an industrialized area of Northern Italy. *Environmental research*, 111(8), 1321-1327.
5. Hosking J., Dora C., Mudu P. (ed). 2011. Health Co-benefits of Climate Change Mitigation: Transport Sector. Geneva: World Health Organization (http://www.who.int/hia/green_economy/transport_sector_health_co-benefits_climate_change_mitigation/en/).
6. Janssen, N. A., Gerlofs-Nijland, M. E., Lanki, T., Salonen, R. O., Cassee, F., Hoek, G., … & Krzyzanowski, M. 2012. Health effects of black carbon. WHO Regional Office for Europe Copenhagen (http://www.euro.who.int/__data/assets/pdf_file/0004/162535/e96541.pdf).
7. Krzyzanowski M. 1997. Methods for assessing the extent of exposure and effects of air pollution. *Occupational and Environmental Medicine*, 54(3):145-151.
8. Prüss-Ustün, A., Mathers, C., Corvalán, C., & Woodward, A. 2003. Introduction and methods: assessing the environmental burden of disease at national and local levels. Geneva: World Health Organization (http://www.who.int/quantifying_ehimpacts/publications/en/9241546204.pdf?ua=1).
9. Smith, K. R., Bruce, N., Balakrishnan, K., Adair-Rohani, H., Balmes, J., Chafe, Z., ... & Rehfuess, E. 2014. Millions dead: how do we know and what does it mean? Methods used in the comparative risk assessment of household air pollution. *Annual review of public health*, 35: 185-206.
10. Tonne, C., Beevers, S., Armstrong, B., Kelly, F., & Wilkinson, P. 2008. Air pollution and mortality benefits of the London Congestion Charge: spatial and socioeconomic inequalities. *Occupational and Environmental Medicine*, 65(9), 620-627.
11. WHO Regional Office for Europe. 2006. Air quality guidelines: global update 2005: particulate matter, ozone, nitrogen dioxide, and sulfur dioxide. Copenhagen: WHO Regional Office for Europe (http://www.euro.who.int/__data/assets/pdf_file/0005/78638/E90038.pdf).
12. WHO Regional Office for Europe. 2013. Health risks of air pollution in Europe – HRAPIE project. Recommendations. Copenhagen: WHO Regional Office for Europe (http://www.euro.who.int/__data/assets/pdf_file/0006/238956/Health-risks-of-air-pollution-in-Europe-HRAPIE-project,-Recommendations-for-concentrationresponse-functions-for-costbenefit-analysis-of-particulate-matter,-ozone-and-nitrogen-dioxide.pdf).
13. WHO Regional Office for Europe. 2014. WHO expert meeting: methods and tools for assessing the health risks of air pollution at local, national and international level (http://www.euro.who.int/__data/assets/pdf_file/0010/263629/WHO-Expert-Meeting-Methods-and-tools-for-assessing-the-health-risks-of-air-pollution-at-local,-national-and-international-level.pdf).
14. WHO. 2014. Burden of disease from Household Air Pollution for 2012. (http://www.who.int/phe/health_topics/outdoorair/databases/FINAL_HAP_AAP_BoD_24March2014.pdf)
15. Yorifuji, T., Yamamoto, E., Tsuda, T., & Kawakami, N. 2005. Health impact assessment of particulate matter in Tokyo, Japan. Archives of environmental & occupational health, 60(4), 179-185.

8.4 ASSESSMENT OF PUBLIC HEALTH RISK ASSOCIATED WITH ATMOSPHERIC EXPOSURE TO PARTICULATE MATTER IN THE VICINITY OF RTB COPPER SMELTER COMPLEX

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ABSTRACT

The objective of this study was to estimate the potential health risk of residents of Bor town due to exposure to polluted air originating from copper mining activities. Two individual risks (pediatric asthma emergency room visits and lifetime excess for lung cancer) were calculated. The data has shown that number of person younger of 18 years who may be affected by the exposure of fine particulate matter are almost equal during smelting operation and during no smelting activities. Results also illustrate lifetime excess lung cancer risks, exceeding the $1x10^{-6}$ threshold for the measured levels of particulate matter and associated heavy metals (arsenic, chromium, cadmium and nickel) on behalf of the population living in the vicinity of copper smelter in Bor.

INTRODUCTION

The Municipality of Bor is located in the eastern part of Serbia. It has a total population of 65000. Bor town is recognized as a black spot of Serbia, as a non-healthy place to live due to its poor air quality.

RTB Mining Company is one of the European largest smelting complexes, with an international reputation as a highly polluted area that has been mined for more than one hundred years. Smelting caused much of the ecological damage via acid rain and elevated levels of various metals in the vicinity of smelters. Principal air pollutants emitted from copper smelters are sulfur dioxide and the particulate matter from the processes. The amount of SO_2 depends on the characteristics of the smelting ores and whether facilities are in place for capturing and converting the SO_2.

Air pollution may results in health effects on the populations, which might be either chronic (arising from long-term exposure) or acute (due to accidents). Air pollution and the problems it causes are not confined by any boundaries. In general, exposure to SO_2 irritates the human upper respiratory tract. The most serious air pollution episodes occurred when there was a synergistic effect of SO_2 with PM and water vapor. SO_2 is the precursor of secondary fine sulfate particles, which in turn affect human health and reduce visibility.

The health effects of PM_{10} and $PM_{2.5}$ are well documented. There is no evidence of a safe level of exposure or a threshold below which no adverse health effects occur. Health effects associated with PM are linked to respiratory, cardiovascular health problems and premature mortality. Many of epidemiological studies focused on associations between daily respiratory symptoms and/or lung function and particulate air pollution (Pope and Arden, 2000). Pope et al (2002) performed a significant project that linked particle pollution ($PM_{2.5}$) to lung cancer (and cardiopulmonary disease).

The five toxic trace metals attached to the particulate matter, As, Cd, Cr, Ni and Pb, are classified according to IARC (2009) as a carcinogenic to humans. Most of those toxic trace metals are in the form of fine particles with a size distribution equivalent to that of aerosols with diameters of 1.0 μm or less. (Pope et al , 2002) In this sense, we have characterized the fine particulates by those five heavy metal contents in order to evaluate possible cancer health effects.

Although, oral arsenic exposure is the predominant exposure route, air is also an important source of arsenic, especially in area with industrial activity. In mining area, arsenic in air is attached to particular matter and is usually present as a mixture of arsenite and arsenate, with negligible amount of organic arsenic species. The US EPA has estimated that approximatelly 40 to 90 ng of arsenic per day are typically inhaled by humans. (US EPA, 2006) The presence of arsenic in air borne particulate matter is considered a risk for certain diseases. The WHO reported moderate increase in lung cancer mortality in population living near copper smelters and other point sources of arsenic. (WHO,2005)

To date, no one study in Serbia has assessed the respiratory effect in children and adults of exposure to industrial air emissions.

Resident areas of Bor town are located close to industrial area and therefore have a high level of exposure. Despite the 150 m tall stack, air quality monitoring in the Bor town measured elevated levels of As, Pb, Cd, Ni and some other elements from site operations. For example, the recorded average levels of As in $PM_{2.5}$ during the period when the smelter works were 46.4 ng/m^3. The typical concentration of As in rural area of Europe ranges 0.2-1.5 ng/m^3 and 0.5-3.0 ng/m^3 in urban areas. (Mandal and Suzuki, 2002) Those concentrations indicate that the content of As in Bor air is about 15 times above what would be expected in an area unaffected by smelting activities and about 5 times higher comparing with the Huelva, the biggest copper mining town in Spain and the second one in Europe in terms of Cu production. (Sanchez-Rodas et al, 2012)

METHODOLOGY

In this research, we investigated the public health risk associated with atmospheric exposure to particulate matter for different observational periods: non-heating season (NHS), heating season (HS), smelter works (SW) and smelter does not work (SOW) in the vicinity of copper smelter in the Bor, Serbia.

The campaign was performed during four intensive observational periods and results were calculated separately according to the data for each period. A total of 104 samples of particulate matter on a daily base were collected from September 2009 until July 2010 with low volume sampler Sven/Leckel LVS3 from the yard of kindergarten "Bosko Buha" located 300 m downwind of RTB Copper smelter. Mass concentrations of loaded filters were determined by gravimetric analysis. The filters were digested in an acid solution and analyzed for elements content by inductively coupled plasma emission spectrometry.

The two individual risks (pediatric asthma emergency room visits and lifetime excess for lung cancer) were calculated using the mean values of PM and associated metals for observed periods as an approximation of diurnal situation for air quality in Bor town. In order to calculate excess cancer risk the fine particulates were characterized by their heavy metal content previously.

Human health risk assessment methodology proposed by US EPA was apply for the assessment of the relationship between the intensity of the environmental contamination with heavy metals associated with particulate matter and the potential risk to human health. (US EPA, 2005).

The unit risk methodology utilized in this assessment to calculate number of pediatric asthma emergency room visits was based on the two study conducted in Atlanta and Seattle by Levy et al (2002). For the calculation of individual risk for pediatric asthma emergency room visit the average body weight of 33.7 kg for the population younger than 18 years and inhalation rate of 1.2 m^3/h were taken from US EPA Exposure Factors Handbook (EFH) (1997) The unit risk for $PM_{2.5}$ exposures is 1% per unit increase (measured in μg/m^3). The unit risk for PM_{10} exposures is 0.7% per unit increase.

Individual lifetime lung cancer risks for the exposed population of Bor town were investigated for five carcinogens (three known and two probable) using the access of Greene1 and Morris (2006). Excess cancer risk (ECR) was calculated for each elements separately in order to estimate the potential carcinogenic risk due to exposure to those metal via inhalation. The exposure concentration used to determine potential carcinogenic effects, however, must be averaged over the entire lifetime (assumed to be 70 years) regardless of the length of time which the receptor is assumed to be exposed.

RESULTS AND DISCUSSION

Figure 1 presents the heavy metal distributions during the four observation periods. Although the mass concentration of fine particulate measured during period when the smelter was out of operations were lower for 14.2 % comparing with value obtained during the working period of smelter, the content of associated five toxic metals were for 72.5 % higher during smelting operations. The distribution of heavy metals also varied during non-heating and heating season. The sum of recorded values of heavy metals during non-heating season was 1.7 times lower comparing with heating season. Lead comprised most of the toxic metal content during the whole observation period. The highest percentage of lead was recorded during period when smelter works (0.48%). Almost the same percentage of lead was calculated during heating season (0.46%) The highest values for arsenic, cadmium and nickel were also recorded during smelter activities. The highest value for chromium was recorded during non-heating season. Cadmium had the lowest content of the heavy metals with 0.020% during smelting activities which is 10 times higher comparing with recorded value for period when the smelter was out of work.

The box plot chats given at Figure 2 illustrate the content of fine particulate matter during different observation periods. The data of mean $PM_{2.5}$ content were used for the calculation of air quality index.

The air quality index was calculated for each observation periods. As could be seen in Table 1, numerical values in the air quality index showed that the average levels during observation periods range from moderate to unhealthy for sensitive groups (during heating season).

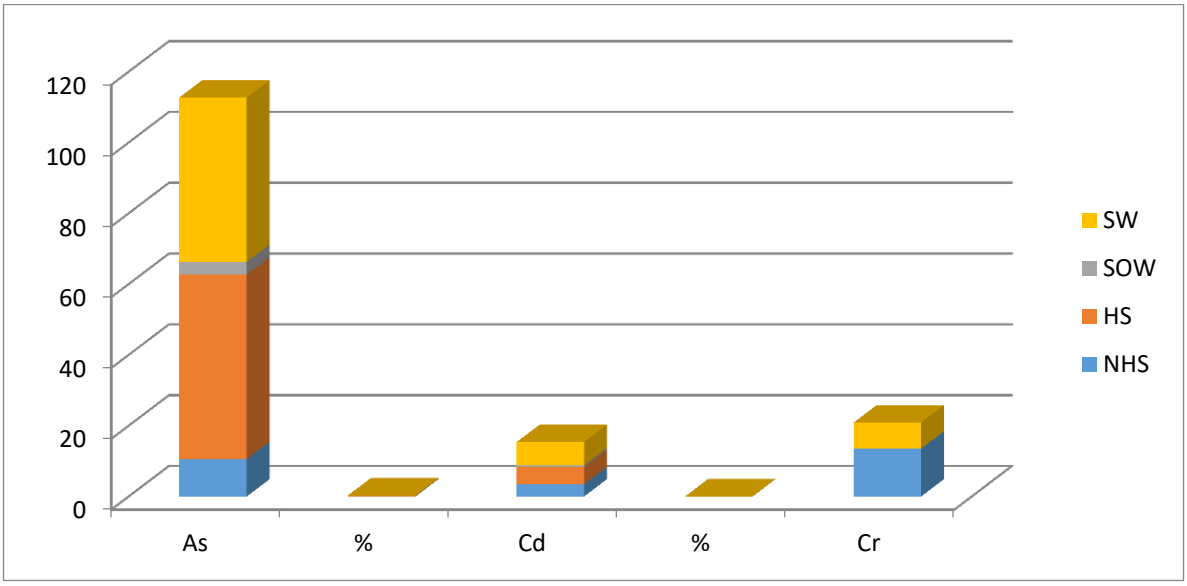

Figure 1. *Mean values for heavy metal content of $PM_{2.5}$ during observation periods*

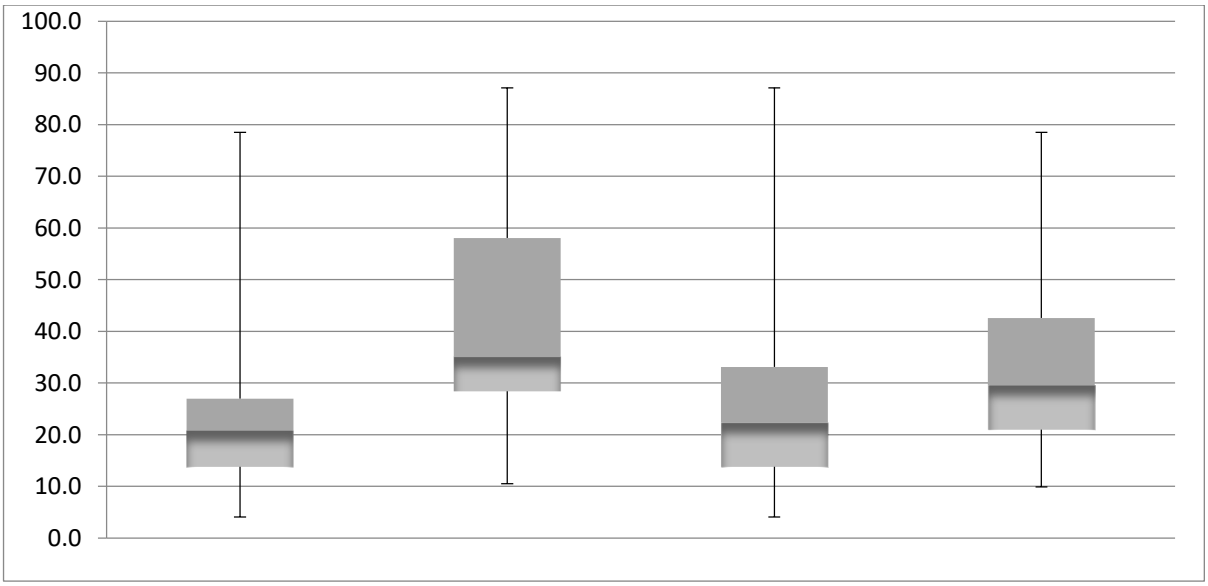

Figure 2. *Box blot for $PM_{2.5}$ during observation periods – NHS, HS, SOW, SW respectively*

The estimated excess cases for pediatric asthma emergency room visit for different observation periods were given in Table 2. Comparing the results for individual risk values in pediatric asthma emergency room visits (target population in this assessment youth < 18 year) when exposed to fine particulate there is not a significant difference between the period when the smelter does not work and works. The data has shown number of person that may be affected by the exposure of $PM_{2.5}$ are almost equal 2.9 during smelting operation and 3.3 during no smelting activities.

The results for the calculated excess cancer risk for different observation periods are summarized in Table 3.

According to the results the most threatening heavy metals to the population of Bor are As and Cr. The As and Cr values of $55.73x10^{-6}$ and $24.70x10^{-6}$ recorded during the period of smelting are the most significant contributors in this assessment for lung cancer risk. The calculated individual excess risk for lung cancer via exposure to As is 18.3 times higher during period when the smelter works. The same results were calculated for Cd, 18.4 times higher. The value for individual excess lung cancer risk for Ni during period when the smelter works was $1.39x10^{-6}$.

Table 1. *Calculated air quality index for different observation periods*

AQI range	AQI category	Calculated AQI				
			NHS	**HS**	**SOW**	**SW**
0-50	Good	Average AQI	63.9	102.9	74.2	70.7
51-100	Moderate					
101-150	Unhealthy for sensitive groups	min	13.3	34.1	13.3	6.6
151-200	Unhealthy					
201-300	Very unhealthy	max	158.5	163.5	163.5	163.4
301-400	Hazardous					
401-500	Hazardous					

Table 2. *Estimated excess cases for pediatric asthma emergency room visit for different observation periods*

	NHS		HS		SOW		SW	
	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$
C x 10^{-3} ($\mu g/m^3$)	33.2	23.3	50.5	42.4	40.3	28.9	41.3	33.7
Ri (%)	0.0232	0.0233	0.0354	0.0424	0.0282	0.0289	0.0289	0.0337
Individuals at risk	2.3	2.3	3.5	4.2	2.8	2.9	2.9	3.3

Table 3. *Calculated excess cancer risk for different observation periods*

ECR x 10^{-6}	NS	GS	TNR	TR
As	**12.10**	**47.19**	**3.04**	**55.73**
Cd	**1.40**	**1.83**	0.18	**3.32**
Pb	0.16	0.50	0.12	0.54
Ni	0.66	-	-	**1.39**
Cr	**42.97**	-	-	**24.70**

The calculated values for individual excess lung cancer risk for Pb, Ni and Cr are lower than $1x10^{-6}$ during period when smelter does not work. According to US EPA any cancer risk lower than $1x10^{-6}$ is considered negligible. The calculated individual excess risk for lung cancer via exposure to Pb were lower than $1x10^{-6}$ during whole observation periods indicating an estimate of the probability for no individual risk of developing lung cancer over a 70 year lifetime via exposure to Pb from outdoor air.

The data reflects a clear distinction between risks during period when smelter works and does not work.

CONCLUSIONS

The current study is the first to assess the risk of exposed to emission from the copper mining activities.

According to the calculation of individual risk of pediatric asthma emergency room visits for the population younger than 18 years there is no significant difference period when the smelter does not work and works.

The results showed that the exposure to some toxic metal via inhalation emitted from smelter represent potential hazard to the health of Bor inhabitants. This study has shown increased individual risk for developing lung cancer during lifetime for the population living in the vicinity of copper smelter in Bor if they are exposed to the recorded values of As, Cd, Ni and Cr via air.

Those worrying results indicate that more rigorous strategies for controlling emissions are needed. Further efforts to reduce exposure of heavy metals attached to particulate matter should be made.

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REFERENCES

1. Greene N.A., Morris V.R. 2006. Assessment of Public Health Risks Associated with Atmospheric Exposure to PM2.5 in Washington, DC, USA, Int. J. Environ. Res. Public Health 3, 86-97.
2. International Agency for Research on Cancer (IARC), 2009. Agents reviewed by the IARC monographs: volumes 1-100A.
3. Levy J.I., Greco S. L., Spengler J.D., 2002. The importance of population susceptibility for air pollution risk assessment: A case study of power plants near Washington, DC. Environmental Health Perspectives, 110, 1253-1260.
4. Mandal B. K., Suzuki K. T., 2002. Arsenic round the world: a review , Talanta, 58, 201-235.
5. Pope, C. Arden III. 2000. Epidemiology of Fine Particulate Air Pollution and Human Health: Biologic Mechanisms and Who's at Risk? Environmental Health Perspectives, 108, 713-723.
6. Pope, C. Arden III; Burnett, Richard T.; Thun, Michael J.; Calle, Eugenia E.; Krewski, Daniel; Ito, Kazuhiko; Thurston, George D., 2002. Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air pollution. Journal of the American Medical Association, 287, 1132-1141.
7. Sanchez-Rodas D., Sanchez de la Campa A., Oliveira V., De la Rosa J., 2012. Health implications of the distribution of arsenic species in airborne particulate matter, Journal of Inorganic Biochemistry, 108, 112-114.
8. U.S. Environmental Protection Agency, 1997. Exposure Factors Handbook, EPA/600/P-95/002Fa
9. US EPA, 2005, Guidelines for Carcinogen Risk Assessment. 70 FR 17765-17817.
10. US EPA, 2006. Inorganic Arsenic, Toxicity and Exposure Assessment for Children's Health. TEACH Chemical Summary, http://www.epa.gov/teach/chem_summ/Arsenic_summary.pdf , Accessed November 2016.
11. WHO, 2005. Air quality guidelines for particulate matter, nitrogen oxide and sulphur dioxide, Summary of risk assessment, Global update

8.5 METALS IN AIRBORNE PARTICULATE MATTER: WHAT DO WE KNOW ABOUT THEIR TOXICITY?

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ABSTRACT

This paper reviews the available information on the toxicity of metals commonly detected as air pollutants. Except for heavy metals, metallic components of PM mainly include transition metals. Experimental studies indicate their action as free radicals and catalysts. Though inhalation of high concentration of transition metals (especially of nanoscale particles) produces metal fume fever, illness with symptoms typical for acute inflammatory reaction, ambient air concentration of metals may be too small to be biologically relevant. On the other side, a substantial number of epidemiologic studies showed significant association between metals in ambient PM and health effects. Though we should have in mind that ambient PM is a complex mixture, with multiple agents which may interact in undefined ways, some results of epidemiology studies seem to be internally consistent in identifying group of transition metals (Fe, Ni, V, Zn) as potentially more harmful than others (As, Cu, Mn, Se).

INTRODUCTION

Particulate air pollution is associated with acute and chronic health effects, primarily affecting respiratory and cardiovascular systems, which are attributed to non-specific underlying mechanisms like inflammatory injury and oxidative damage. The generally accepted view is that the size of the airborne particles and their surface area determine the potential to generate biological effects and much less is known about the influence of particle composition. Anthropogenic air pollution is mostly caused by the coal and oil combustion, traffic and industrial processes. Depending on a source, particles contain carbonaceous components, minerals, ions (like sulfate or nitrate) and various metals. (WHO, 2006) However, little information is and available on contribution of metallic fraction to the particulate matter (PM) toxicity.

This paper reviews the available information on the toxicity of metals which are most commonly detected worldwide as air pollutants.

HEAVY METALS

Metallic components of PM mainly include transition metals (Cakmak et al, 2014). Some of them, belonging into the group of heavy metals, like lead (Pb), mercury (Hg) and cadmium (Cd), are well known for their toxicity (WHO, 2007). Air pollution is just one among many sources of exposure to these metals, but because of their persistence and potential for global atmospheric transfer, their concentration in the air is routinely controlled as part of total suspended particles or PM.

Long term lead exposures have adverse effects on central nervous system in fetuses, infants and children resulting in intellectual and behavioral disorders (Chen et al, 2005; Jusko et al, 2008). Poisoning resulting from acute massive exposure to lead by inhalation or ingestion is manifested by abdominal colic, encephalopathy, anemia, neuropathy and nephropathy. Chronic lead nephropathy, which is a slowly progressive interstitial nephritis resulting from excessive cumulative exposure to lead is frequently associated with hypertension and gout. Furthermore, lead exposure at much lower levels acts as a cofactor with other more established renal risk factors for chronic kidney disease. Adverse renal effects have been reported at mean blood lead levels of less than 5 mcg/dL. Cumulative lead dose has also been associated with worse renal function. It may be additional cause of hypertension which has been associated epidemiologically with lead exposure (Navas-Acien et al, 2007).

In vivo and in vitro studies have shown that chronic lead exposure causes oxidative stress, promotes inflammation, raises vasoconstrictor and lowers vasodilator activity, alters the renin-angiotensin system. These actions and other subtle mechanisms of lead toxicity may promote hypertension, atherosclerosis, thrombosis, and cardiovascular disease (Vaziri 2008).

Mercury is toxic in the elemental and inorganic forms, but the main concern is associated with the organic compounds, especially methylmercury, that accumulate in the food chain, which is the main route of general population exposure. Fetuses exposed in utero are the most severely affected. Mercury toxicity most commonly affects the neurologic, gastrointestinal and renal organ systems. Neurological and behavioral disorders may be observed after inhalation, ingestion or dermal exposure to different mercury compounds. Symptoms include tremors, insomnia, memory loss, neuromuscular effects, headache, cognitive and motor dysfunction. Acute exposure caused by inhaled elemental mercury can lead to pulmonary symptoms resembling metal fume fever. Mild, subclinical signs of central nervous system toxicity can be seen in workers exposed to an elemental mercury. Kidney effects have also been reported (European Commission 2002, Bernhoft 2012).

The major sources of inhaled cadmium are cigarette smoke and some industrial processes. Exposure to high concentration of cadmium in the air in occupational settings may produce acute metal fume fever. Long term cadmium exposures are associated with kidney and bone damage. Even minimal environmental exposure to cadmium is supposed to cause skeletal demineralisation (Staessen 1999). Cadmium has also been identified as a potential human carcinogen, causing lung and renal cancer. (Il'yasova et al, 2005; Godt et al, 2006; Park et al, 2012).

TRANSITION METALS

Except for heavy metals, based on their prevalence in ambient air and toxicity, review of the literature identified following metals and metalloids which may pose the greatest potential risk to human health: arsenic (As), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), selenium (Se), titanium (Ti), vanadium (V), and zinc (Zn) (Cakmak et al, 2014). Many of them are normal constituents of the human body and are essential for activation of certain enzymes necessary for normal physiological functions. Transition metals can exist in different oxidation states, which may influence their bioavailability and toxicity. They probably cause local damage by generating ROS during redox cycling between lower and higher-valent forms. Thus Cr^{6+} is classified as carcinogenic, while Cr^{3+} is not. Metal carcinogenicity is probably primarily related to the particular metal compound or complex, rather than to the metal in general. Complex and chelate formation is a common characteristic of metal ions that are found to have carcinogenic properties. Metals may contribute to oxidative stress produced by organic compounds through redox cycling of quinone-based radicals which includes complexing of metal resulting in depletion of antioxidants by reactions between quinones and thiol-containing compounds. Metals directly support electron transport to generate oxidants and also diminish levels of antioxidants (Halliwell et al, 1984).

Toxicity in occupational settings

Though occupational studies may not be representative for general population exposure, they provide some valuable information on metals toxicity. Metal fume fever is influenza-like syndrome that occurs several hours after exposure to fumes of metals, usually zinc, but also copper and some other metals and their oxides (Mueller et al, 1985). Pathophysiology of this disease includes toxic and immunologic mechanisms via free oxygen radical formation and cytokine responses (Blanc et al, 1993, Fine et al, 1997, Kuschner et al, 1997, Lindahl et al, 1998). If we have in mind that a free-radical may be defined as any species that has one or more unpaired electrons, this broad definition, except for the oxygen molecule itself, the hydrogen atom (one un-paired electron), also includes most transition metals.

Chronic inhalation of copper sulfate produces pulmonary fibrosis with histiocytic granulomas (“vineyard sprayer’s lung”) and adenocarcinomas or sarcomas (Kuratsune et al, 1974, Plamenac et al, 1985). Copper ions mediate site-specific tissue damage by generating –OH (Samuni et al, 1981). Nickel is classified as carcinogenic, and inhalation is associated with specific histological changes in the nasopharynx and upper respiratory tract, asthma, pulmonary fibrosis, nasal and lung tumors (IARC 1990, Grimsrud et al, 2002). In occupational settings selenium appears to primarily produce respiratory symptoms, but there is a possibility of concurrent exposure to many other compounds in workplace. Some selenium compounds act as sever irritants of respiratory tract (Fan et al, 2015). High concentration of Fe may accumulate in the lung, but there is no significant impairment of lung function. However, occupational siderosis and welders' lung may be associated with obstructive airways disease and pulmonary fibrosis (Billings et al, 1993). Exposure to zinc during galvanization process is associated with a high prevalence rate of metal fume fever (Cooper 2008).

Exposure to Transition Metals in Ambient Air

Association between morbidity and mortality with levels of individual transition metals in ambient PM was examined by numerous epidemiological studies and some evidence suggests that this fraction may contribute to adverse health effects.

Assessment of association between particulate and gas-phase components of urban air pollution and daily mortality in eight Canadian cities showed possitive correlation for PM2.5, Zn, Ni, and Fe, and mortality from lag 1 day data (Burnett et al, 2000). Both single and multi-pollutant models showed similar percent increases for Zn, Fe, and Ni in daily non-accidental deaths. Correlations were not found for As, Cr, Cu, Mn, Se, Ti and V. Study conducted in six US cities indicated that Pb and Ni were associated with total mortality (Laden et al, 2000). V and Fe were statistically associated with increases in daily mortality when evaluated separately, but were no longer significant if modeled simultaneously with sulfur, Ni and Pb. Daily cardiovascular mortality rates in 60 cities were associated with Ni and V. No significant associations were reported for As, Cr, Cu, Fe, Mn, Se, or Zn (Lippmann et al, 2006). Results of this epidemiological study were not supported by the results of the mouse model of atherosclerosis in experiment conducted by the same group of investigators. They concluded that known biological mechanisms cannot account for the significant associations between Ni and acute cardiac function changes in mice or with cardiovascular mortality in people at low ambient air concentrations. PM2.5 mass and several constituents were associated with multiple mortality categories, especially cardiovascular deaths in six California counties. Among metal components, significant association was found with Cu, Fe, Ti, V and Zn, but not Mn or Ni (Ostro et al, 2007). Study conducted in 25 US communities showed the increase of 0,74% in nonaccidental deaths associated with a 10 microg/m^3 increase in 2-day averaged PM2.5 mass concentration. It was more pronounced when PM2.5 mass contained a higher proportion of Al, As, sulfate, Si and Ni. No significant associations were found for Cr, Fe, Mn, V, or Zn (Franklin et al, 2008).

Elderly people are expected to be more susceptible to air pollution and many studies focus on aging population. Significant positive association between short-term changes in V concentration in the air (average concentration of 3 ng/m^3) and Ni (average concentration of 2 ng/m^3) and a higher risk of cardiovascular and respiratory hospitalization for persons aged 65 or older was found for 106 US continental counties with available PM2.5 and hospital admissions data (Bell et al, 2009). Results of CALFINE study (Ostro et al, 2007*)* showed increases in mortality associated with Zn for 1 and 3-day lags for people older than 65. There were also associations for Cu, Fe, Mn, Ti, V and Zn (but not for Ni) and daily mortality during the cooler months (average concentration for Fe was 124 ng/m^3, for the other metals 2-12 ng/m^3).

Air quality data on trace metals, other constituents of PM2.5 and criteria air pollutants were used to examine relationships with long-term mortality in a cohort of male US military veterans (aged 60 years or older), along with data on vehicular traffic density (Lipfert et al, 2006). Long-term mortality (during 1997-2001 period) was associated with Ni (average concentration of 1.73 ng/m^3) and V (average concentration of 1.90 ng/m^3), but not with As, Cu, Fe, Mn, Se or Zn. Study of hospital admissions because of cardiovascular disorders in Atlanta from 1998 to 2006 in 64-year or older people indicated that Cu, Fe oxides, Mn, Ti and Zn 24-h concentrations were associated with increased odds for hospital admissions (Suh et al, 2011).

Children may be the most vulnerable subpopulation exposed to air pollution. Short term association between ambient Zn and pediatric asthma exacerbations in 17-year or younger children was examined by Hirshon et al, (2008). Previous day medium levels of Zn (8.63-20.76 ng/m^3) were associated with 1.23 times higher risks of pulmonary function worsening comparing with previous day low levels of zinc (below 8.63 ng/m^3). Higher levels of Zn (above 20.76 ng/m^3) were associated with a 1.16 times higher risk. Another study on children, aged 2 years and younger living in certain New York areas, showed that increases in ambient Ni and V concentrations were associated significantly with increased probability of wheeze. Total PM2.5 was not associated with wheeze or cough and Zn was significantly negatively associate (Patel et al, 2009). Study conducted in California indicated positive correlation between increase in concentrations of Cu, Fe, K and Zn and hospital admissions for all respiratory symptoms at 1 and 3-day lags in 19-year old or younger persons (especially under 5 years old) (Ostro et al, 2009).

More reliable data were expected form studies on human volunteers, but they provided only weak evidence for the involvement of metals. Studies included measurements of pulmonary and cardiovascular functions parameters or analyses of indicators of inflammation and ROS in persons exposed to various levels of ambient PM containing transition metals. Association between pulmonary function in twenty-nine patients with chronic

obstructive bronchitis, asthma, or ischemic heart disease and air pollution (PM10 and PM2.5 including content of Cd, Cr, Fe, Ni, Pb, V, and Zn) was investigated in two one-month surveys (Lagorio et al, 2006). Spirometry testing results (expressed as ratio of forced expiratory volume to forced vital capacity) were in negative correlation with increasing concentrations of PM2.5, NO2, Zn and Fe in patients with chronic obstructive bronchitis. There was no association between any air pollutant and lung function in patients with heart diseases. Sorensen et al, (2005) examined the relationship between the personal exposure to water-soluble transition metals (V, Cr, Fe, Ni, Cu, Pt) in PM2.5 and oxidative DNA damage in 49 students from Copenhagen. Results indicate possible role of V and Cr independent of particle mass and/or other possible toxic compounds contained within this particulate mixture.

CONCLUSION

Basic and experimental studies indicate that metals may act as free radicals and catalysts. Inhalation of high concentration of metals (especially nanoscale particles of transition metals) produces metal fume fever, illness which symptoms are typical for acute inflammatory reaction. Though occupational inhalation of metals can produce many other significant health effects, in more modern environments, with lower permissible limits of metals in the air, exposures do not show an increased risk of mortality, cancer and other morbidity. These observations are consistent with the results of experiments in vivo and in vitro demonstrated that individual metals and extracts of metals from ambient PM can produce acute inflammatory responses only in doses which are much greater than in ambient air. From the medical point of view, the great majority of metallic constituents of PM are normal constituents of the human body and we may suppose that relatively low ambient air concentration may be controlled by body homeostasis, which means that metals concentrations in PM are too small to be biologically relevant.

On the other side, a substantial number of epidemiologic studies showed statistically significant association between metals in ambient PM and health effects (respiratory and cardiovascular morbidity and mortality). The limitations of the epidemiological studies to define the role of transition metals in health effects are primarily related to the presence of co-pollutants and characterization of exposure on an individual and population level. Though we should have in mind that ambient PM is a complex mixture, with multiple agents which may interact in undefined ways, some results of epidemiology studies seem to be internally consistent in identifying group of transition metals (Fe, Ni, V, Zn) as potentially more harmful than others (As, Cu, Mn, Se).

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REFERENCES

1. Joint WHO/Convention Task Force on the Health Aspects of Air Pollution. Health risks of particulate matter from long-range transboundary air pollution. World Health Organization 2006. Available at: http://www.euro.who.int/__ data/assets/pdf_file/0006/78657/E88189.pdf.
2. Cakmak, S., Dales, R., Kauri, L.M., Mahmud, M., Van Ryswyk, K., Vanos, J., Liu, L., Kumarathasan, P., Thomson, E., Vincent, R., Weichenthal, S. 2014. Metal composition of fine particulate air pollution and acute changes in cardiorespiratory physiology. Environ. Pollut. 189, 208-214.
3. Joint WHO/Convention Task Force on the Health Aspects of Air Pollution. Health risks of heavy metals from long-range transboundary air pollution. Available at : http://www.euro. who. int/__data/assets/pdf_file/0007/78649/E91044.pdf .
4. Chen, A., Dietrich, K.N., Ware, J.H., Radcliffe, J., Rogan, W.J. 2005. IQ and blood lead from 2 to 7 years of age: are the effects in older children the residual of high blood lead concentrations in 2-year-olds?. Environ. Health Perspect., 113 (5), 597-601.
5. Jusko, T.A., Henderson, C.R, Lanphear, B.P., Cory-Slechta, D.A., Parsons, P.J., Canfield, R.L. 2008. Blood lead concentrations < 10 microg/dL and child intelligence at 6 years of age. Environ. Health Perspect., 116(2), 243-248.
6. Navas-Acien, A., Guallar, E., Silbergeld, E.K., Rothenberg, S.J. 2007. Lead exposure and cardiovascular disease -a systematic review. Environ. Health Perspect., 115, 472–482.
7. Vaziri, N. Mechanisms of lead-induced hypertension and cardiovascular disease. 2008. Am. J. Physiol., 295 (2), H454-H465.

8. Bernhoft, R. 2012. Mercury Toxicity and Treatment: A Review of the Literature. J. Environ. Public Health, Article ID 460508, 10 pages, http://dx.doi.org/10.1155/2012/460508 .
9. European Commission. Ambient Air Pollution by Mercury (Hg) Position Paper. Luxembourg: Office for Official Publications of the European Communities, 2002, ISBN 92-894-4260-3.
10. Staessen, J.A., Roels, H.A., Emelianov, D., Kuznetsova, T., Thijs, L., Vangronsveld, J., Fagard, R. 1999. Environmental exposure to cadmium, forearm bone density, and risk of fractures: prospective population study. Public Health and Environmental Exposure to Cadmium (PheeCad) Study Group. Lancet, 353, 140–1144.
11. Godt, J., Scheidig, F., Grosse-Siestrup, C., Esche, V., Branderburg, P., Reich, A., Groneberg, D. 2006. The toxicity of cadmium and resulting hazards for human health. J. Occup. Med, Toxicol., 1, 22.
12. Park, R.M., Stayner, L.T., Petersen, M.R., Finley-Couch, M., Hornung, R., Rice, C. 2012. Cadmium and lung cancer mortality accounting for simultaneous arsenic exposure. Occup. Environ. Med., 69(5), 303-309.
13. Il'yasova, D., Schwartz, G.G. 2005. Cadmium and renal cancer. Toxicol. Appl. Pharmacol., 207(2), 179-186.
14. Halliwell, B., Gutteridge, J. 1984. Oxygen toxicity, oxygen radicals, transition metals and disease. Biochem. J., 219, 1-14.
15. Mueller, E., Opens overlay Seger, D. 1985. Metal fume fever—A review. J Emerg Med., 2(4), 271-274.
16. Blanc, P.D., Boushey, H.A., Wong, H., Wintermeyer, S.F., Bernstein, M.S. 1993. Cytokines in metal fume fever. Am. Rev. Respir. Dis., 147(1), 134-138.
17. Fine, J.M., Gordon, T.,Chen, L.C., Kinney, P., Falcone, G., Beckett, W.S. 1997. Metal fume fever: characterization of clinical and plasma IL-responses in controlled human exposures to zinc oxide fume at and below the TLV. J. Occup. Environ. Med., 39, 722–726.
18. Kuschner, W.G., D'Alessandro, A., Wong, H., Blanc, P.D. 1997. Early pulmonary cytokine responses to zinc oxide fume inhalation. Environ. Res., 75, 7–11.
19. Lindahl, M., Leanderson, P., Tagesson, C. 1998. Novel aspect on metal fume fever: zinc stimulates oxygen radical formation in human neutrophils. Hum. Exp. Toxicol., 17, 105–110.
20. Plamenac, P., Santic, Z., Nikulin, A. 1985. Cyotologic changes of the respiratory tract in vineyard spraying workers. Eur. J. Respir. Dis., 67, 50-55.
21. Kuratsune, M., Tokudome, S., Shirakusa, T., Yoshida, M., Tokumitsu, Y. 1974. Occupational lung cancer among copper smelters. Int. J. Cancer., 13(4), 552-558.
22. Samuni, A., Chevion, M., Czapski, G. 1981. Unusual copper-induced sensitization of the biological damage due to superoxide radicals. J. Biol. Chem., 256,12632–12635.
23. International Agency for Research on Cancer. Chromium, nickel and welding. Lyon, France: International Agency for Research on Cancer, 1990:257–445. (IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, vol 49).
24. Grimsrud, T.K., Berge, S.R., Haldorsen, T., Andersen, A. 2002. Exposure to different forms of nickel and risk of lung cancer. Am. J. Epidemiol., 156(12), 1123-1132.
25. Fan, A.M., Vinceti, M. Selenium and its compounds. 2015. In: Raymond, D. Harbison, R.D., Marie, M., Bourgeois, M.M., Giffe,T. J., editors. Hamilton and Hardy's Industrial Toxicology, 6th ed, John Wiley & Sons, 2015, pp. 205-228.
26. Billings, C.G., Howard, P. 1993. Occupational siderosis and welders' lung: a review. Monaldi Arch. Chest Dis., 48(4), 304-314.
27. Cooper, R. G. 2008. Zinc toxicology following particulate inhalation. Indian J. Occup. Environ. Med., 12(1), 10–13.
28. Burnett, R.T., Brook, J., Dann, T., Delocla, C., Philips, O., Cakmak, S., Vincent, R., Goldberg, M.S., Drewski, D. 2000. Association between particulate- and gas-phase components of urban air pollution and daily mortality in eight Canadian cities. Inhal. Toxicol., 12(Suppl 4), 15–39.
29. Laden, F., Neas, L.M., Dockery, D.W., Schwartz, J. 2000. Association of fine particulate matter from different sources with daily mortality in six U.S. cities. Environ. Health Perspect., 108(10), 941–947.
30. Lippmann, M., Ito, K., Hwang, J.S., Maciejczyk, P., Chen, L.C. 2006. Cardiovascular effects of nickel in ambient air. Environ. Health Perspect., 114(11), 1662–1669.
31. Ostro, B., Feng, W.Y., Broadwin, R., Green, S., Lipsett, M. 2007. The effects of components of fi ne particulate air pollution on mortality in California: results from CALFINE. Environ. Health Perspect., 115(1), 13–19.
32. Franklin, M., Koutrakis, P., Schwartz, P. 2008. The role of particle composition on the association between PM2.5 and mortality. Epidemiology, 19(5), 680–689.
33. Bell, M.L., Ebisu, K., Peng, R.D., Samet, J.M., Dominici, F. 2009. Hospital admissions and chemical composition of fine particle air pollution. Am. J. Respir. Crit. Care Med., 179(12), 1115–1120.
34. Ostro, B.D., Feng, W.Y., Broadwin, R., Malig, B.J., Green, R.S., Lipsett, M.J. 2008. The impact of components of fine particulate matter on cardiovascular mortality in susceptible subpopulations. Occup. Environ. Med., 65(11), 750–756.
35. Lipfert, F.W., Baty, J.D., Miller, J.P., Wyzga, R.E. 2006. PM2.5 constituents and related air quality variables as predictors of survival in a cohort of U.S. military veterans. Inhal. Toxicol., 18(9), 645–657.
36. Suh, H.H., Zanobetti, A., Schwartz, J., Coull, B.A. 2011. Chemical properties of air pollutants and cause-specific hospital admissions among the elderly in Atlanta, Georgia. Environ. Health Perspect., 119, 1421–1428.
37. Patel, M.M., Hoepner, L., Garfinkel, R., Chillrud, S., Reyes, A., Quinn, J.W., Perera, F., Miller, R.L. 2009. Ambient metals, elemental carbon, and wheeze and cough in New York City children through 24 months of age. Am. J. Respir. Crit. Care Med., 180(11), 1107–1113.

38. Hirshon, J.M., Shardell, M., Alles, S., Powell, J.L., Squibb, K., Ondov, J., Blaisdell, D.J. 2008. Elevated ambient air zinc increases pediatric asthma morbidity. Environ. Health Perspect., 116(6), 826–831.
39. Lagorio, S., Forastiere, F., Pistelli, R., Iavarone, I., Michelozzi, P., Fano, V., Marcon, A., Ziemacki, G., Ostro, B.D. 2006. Air pollution and lung function among susceptible adult subjects: a panel study. Environ. Health, 5(1), 11–12.
40. Sorensen, M., Schins, R.P., Hertel, O., Loft, S. 2005. Transition metals in personal samples of PM2.5 and oxidative stress in human volunteers. Cancer Epidemiol. Biomarkers Prev., 14(5), 1340–1343.

8.6 THE ASSOCIATION BETWEEN SHORT-TERM EXPOSURE TO PM10 AND SOOT AND CIRCULATORY SYSTEM-RELATED MORTALITY IN BELGRADE AREA

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ABSTRACT

In this study we estimated the relationship between exposure to particulate matter and daily mortality counts attributed to circulatory system diseases in Belgrade area (Serbia). The analysis is based on the 2-year pollutant monitoring (2010-2011) and the corresponding administrative records on mortality. A slightly modified methodological approach is introduced in order to estimate the impact of increased pollutant exposure over the last few days preceding death. The circulatory system-related-mortality rates for the observed period in Belgrade area were among the highest in the EU region. According to the results, a 10-μg m^{-3} increase in PM_{10} concentrations is followed by an increase in cardiovascular outcomes in the range from 1.28 to 1.47% in elderly population. The impact of air pollution on health is well documented, and thus it is necessary to introduce rigorous emission control regulations in developing countries to ensure improvement of ambient air quality and public health indicators.

INTRODUCTION

Epidemiological studies have provided convincing evidence in support of a positive causal relationship between particulate matter (PM_{10}) and mortality occurring as a result of ischemic heart disease, cardiac arrhythmia, cardiac arrest, increased blood markers of risk and subclinical atherosclerosis (Künzli et al,, 2005). Thereby, vulnerable young and elderly populations in urban areas, along with the people with low educational attainment and socioeconomic status, disproportionately experience a pollution-related health burden (Barret, 2015). The principal purpose of this study is to examine the effects of short-term exposure to PM_{10} and soot on cardiovascular mortality in the urban area of Belgrade based on the 2-year pollutant monitoring and the corresponding administrative records on mortality. Mortality rate is chosen as an indicator since it represents a clear outcome which is not likely to be misinterpreted and unregistered like subtle health conditions (Bell et al,, 2011). Unlike previous studies that dealt with the short-term effects using lags of 0, 1, and 2 days, the present one introduces a slightly modified methodological approach in order to estimate the effects of cumulative pollutant exposure during the 3, 7 or 30 days preceding death. According to the data obtained from the Statistical Office of the Republic of Serbia (2015), circulatory system diseases were the leading cause of death in the Belgrade area with high related rates in the range from 635 to 677 per 100 000 inhabitants over the last 15 years. Comparable rates have been registered in the neighbouring countries, namely in Romania and Hungary, and are among the highest values in the EU region (The European Detailed Mortality Database).

METHODOLOGY

Daily time series data on total mortality and mortality trends due to circulatory system diseases for the years 2010 and 2011 were obtained from the Institute of Public Health in Belgrade. The concentrations of PM_{10} and soot were measured at 7 and 17 monitoring stations, respectively, uniformly distributed over the city area. Meteorological data obtained from the Global Data Assimilation System with spatial resolution of 1 degree were collapsed over a 24-hour period to provide a mean, median, maximum, minimum and range for temperature, relative humidity and atmospheric pressure. The relationship between daily counts of circulatory system related mortality and the levels of air pollutants were modeled using quasi-Poisson regression. Based on the previous studies (Samet et al, 2000a; Samet et al, 2000b; Le Tertre et al, 2002; Dominici et al, 2006; Bell et al, 2008; Peng and Dominici, 2008; Brook et al, 2010; Shah et al, 2015), the selected major confounding factors included days of the week, seasonality, nonlinear function of temperature, pressure and relative humidity.

Two separate models were specified; one for PM_{10} and the other one for soot.

The models were specified as follows, respectively:

$E(Y_t) = \exp\{\beta_1 PM\Delta 3_t + \beta_2 PM\Delta 7_t + \beta_3 PM30MA_t + \beta_4 PRSS_t + \beta_5 RH2M_t + S(time, \lambda_1) + S(temp, \lambda_2) + \alpha DOW_t\}$

$E(Y_t) = \exp\{\beta_1 Soot\Delta 3_t + \beta_2 Soot\Delta 7_t + \beta_3 Soot30MA_t + \beta_4 PRSS_t + \beta_5 RH2M_t + S(time, \lambda_1) + S(temp, \lambda_2) + \alpha DOW_t\}$

Y_t – the expected number of circulatory disease related deaths on day t; $PM\Delta 3_t$ ($Soot\Delta 3_t$) – difference between 3-day simple moving average and 7-day simple moving average of mean concentration (μg m^{-3}) of the air pollutant ending on day t; $PM\Delta 7_t$ ($Soot\Delta 7_t$) – difference between 7-day simple moving average and 30-day simple moving average of mean concentration (μg m^{-3}) of the air pollutant ending on day t; $PM30MA_t$ ($Soot30MA_t$) – 30-day simple moving average of mean concentration (μg m^{-3}) of the air pollutant ending on day t; $PRSS_t$ – daily range of pressure at surface (hPa) on day t; $RH2M_t$ – daily range of relative humidity at 2m AGL (%) on day t; $S(.,\lambda)$ – natural cubic spline of time with λ degrees of freedom (five/year for time and three in total for temperature); DOW_t – day of the week on day *t*; β_n – regression coefficients relating covariate levels to the number of deaths; and α – regression coefficient relating the day of the week to the number of deaths.

The smooth function $S(.,\lambda)$ in the model is used to adjust smooth fluctuations in mortality over time so that only short-term variation in mortality and air pollution is used to estimate β (Dominici et al, 2003).

RESULTS AND DISCUSSION

The daily mortality counts in Belgrade area for the years 2010 and 2011 included 37,540 deaths, out of which 20,081 were attributed to circulatory diseases. In general, the lowest circulatory related-death rates registered in the spring and autumn season are followed by a steady increase and prominent peaks in the middle of summer and the start of winter period. The model estimates of the association between pollutant concentrations and related mortality are shown in Table 1 and Table 2. In the presented solution, PM_{10} and soot were modelled as separate air quality indicators. Their effects on young people (<30) and individuals of non-identified age are not considered herein due to a relatively small number of observations. In the case when both pollutants were included in the model, soot has taken over explanatory power, probably due to the fact that it includes the combustion-related PM_{10} fraction originating from traffic, solid fuel burning, shipping and industrial sources, which proved to be more harmful than the secondary organic aerosol formed through photochemical reactions (Janssen et al, 2011).

The percent changes in circulatory system-related mortality with a 10-μg m^{-3} increase in PM_{10} and soot concentrations are shown in Table 3. According to the results, the death outcomes triggered by air pollution events are not immediate, but may take few days to occur. This is in compliance with the previous studies reporting that PM_{10} effects on cardiovascular mortality usually occur after a time lag of about two days (Pope and Dockery, 2006). The short-term effects of exposure to elevated PM_{10} concentrations are observed to be particularly significant in elderly population, as this group is generally more susceptible to the effects of air pollution. For them, the 10-μg m^{-3} increase in PM_{10} concentrations is followed by a moderate increase in cardiovascular outcomes ranging from 1.28 to 1.47%. Similarly, the daily number of circulatory-related deaths among all age groups increased by 1.33% for the same increment in pollutant concentrations. The higher effects of PM_{10} exposure (2.12%) over the period of 3 and 7 days preceding the fatal outcome are observed solely for the middle-aged male group. As regards soot, the higher levels do not appear to be statistically significant with the exception of elevated concentrations over the last 30 *i.e.* 7 days preceding the fatal outcome (30-day moving average and 7-day delta values) that also exert the pronounced effects on middle-aged males.

The observed impact of increased pollutant concentrations on males aged 30-65 can be explained by two factors. Firstly, unlike the elderly people who spend more time indoors, the younger population is more active and their activity patterns might have a substantial impact on timing, location and degree of pollutant exposure (Klepeis et al, 2001). Secondly, the observed gender-dependent difference in size effect of both particles for the middle-aged group may be explained by a larger diameter of upper respiratory airways and higher respiratory minute volume in males (Gehr and Heyder, 2000).

Table 1. *Model estimate of the association between PM_{10} and circulatory system-related mortality.*

	Total	Middle-aged males	Middle-aged females	Elderly males	Elderly females
PM_{10} 3 days delta	0.001***	0.002	-0.001	0.001**	0.001**
	(0.0005, 0.002)	(-0.001, 0.004)	(-0.005, 0.004)	(0.0001, 0.003)	(0.0001, 0.002)
PM_{10} 7 days delta	0.001*	0.002*	-0.003	0.001*	0.0002
	(-0.0001, 0.001)	(-0.0002, 0.004)	(-0.007, 0.001)	(-0.0001, 0.002)	(-0.001, 0.001)
PM_{10} 30 days MA	0.0004	0.003	-0.003	0.0001	0.0004
	(-0.001, 0.002)	(-0.001, 0.007)	(-0.010, 0.003)	(-0.002, 0.002)	(-0.001, 0.002)
PRSS range	-0.006*	-0.005	0.008	-0.009*	-0.005
	(-0.012, 0.0002)	(-0.026, 0.016)	(-0.021, 0.038)	(-0.019, 0.001)	(-0.014, 0.004)
RH2M range	-0.001	-0.006**	-0.001	-0.001	-0.001
	(-0.003, 0.0005)	(-0.012, -0.001)	(-0.009, 0.007)	(-0.004, 0.002)	(-0.003, 0.002)
Tuesday	-0.052*	-0.183*	-0.141	0.03	-0.087**
	(-0.106, 0.002)	(-0.371, 0.005)	(-0.402, 0.120)	(-0.055, 0.116)	(-0.164, -0.010)
Wednesday	-0.055**	-0.04	-0.123	-0.029	-0.076*
	(-0.109, -0.001)	(-0.221, 0.142)	(-0.382, 0.137)	(-0.116, 0.058)	(-0.152, 0.001)
Thursday	-0.085***	-0.029	-0.191	-0.059	-0.106***
	(-0.139, -0.031)	(-0.209, 0.152)	(-0.455, 0.074)	(-0.147, 0.028)	(-0.183, -0.029)
Friday	-0.085***	-0.158*	-0.217	-0.072	-0.073*
	(-0.139, -0.030)	(-0.345, 0.029)	(-0.483, 0.050)	(-0.160, 0.016)	(-0.149, 0.003)
Saturday	-0.060**	-0.049	-0.017	-0.021	-0.093**
	(-0.114, -0.006)	(-0.230, 0.132)	(-0.269, 0.236)	(-0.108, 0.066)	(-0.170, -0.016)
Sunday	-0.044	0.04	-0.138	-0.04	-0.055
	(-0.097, 0.010)	(-0.137, 0.217)	(-0.399, 0.122)	(-0.127, 0.047)	(-0.131, 0.021)
nsTime1	-0.197	-0.003	-0.139	-0.317	-0.165
	(-0.451, 0.057)	(-0.860, 0.854)	(-1.403, 1.124)	(-0.720, 0.086)	(-0.527, 0.197)
nsTime2	-0.729***	-0.202	-1.093	-0.898***	-0.703***
	(-1.054, -0.403)	(-1.310, 0.905)	(-2.696, 0.509)	(-1.416, -0.380)	(-1.165, -0.240)
nsTime3	-0.08	-0.312	-0.029	-0.244	0.057
	(-0.359, 0.199)	(-1.265, 0.640)	(-1.404, 1.346)	(-0.688, 0.200)	(-0.340, 0.454)
nsTime4	-0.274**	0.042	-0.291	-0.343*	-0.29
	(-0.526, -0.022)	(-0.821, 0.904)	(-1.531, 0.949)	(-0.742, 0.056)	(-0.649, 0.069)
nsTime5	0.019	-0.258	0.183	-0.164	0.16
	(-0.241, 0.278)	(-1.152, 0.637)	(-1.092, 1.458)	(-0.577, 0.248)	(-0.209, 0.529)
nsTime6	-0.337**	-0.034	-0.942	-0.409*	-0.308
	(-0.639, -0.034)	(-1.067, 0.998)	(-2.458, 0.574)	(-0.889, 0.071)	(-0.738, 0.122)
nsTime7	-0.686***	-0.807	-0.731	-0.846***	-0.584***
	(-0.988, -0.385)	(-1.840, 0.226)	(-2.225, 0.763)	(-1.324, -0.367)	(-1.013, -0.155)
nsTime8	-0.228**	0.18	-0.748	-0.226	-0.281**
	(-0.422, -0.034)	(-0.468, 0.827)	(-1.741, 0.245)	(-0.534, 0.081)	(-0.559, -0.004)
nsTime9	-0.493*	-0.333	-0.791	-0.805*	-0.324
	(-1.033, 0.046)	(-2.180, 1.514)	(-3.447, 1.866)	(-1.661, 0.052)	(-1.091, 0.444)
nsTime10	-0.059	-0.07	0.311	-0.152	-0.015
	(-0.188, 0.070)	(-0.509, 0.369)	(-0.308, 0.930)	(-0.361, 0.058)	(-0.196, 0.166)
nsTemp1	-0.052	0.458**	0.064	-0.051	-0.142
	(-0.184, 0.081)	(0.014, 0.902)	(-0.587, 0.715)	(-0.263, 0.162)	(-0.330, 0.046)
nsTemp2	0.221	1.210**	-0.398	0.351	0.036
	(-0.049, 0.491)	(0.251, 2.170)	(-1.684, 0.888)	(-0.083, 0.784)	(-0.344, 0.417)
nsTemp3	0.360***	0.279	0.259	0.338***	0.406***
	(0.220, 0.499)	(-0.195, 0.753)	(-0.429, 0.948)	(0.115, 0.562)	(0.209, 0.603)
Constant	3.675***	0.52	0.9	2.747***	3.030***
	(3.403, 3.946)	(-0.413, 1.453)	(-0.444, 2.245)	(2.317, 3.178)	(2.644, 3.416)

Note: *p<0.1; **p<0.05; ***p<0.01. Middle-aged – 30-65 years; Elderly - >65 years; PRSS – pressure at surface; RH2M – relative humidity at 2 m AGL.

Table 2. *Model estimate of the association between soot and circulatory system-related mortality.*

	Total	**Middle-aged males**	**Middle-aged females**	**Elderly males**	**Elderly females**
Soot 3 days delta	0.002	0.006	-0.005	-0.001	0.003
	(-0.001, 0.005)	(-0.004, 0.015)	(-0.020, 0.010)	(-0.005, 0.004)	(-0.001, 0.007)
Soot 7 days delta	0.002	0.009*	-0.008	0.001	0.002
	(-0.002, 0.005)	(-0.001, 0.018)	(-0.023, 0.008)	(-0.004, 0.006)	(-0.003, 0.006)
Soot 30 days MA	0.001	0.030***	-0.002	0.0001	-0.004
	(-0.006, 0.007)	(0.008, 0.052)	(-0.034, 0.029)	(-0.010, 0.011)	(-0.013, 0.005)
PRSS range	-0.007**	-0.008	0.009	-0.011**	-0.005
	(-0.013, -0.0003)	(-0.029, 0.013)	(-0.021, 0.039)	(-0.021, -0.0003)	(-0.014, 0.004)
RH2M range	-0.001	-0.006**	-0.0004	-0.0005	-0.0004
	(-0.003, 0.001)	(-0.012, -0.001)	(-0.008, 0.008)	(-0.003, 0.002)	(-0.003, 0.002)
Tuesday	-0.051*	-0.187*	-0.14	0.032	-0.085**
	(-0.105, 0.003)	(-0.374, 0.001)	(-0.401, 0.121)	(-0.054, 0.118)	(-0.162, -0.009)
Wednesday	-0.051*	-0.04	-0.121	-0.024	-0.072*
	(-0.106, 0.003)	(-0.220, 0.141)	(-0.381, 0.138)	(-0.111, 0.063)	(-0.149, 0.004)
Thursday	-0.080***	-0.026	-0.189	-0.053	-0.102***
	(-0.135, -0.026)	(-0.206, 0.154)	(-0.454, 0.076)	(-0.140, 0.035)	(-0.179, -0.025)
Friday	-0.080***	-0.155	-0.215	-0.065	-0.069*
	(-0.134, -0.025)	(-0.341, 0.032)	(-0.481, 0.051)	(-0.154, 0.023)	(-0.145, 0.007)
Saturday	-0.055**	-0.046	-0.014	-0.013	-0.091**
	(-0.110, -0.001)	(-0.227, 0.135)	(-0.267, 0.239)	(-0.101, 0.074)	(-0.168, -0.014)
Sunday	-0.042	0.04	-0.137	-0.038	-0.054
	(-0.096, 0.012)	(-0.137, 0.217)	(-0.398, 0.124)	(-0.125, 0.050)	(-0.129, 0.022)
nsTime1	-0.199	-0.028	0.029	-0.319	-0.173
	(-0.444, 0.046)	(-0.853, 0.798)	(-1.178, 1.236)	(-0.707, 0.068)	(-0.520, 0.175)
nsTime2	-0.741***	0.202	-0.972	-0.943***	-0.765***
	(-1.083, -0.399)	(-0.959, 1.364)	(-2.645, 0.700)	(-1.487, -0.400)	(-1.247, -0.282)
nsTime3	-0.076	-0.33	0.113	-0.236	0.05
	(-0.352, 0.200)	(-1.273, 0.612)	(-1.231, 1.457)	(-0.674, 0.201)	(-0.340, 0.440)
nsTime4	-0.273**	0.145	-0.311	-0.363*	-0.287
	(-0.527, -0.019)	(-0.727, 1.018)	(-1.553, 0.931)	(-0.765, 0.038)	(-0.647, 0.072)
nsTime5	0.02	0.315	0.174	-0.207	0.1
	(-0.267, 0.308)	(-0.670, 1.299)	(-1.233, 1.581)	(-0.664, 0.250)	(-0.307, 0.506)
nsTime6	-0.332**	0.419	-0.8	-0.414	-0.378
	(-0.654, -0.010)	(-0.675, 1.513)	(-2.398, 0.799)	(-0.925, 0.097)	(-0.833, 0.077)
nsTime7	-0.687***	-0.285	-0.618	-0.879***	-0.655***
	(-1.015, -0.359)	(-1.402, 0.832)	(-2.232, 0.997)	(-1.399, -0.358)	(-1.118, -0.191)
nsTime8	-0.189*	0.752**	-0.895	-0.196	-0.311**
	(-0.405, 0.028)	(0.025, 1.478)	(-1.984, 0.194)	(-0.540, 0.149)	(-0.617, -0.005)
nsTime9	-0.483*	0.255	-0.798	-0.861*	-0.36
	(-1.037, 0.070)	(-1.638, 2.147)	(-3.515, 1.918)	(-1.738, 0.017)	(-1.142, 0.423)
nsTime10	-0.048	0.224	0.189	-0.177*	-0.019
	(-0.166, 0.070)	(-0.164, 0.613)	(-0.392, 0.769)	(-0.367, 0.013)	(-0.185, 0.146)
nsTemp1	-0.1	0.337	0.141	-0.109	-0.178*
	(-0.234, 0.035)	(-0.103, 0.777)	(-0.522, 0.805)	(-0.323, 0.105)	(-0.368, 0.011)
nsTemp2	0.122	0.774	-0.28	0.234	-0.01
	(-0.151, 0.395)	(-0.181, 1.730)	(-1.583, 1.024)	(-0.205, 0.672)	(-0.393, 0.372)
nsTemp3	0.346***	0.241	0.258	0.330***	0.391***
	(0.205, 0.487)	(-0.233, 0.715)	(-0.437, 0.953)	(0.105, 0.555)	(0.192, 0.589)
Constant	3.729***	0.21	0.614	2.820***	3.154***
	(3.442, 4.016)	(-0.777, 1.196)	(-0.782, 2.009)	(2.365, 3.274)	(2.749, 3.558)

Note: *p<0.1; **p<0.05; ***p<0.01. Middle-aged – 30-65 years; Elderly - >65 years; PRSS – pressure at surface; RH2M – relative humidity at 2 m AGL.

Table 3. *The percent changes in circulatory system-related mortality with a 10-μg m^{-3} increase in pollutant concentrations.*

Model 1	Total	Middle-aged males	Middle-aged females	Elderly males	Elderly females
PM10 3 days delta	1.33%	1.52%	-0.54%	1.47%	1.28%
PM10 7 days delta	0.62%	2.12%	-2.58%	1.09%	0.24%
PM10 30 days MA	0.40%	3.24%	-3.34%	0.06%	0.39%
PRSS range	-0.61%	-0.47%	0.83%	-0.90%	-0.52%
RH2M range	-0.12%	-0.62%	-0.07%	-0.09%	-0.05%
Model 2	**Total**	**Middle-aged males**	**Middle-aged females**	**Elderly males**	**Elderly females**
Soot 3 days delta	1.52%	5.64%	-5.04%	-0.60%	2.89%
Soot 7 days delta	1.59%	8.60%	-7.66%	0.91%	1.50%
Soot 30 days MA	0.62%	30.61%	-2.14%	0.10%	-3.82%
PRSS range	-0.67%	-0.79%	0.88%	-1.06%	-0.46%
RH2M range	-0.10%	-0.63%	-0.04%	-0.05%	-0.04%

Note: Middle-aged – 30-65 years; Elderly - >65 years; PRSS – pressure at surface; RH2M – relative humidity at 2 m AGL.

It is worth noting that retrospective studies have certain limitations. For instance, the exposure measurements resulting from a number of centrally located monitors can affect the estimated health risk in a way that is difficult to predict because these data do not reflect the individual exposure. An additional source of uncertainty for health risk estimation lies in the fact that, in uncontrolled retrospective studies, conclusions are made under the assumption that negligible variations in people's lifestyle occurred during the observation period, which doesn't have to be the case in the real world.

CONCLUSIONS

In this study, we calculated the relative rate (expressed as % increase) in circulatory system related-mortality per unit increase in daily PM_{10} and soot concentrations. These findings reflect not only the harvesting or aggravation of the pre-existing conditions among the most vulnerable group of people, but they also point to the importance of the day to day accumulation effect during the long-term PM_{10} and soot exposure. In order to better understand the air pollution effects on healthy people, as well as its long-term consequences, further attempts should include longer time-series and if possible, data for separate regions that could reflect the individual exposure more precisely. Further studies in the area are also required to fully understand the complex biological responses elicited by potentially additive and/or synergistic combinations of air pollutants. The results obtained could provide useful information for establishing environmental legal framework in developing countries.

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REFERENCES

1. Barrett, J. R., 2015. "Exported" Deaths and Short-Term PM10 Exposure: Factoring the Impact of Commuting into Mortality Estimates. *Environmental Health Perspectives*, *123*(1), A22.
2. Bell, M. L., Ebisu, K., Peng, R. D., Walker, J., Samet, J. M., Zeger, S. L., Dominici, F., 2008. Seasonal and regional short-term effects of fine particles on hospital admissions in 202 US counties, 1999–2005. *American Journal of Epidemiology*, *168*(11), 1301-1310.
3. Bell, M. L., Morgenstern, R. D., & Harrington, W., 2011. Quantifying the human health benefits of air pollution policies: Review of recent studies and new directions in accountability research. *Environmental Science & Policy*, *14*(4), 357-368.
4. Brook, R. D., Rajagopalan, S., Pope, C. A., Brook, J. R., Bhatnagar, A., Diez-Roux, A. V., ... & Kaufman, J. D., 2010. Particulate matter air pollution and cardiovascular disease an update to the scientific statement from the American Heart Association. *Circulation*, *121*(21), 2331-2378.

5. Detailed Mortality Database, World Health Organization, Regional Office for Europe, available at: http://data.euro.who.int/dmdb/
6. Dominici, F., Peng, R. D., Bell, M. L., Pham, L., McDermott, A., Zeger, S. L., Samet, J. M., 2006. Fine particulate air pollution and hospital admission for cardiovascular and respiratory diseases. *Jama*, *295*(10), 1127-1134.
7. Dominici, F., Sheppard, L., & Clyde, M., 2003. Health effects of air pollution: a statistical review. *International Statistical Review*, *71*(2), 243-276.
8. Gehr, P., & Heyder, J. (Eds.), 2000. *Particle-lung Interactions*. CRC Press.
9. Janssen, N. A., Hoek, G., Simic-Lawson, M., Fischer, P., Van Bree, L., Ten Brink, H., ... & Cassee, F. R. , 2011. Black carbon as an additional indicator of the adverse health effects of airborne particles compared with PM10 and PM2. 5. *Environmental Health Perspectives*, *119*(12), 1691-1699.
10. Klepeis, N. E., Nelson, W. C., Ott, W. R., Robinson, J. P., Tsang, A. M., Switzer, P., ... & Engelmann, W. H. , 2001. The National Human Activity Pattern Survey (NHAPS): a resource for assessing exposure to environmental pollutants. *Journal of Exposure Analysis and Environmental Epidemiology*, *11*(3), 231-252.
11. Künzli, N., Jerrett, M., Mack, W. J., Beckerman, B., LaBree, L., Gilliland, F., ... & Hodis, H. N., 2005. Ambient air pollution and atherosclerosis in Los Angeles. *Environmental Health Perspectives*, 201-206.
12. Le Tertre, A., Medina, S., Samoli, E., Forsberg, B., Michelozzi, P., Boumghar, A., ... & Katsouyanni, K., 2002. Short-term effects of particulate air pollution on cardiovascular diseases in eight European cities. *Journal of Epidemiology and Community Health*, *56*(10), 773-779.
13. Peng, R. D., & Dominici, F., 2008. Statistical methods for environmental epidemiology with R. In *R: A Case Study in Air Pollution and Health*. Springer Publishing Company New York, NY.
14. Pope III, C. A., & Dockery, D. W., 2006. Health effects of fine particulate air pollution: lines that connect. Journal of the Air & Waste Management Association, 56(6), 709-742.
15. Samet, J. M., Dominici, F., Zeger, S. L., Schwartz, J., & Dockery, D. W. ,2000a. The National Morbidity, Mortality, and Air Pollution Study. Part I: Methods and methodologic issues. *Research Report (Health Effects Institute)*, (94 Pt 1), 5-14.
16. Samet, J. M., Zeger, S. L., Dominici, F., Curriero, F., Coursac, I., Dockery, D., ... & Zanobetti, A.,2000b. The National Morbidity, Mortality, and Air Pollution Study (HEI project no. 96-7): morbidity and mortality from air pollution in the United States. *Cambridge, MA: Health Effects Institute*. Available at: http://www.ncbi.nlm.nih.gov/pubmed/11354823
17. Shah, A. S., Lee, K. K., McAllister, D. A., Hunter, A., Nair, H., Whiteley, W., Langrish J.P., Newby D.E.**,** Mills, N. L., 2015. Short term exposure to air pollution and stroke: systematic review and meta-analysis. *bmj*, *350*, h1295., doi: http://dx.doi.org/10.1136/bmj.h1295
18. Statistical Office of the Republic of Serbia, 2015. The additionally processed mortality data, Vital statistics

8.7 AEROSOL TRANSMISSION OF LEGIONELLA PNEUMOPHILA AS A PUBLIC HEALTH THREAT

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ABSTRACT

The bacterium *Legionella pneumophila* was first discovered in 1976 after the outbreak of pneumonia among the American legionnaires in Philadelphia. Atypical pneumonia is a major clinical characteristic of disease. Although the disease occurs throughout the year, it is much more common in summer because of the greater human exposure to the sources of bacteria such as humidified air, air conditioners and swimming pools. Natural residence of bacteria are rivers, lakes, streams and hot, polluted water. Bacteria can survive in a wide range of environmental conditions. The primary task in the prevention is control and disinfection of the reservoirs of infection, especially water distribution network. As the bacteria is resistant to chlorine it is important to apply the other methods for its inactivation and removal such as filtration, heating at a temperature up to 70 ° C, copper - silver ionization etc. Detection of bacterial presence in various samples is performed only in specialized laboratories, and the PCR methodology is a sovereign procedure for detection of *L.pneumophila* in the environmental samples.

LEGIONELLA SPP. – MICROBIOLOGICAL FEATURES

The motile, aerobic Gram negative bacterium *Legionella pneumophila* was first discovered in 1976 after the outbreak of pneumonia among the American legionnaires in a hotel in Philadelphia. The disease affected 182 people, and resulted in 29 died and 147 hospitalized persons (Fraser et al, 1977).

The bacteria belong to the family *Legionnellaceae*. *Legionella* species are small (0,3 – 0,9 μm in width and approximately 2 μm in length) with polar flagella. The genomes are conserved in size (3.3 to 3.5 Mb), with 88 to 90.2% of coding regions, the GC content - 38% and 3,001 to 3,259 of predicted genes. Legionellae grow on the culture media, that is enriched with iron, and L- cysteine. They use amino acids but not carbohydrates. Some strains grow better in the addition of CO_2. The colonies are "cut-glass", shiny, convex and can be seen after 2-3 days (Gomez-Valero, et al, 2009).

Since *L. pneumophila* was first identified as a human pathogen, more than 50 species of *Legionella* have been recognized, eighteen of them have been associated with human disease. *L. pneumophila* serogroup 1 is responsible for over 84% of human disease cases worldwide. *L.bozemanii*, *L. micdadei*, and *L. longbeachae* are the next most common etiological agents of Legionnaires' disease and together account for approximately 2 to 7% of *Legionella* infections worldwide (Greenwood, et al, 2012).

ECOLOGICAL AND ENVIRONMENTAL CHARACTERISTICS

Legionella bacteria are ubiquitous organisms within freshwater environments and rarely they can be find in soil. Natural residence of bacteria are rivers, lakes, streams and hot, polluted water. Bacteria can survive in a wide range of environmental conditions, from 0ºC to 63ºC, and pH range from 5.0 to 8.5. It survives for years in the water at a temperature of 2 ° C to 8 ° C, it is tolerant to chlorine and resistant to chlorination process of water. It can be found in tanks of water. Colonization of the water distribution network is an important way of *Legionella* spreading. Unlike most other bacteria, legionellae can survive 140 days in pure distilled water at room temperature and more than a year in tap water where they use cysteine from dead bacteria and iron from water pipes for their feed. However, they are so scarce that requires taking large amounts of water to be detected. Widely reported sources linked to outbreaks include cooling towers (CTs) and other aerosol-producing devices. CTs can give rise to large outbreaks accounting for hundreds of LD cases, because of their capacity to disperse contaminated aerosols over long distances (Dondero et al, 1980). Legionellae might be transmitted via showers. Studies also show that disinfection of showerheads by chemicals or cleaning is ineffective long term given the fact that *Legionella* recolonizes the showerheads from existing biofilms in the pipes of the plumbing system. If

the shower hasn't been used for a couple of days, point it towards the floor and let the water flow for a couple of minutes. Try to keep away during this time. Than ventilate the bathroom.

The sources of contaminated aerosols can be air conditioners and objects that are usually air-conditioned, such as hospitals, hotels or guesthouses. Source of infection are often fountains, installations for hydrotherapy, humidifiers, swimming pools with turbulent flow of water, even ice machines. The infection can be also transmitted during the various invasive diagnostic procedures in the respiratory tract, and it is possible to transfer bacteria from human to human. Within human-made water systems, *Legionella* bacteria are found almost exclusively within complex biofilms (Rogers et al, 1994). The primary task in the prevention is control and disinfection of the reservoirs of infection, especially water distribution network. As the bacteria is resistant to chlorine it is important to apply the other methods for its inactivation and removal such as filtration, heating at a temperature up to 70 ° C, copper - silver ionization etc.

Water temperature is is significant for the replication of bacteria. The optimal temperature for colonization of the water heating system is between 40^0C and 50^0C. Chemical parameters such as water hardness, the concentration of free chlorine and the concentration of trace elements also contribute to colonization. Therefore, in the water systems, cold water should be really cold , and the water temperature at the tap should not exceed 20^0C. For the same reason, the water pipes leading to the building must not be placed too shallow. Legionellae also survive in cooling towers and in open channels for water cooling systems (roof above the hotel in Philadelphia). To save energy, the water in these channels (which were placed with the suction pipe air-conditioning system) is constantly circular passage of mourning cooling coils. It gradually increased the temperature of the environment in the channels and started to flourish airborne blue-green algae. The sun's rays are accelerated growth of algae in open channels with hot water supplying thus legionella food, and they are breeding reached a density that are not found in nature. As water is saturated with *Legionellae spp.* so the steam particles sucked into pipes of the ventilation system are spread throughout the building aerosol storm.Today, the air conditioning systems on board used indoor water channels and in office buildings, hospitals and hotels regularly examines the presence of legionella in water systems (Fliermans et al, 1981).

During the past years, there have been many small community outbreaks in which CTs were implicated as the most likely sources of contamination. Ten years ago, an outbreak of legionnaires disease occurred in the northern France with 18 deaths (21%) among the total of 86 cases found within a radius of 10 km around a petrochemical plant that was the probable source of contamination. The only known contamination vector is the aerosol. Smoking, silicosis, and spending more than 100 min outdoors daily as risk factors for acquiring the disease. The dispersion extended over a distance of at least 6 km from plant A, that was to long distance because studies conducted before found that legionella can survive in aerosol droplets (5μm) on the way to 1000-2000 meters from the source. The bacteria can be present in all segments of the water supply system tolerating heat (due to fatty acids, branched chain, as in thermophilic archaea) (Che et al, 2003).

Legionellae are not free-living bacteria, they usually parasitize or form a commensal relationship with free-living, freshwater,and soil amoebae. *Legionella* species multiply intracellularly in protozoas, while parasites protect bacteriafrom environmental conditions, including the effects of biocides, antibiotics, acid, and osmotic and thermal stress. Furthermore, some amoebal species expel biocide-resistant vesicles with large numbers of *L. pneumophila* bacteria, which may act as airborne agents for bacterial transmission.

L.PNEUMOPHYLA AS A PUBLIH HEALTH THREAT: CLINICAL AND EPIDEMIOLOGICAL SIGNIFICANCE

Legionnaires' disease is most strongly associated with human-made aquatic environments that contain water at elevated temperatures. Many disease outbreaks are linked to air-conditioning cooling towers and evaporative condensers, which can produce contaminated water droplets that are inhaled. *L. pneumophila* is an environmental organism and, therefore, an opportunistic and accidental pathogen of humans. Because of that, the accidental human infection is a dead end for *Legionella* replication, and person-to-person transmission has never been reported. Each year in the US and Canada are diagnosed around 18,000 people with Legionnaires' disease while in the European Union are so far reported 600 outbreaks. The incidence of disease dramatically increases in the recent years due to the installation of central air-conditioning systems in large buildings, such as office buildings, hospitals and hotels. The disease occurs when the bacteria with the air-droplets reach the pulmonary alveoli. However, new evidence suggests that another way of contracting *Legionella* is aspiration, that means choking such that secretions in the mouth get past the choking reflexes and instead of going into the esophagus and

stomach, mistakenly, enter the lung. The protective mechanisms to prevent aspiration are defective in patients who smoke or have lung disease (Newton et al, 2010).

The incubation period is 2 to 10 days. Severe atypical pneumonia is a major clinical characteristic of disease. After the prodromal symptoms, the disease begins sudden onset of dry cough and high fever (40^0C and more) with chills. Radiograph of the lungs initially shows typical infiltrates, which may progress to the consolidation of the five lobes. Bilateral infiltrates are present in 2/3 of the patients. The abscess cavity, particularly in immunocompromised patients may also appear. Liver, kidneys, gastrointestinal tract and central nervous system can be also affected (Mc Dade et al, 1977). *Legionella* can survive and multiply inside phagocytic cells, especially macrophages. Extensive lysis of phagocytic cells occurs where the bacteria rich high numbers (Cazalet et al, 2004). Milder clinical form is Pontiac fever which is the acute respiratory illness without pneumonia. It resembles viral flu. It can be predominantly caused by *L.micdadei*. The symptoms include fever, muscle pain, headache, sometimes a cough, chest and pharynx pain, diarrhea (Muder & Yu, 2002). Although the disease occurs throughout the year, it is much more common in summer because of the greater human exposure to the sources of bacteria such as humidified air, air conditioners and swimming pools. Mortality of legionnaires' disease in untreated patients ranges from 0 to 20%. All exposed persons can be ill, but increased risk of infection are for immunocompromised persons, persons with chronic lung disease, the elderly, smokers, and those receiving immunosuppressive therapy. Recent technical innovation contributing to the rise of infection with legionellae is the use of ventilators to assist very ill patients to breathe where the water that can be contaminated is used to humidify the air that is pumped in the lungs (Marston et al, 1997). Legionellae have rarely been associated with prosthetic valve endocarditits or wound infections, these are usually nosocomial infections (Higa et al, 2008).

Prompt diagnosis and treatment with effective antibiotics are important since *L.pneumophila* infection can be fatal. Respiratory samples (sputum, aspirates, washings, pleural fluids, biopsy or autopsy materials) can be examinated by microscopy or cultivation. The polymerase chain reaction – PCR can be used to detect and type legionellae in clinical and environmental samples. The detection of legionella antigen can be performed in urine samples using ELISA test. Antibodies to *L.pneumophila* can be detected in sera 8-10 days after the onset of infection and it can be useful diagnostic and epidemiological tool. Antibodies can persists for month or years and can cross-react with *Campylobacter spp*. An intravenous macrolides are also often used for treatment of pneumonia, with addition of fluoroquinolones or rifampicin in severe cases. Erythromycin is currently the drug of choice for treating legionellosis (Amsden, 2005). Serological studies have shown a significant percentage of the population with antibodies to *Legionella* spp. Considering these studies it can be concluded on frequent contact, and asymptomatic immunity after infection. Immunity to the disease is primarily cell-mediated and humoral immunity plays a minor role. Particularly vulnerable are people with impaired cellular immunity (eg, patients with AIDS). Because *L.pneumophila* is an environmental organism, there has been no selective pressure on its evolution from the mammalian immune system. Early inflammatory response is believed to control bacterial replication while cell-mediated immunity contributes to the resolution of the infection and bacterial clearance (Greig et al, 2004).

Most of Legionnaires' Disease occur as sporadic cases or epidemic may break out due to the contamination of hot and cold water, cooling towers, a spa-pools, thermal pools, respiratory therapy equipment, decorative fountains, pools with bubbles (jacuzzi, whirlpool, etc.).An obvious way of preventing infection is to eliminate bacteria from water-supplies that might produce aerosols, which would be inhaled by humans. Efforts are also made to develop a vaccine against Legionnaires disease.

MONITORING AND PREVENTION

Legionellae are environmental bacteria and as such represents a public health problem, and their research and possible prevention are area of work of the various organizations. Knowing the risk factors for colonization of legionella in artificial water systems can greatly assist in the development of strategies for the prevention of legionellosis. The surveillance of the bacterial presence can be conduct in the following environmental samples: water (wastewater, water from water bodies or drinking water), washes from environmental objects, biofilms scraped from internal surface of water-supply, industrial, and other types of equipment (i.e.from trays in air-conditioners), or soil (Tran, 2006; Baskerville et al, 1981). Water samples for detection of legionellae (mainly 1L) are collected in polyethylene bottles. If the bottles are previously used, must be cleaned, washed with distilled water and sterilized by autoclaving (if you can not bear such a way sterilization, should be pasteurized). Chlorine and other oxidizing biocides have been inactivated by the addition of potassium thiosulfate or sodium

thiosulfate in the container (Cianciotto, 2007). The samples are transported at a temperature 6°C - 18°C. As a rule of microbiological analysis, the sample should be processed as soon as possible after receipt of the sample water (preferably on the day of sampling, especially if the samples contain biocides). The higher concentration of bacteria is obtained by membrane filtration or centrifugation. The cultivation is carried out on buffered charcoal extract (BCYE) agar / 72 h , 36°C. PCR method is also useful, rapid, specific and high sensitive tool in the examinating of environmental samples.

Prevention of infection is achieved by heating the water in contaminated systems to 55-75°C, hyper – chlorination, periodic flushing of infrequently used taps. Cold water supplies should be kept below 20°C. Multicomponent disinfectants based on hydrogen peroxide, biocides or silver - copper ionization can be used for the prevention of the growth of legionellae and supporting organisms (algae and amoebe). In the infected water system it would be necessary to dose a suitable biocides.

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REFERENCES

1. Amsden, G.W. , 2005. Treatment of legionnaires' disease, Drugs 65, 605-614.
2. Baskerville, A., Fitzgeorge, R. B.,Broster, M., Hambleton, P., Dennis, P.J., 1981. Experimental transmission of Legionnaires' disease by exposure to aerosols of *Legionella pneumophila*. Lancet ii:1389–1390.
3. Cazalet, C., Rusniok, C., Bruggemann, H., Zidane, N., Magnier, A., Ma, L., Tichit, M., Jarraud, S., Bouchier, C., Vandenesch, F., Kunst,F., Etienne, J., Glaser, P., Buchrieser, C., 2004. Evidence in the *Legionella pneumophila* genome for exploitation of host cell functions and high genome plasticity.Nat. Genet. 36:1165–1173.
4. Che, D., Decludt, B., Campese, C., Desenclos, J.C. , 2003. Sporadic cases of community acquired Legionnaires' disease: an ecological study to identify new sources of contamination. J Epidemiol Community Health, 57, 466–9.
5. Cianciotto, N. P., 2007. Iron acquisition by *Legionella pneumophila*. Biometals, 20, 23–331.
6. Dondero, T.J., Rendtorff, R.C., Mallison, G.F.et al, 1980. An outbreak of Legionnaires'disease associated with a contaminated air-conditioning cooling tower. N Engl J Med. 302:365–70.
7. Fliermans, C. B., Cherry, W. B.,Orrison, L. H., Smith, S. J., Tison, D. L., Pope, D.H.(1981). Ecological distribution of *Legionella pneumophila*. Appl.Environ. Microbiol. 41:9–16.
8. Fraser, D.W., Tsai , T.R., Orenstein, W., et al, 1977. Legionnaires' disease: description of an epidemic of pneumonia. N Engl J Med. 297:1189–97.
9. Gomez-Valero, L., Rusniok, C., Buchrieser, C., 2009. *Legionella pneumophila*:population genetics, phylogeny and genomics. Infect. Genet. Evol.9:727–739.
10. Greenwood,D.,Barer,M.,Slack,R.,Irving, W., 2012. Medical Microbiology Elsevier.Churchill Livingstone.339-342
11. Greig, J.E., Carnie, J.A., Tallis, G.F., et al, 2004. An outbreak of Legionnaires' disease at the Melbourne Aquarium, April 2000: investigation and case-control studies. Med J Aust. 180:566–72.
12. Higa, F., Fujita, J., Koide, M., Haranaga, S.,Tateyama, M., 2008. Clinical features of two cases of Legionnaires' disease with persistence of *Legionella* urinary antigen excretion. Intern. Med. 47:173–178.
13. Marston, B. J., Plouffe, J. F., File, T. M., Hackman, B.A., Salstrom, S.J., Lipman, H.B., Kolczak, M.S., Breiman, R.F., 1997. Incidence of community-acquired pneumonia requiring hospitalization. Results of a population-based active surveillance study in Ohio. The Community-Based Pneumonia Incidence Study Group. Arch. Intern. Med. 157:1709–1718.
14. McDade, J.E., Shepard, C.C., Fraser, D.W., Tsai T.R., Redus M.A., Dowdle, W.R., 1977. Legionnaires' disease: isolation of a bacterium and demonstration of its role in other respiratory disease. N Engl J Med 297:1197–203.
15. Muder, R. R., Yu, V.L., 2002. Infection due to *Legionella* species other than *L. pneumophila*. Clin. Infect. Dis. 35:990–998.
16. Newton, H.J., Ang, D.K., van Driel, I.R.,Hartland E.L., 2010. Molecular pathogenesis of infection caused by Legionella pneumophila, Clinical Microbiology Reviews, 23, 274-298.
17. Rogers, J., Dowsett, A. B., Dennis, P.J., Lee, J.V., Keevil, C.V., 1994. Influence of temperature and plumbing material selection on biofilm formation and growth of *Legionella pneumophila* in a model potable water system containing complex microbial flora. Appl. Environ. Microbiol.,60, 1585–1592.
18. Tran, M.et al. 2006. A Community-Wide Outbreak of Legionnaires Disease Linked to Industrial Cooling Towers—How Far Can Contaminated Aerosols Spread? J Infect Dis 193,102 -111

8.8 EXPOSURE TO AIR POLLUTION AND RESPIRATORY OUTCOMES AMONG SCHOOLCHILDREN IN NIŠ, SERBIA

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ABSTRACT

Ambient air pollution is a major risk factor for the health of the exposed population and the respiratory tract is the primary target for air pollutants, especially among children. Studies of the respiratory effects of air pollution in Serbia published in peer-reviewed journals have been infrequent. Air pollution monitoring in Niš (Serbia) started in 1966 by Public Health Institute at two monitoring sites by measuring daily concentrations of sulphur dioxide, black smoke and sediments. Health impact of air pollution to schoolchildren was studied over the last forty years, started in 1974. In this review we summarize three published studies that focus on the association between ambient air pollution and respiratory outcomes among schoolchildren in Niš. All studies demonstrate that air pollution significantly affect schoolchildren's health and increase of respiratory morbidity.

INTRODUCTION

The respiratory tract is the primary target for urban air pollutants and the respiratory effects of chronic exposure to ambient air pollution are well established (WHO, 2013). These effects manifest as inflammation of the bronchial airways, and episodes of reversible bronchoconstriction, sputum production, wheezing and asthma (Pope , Dockery, 2006; Yogev-Baggio et al, 2010; Portnov et al, 2012; WHO, 2013;Braman, 2006.). Children are more susceptible to airpollution than adults due to many reasons. Firstly, more than eighty percent of alveoli are formed postpartum, and changes in the lung continue through adolescence . Secondly, children have a larger lung surface area per kilogram of body weight than adults and, under normal breathing, they breathe 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. Several studies also indicated that exposure to air pollution tends to increase the risk of chronic respiratory symptoms (including asthma) that are associated with decreased life expectancy and may exert a lifelong effect on children's health (GINA, 2013; Zuraimi et al, 2011; Dominici et al, 2015.).

In undeveloped countries as well as in transitional countries, there is the medical and economic burden of asthma (Bateman, 2006; Fedortsiv etal, 2012.).Children living in the urban areas are particularly vulnerable (Samet, Maynard, 2005; Nordling, E. et al, 2008;). Asthma is also a major health concern in Serbia, affecting from 2.5% to 9.8% children (Zivkovic et al, 2010). The possible explanations for this worldwide increase are either genetic variability or changes in environmental factor exposure. The impact of environmental factors on respiratory diseases, particularly air pollution, seems to vary in different parts of the globe, probably owing to individual susceptibility.

Serbian National Monitoring Network Program of air quality control has been conducted from 1992 on 82 sites where 20 pollutants are being monitored (Nikic et al, 2009.). However, air pollution monitoring in Niš (Serbia) started in 1966 by Public Health Institute at two monitoring sites by measuring daily concentrations of sulphur dioxide, black smoke and sediments. Only few epidemiological studies about air pollution health effects were conducted in Serbia until 1990 (6-9) and Niš is one of the rare Serbian cities where epidemiological studies are regularly performed monitoring the health effect of air pollution.

Up to the early nineties of the previous century, Niš was an industrially developed city. The dominant sources of air pollution were industry and local heating. During the nineties, Niš, among other cities in Serbia, underwent a very difficult period being under economic sanctions and poverty.The main sources of air pollution in Niš today are energy production facilities and transportation.

In this review we summarize published studies that focus on the association between ambient air pollution and respiratory outcomes among schoolchildren in Niš.

METHODOLOGY

We searched the relevant articles, conference proceedings, and Master and PhD thesis up to 1st October 2015 regarding the objective of the paper.

RESULTS AND DISCUSSION

Health impact of air pollution to schoolchildren was studied over the last forty years, starting in 1974. Over the past decades, several studies have attemped to investigate the effects of air pollutants on respiratory morbidity of children in Niš.

In a cross-sectional population study, the author (Jevtic,1980) estimates of long-term exposure to air pollution and its association with children's lung function development. A total of 2666 children participated from 7 to 15 years [1309 males (49%) and 1357 females (51%)]. The exposed group of children were attending the two schools located in a city of Niš (considered a highly polluted area), while the children of non-exposed group, were attending the school in village Gornji Matejevac (a non-polluted area). A standardized MRC questionnaire was used to collect self-reported respiratory health and risk factor data from the parents/guardians of children attending primary schools in the study area. The long-term effects of ambient air pollution have been investigated by spirometry and anthropometric measurements were done during 5-year investigation period.The effect of increased concentrations of air pollutants on development bronchitis was observed in urban children and positive association between the estimated levels of exposure and reduced lung function forced expiratory volume in the first second (FEV1), increased incidence of respiratory symptoms and higher prevalence rate of chronic bronchitis), without effects on growth and development.

In another study, using average monthly measurements and daily concentration of soot and sulphur dioxide, the author compared associations between the long-term effects of investigated ambient air pollutants and health of the schoolchildren (Nikolic, 2000.). The exposed group of children (N=215), aged 11–14 years, were attending the school located in a city of Niš (Serbia) with a higher level of air pollution, while the children (N=139) of non-exposed group, were attending the school in the area with a lower level of air pollution. The ambient air concentrations of air pollutants were determined in ten-year period. The standardized original structured questionnaire was completed by the parents. The study revealed a difference in the prevalence of asthma ($\chi2=0,720 < \chi2=3,841$, $p>0,05$), opstructive bronchitis ($\chi2=4,084 > \chi2=3,841$, $p<0,05$), and upper respiratory symptoms like sore throat, runny or blocked nose, cough ($\chi2=6,635$, $p < 0,01$) in children exposed to higher concentrations of air pollutants compared to the control group, and air pollution increases the risk of ambulatory visits among schoolchildren.

In another study Nikic and team (Nikic et al, 2008.) investigated impact of ordinary air pollutants (sulfur dioxide and black smoke) in concentrations regulary reported during monitoring on hospital admissions for respiratory diseases among children. The authors compared daily data of sulphur dioxide and black smoke concentrations in air with data of daily hospital admissions for respiratory diseases in children 0−14 years of age in two periods (1992−1995 and 2002−2005) in Niš, Serbia. There were totally 4 283 and 3 842 hospital admissions for respiratory diseases in children in the first (1992−1995), and the second (2002−2005) period observed, respectively. The highest number of hospital admissions was registered in children aged 0−4 years, and the lowest one in children aged 10−14 years. Statistically significant influence of pollutants on the number of hospital admissions for respiratory diseases was observed in the period 1992−1995 in children aged 0−4 years. Overall, a 10 μg/m3 increase in black smoke concentration was associated with a 3.95% (95% CI 1.29−6.67%) increase in the rate of hospital admission for respiratory diseases after three days, 4.50% (1.77−7.30%) after four days and 7.15% (1.21−13.44%) after seven days. A 10 μg/m3 increase in sulphur dioxide concentration was associated with a 1.29% (0.03−2.56%) increases in the rate of hospital admission for respiratory illness after three days. The influence of air pollution on the number of hospital admissions in older groups of children, as well as in the period 2002-2005 was not statistically significant.

The presented studies demonstrate that air pollution significantly affect children's health and increase of respiratory morbidity. It was confirmed that even relatively low levels of air pollution had impact on respiratory system of schoolchildren. Compromised air quality, as an exogenous component, together with other biological, economic and/or social factors, are significant aggravators of respiratory diseases.

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

These results concur with the results found in another studies carried out on children of the same age (Ronchetti , R et al, 2001; Wright, R.J. Brunst, K.J.,2004.) which showed that children living in highly polluted areas display a higher prevalence of respiratory symptoms and impaired lung function than those living in moderately and less. These findings are consistent with a negative impact of industrial pollution on the respiratory health of schoolchildren.

The studies provided important information (e.g. on potential confounders) that could be used in further research in the field, for example in population-level studies (multiple-group ecological studies). This type of study is strongly needed since new sources of pollution constantly appear.Moreover, based on the results of the study, a framework for environmental health interventions at the individual/ intrapersonal, interpersonal, organizational, community, and society/policy level, as well as targets for change (e.g. resources, policies, community capacity, social networks and behaviour) could be set."Primary strategies" which reduce the release of air pollutants are critical for the reduction of regional ambient air pollution levels and local traffic-related pollutant levels. Such strategies require the stringent control of automobile and truck emissions. Even under current regulatory levels of air pollutants, adverse effects of air pollution occur for many respiratory illnesses including asthma, low lung function growth, and airway inflammation. "Secondary strategies" to reduce exposure or to decrease personal susceptibility may also be required. Such strategies could include siting schools and parks away from roads with high traffic volumes; issuing warnings to the public with recommendations for reducing outdoor activity on high pollution days; and minimizing commuting time on roads especially for school commutes.

As in most studies of this type, unmeasured confounding is a real concern. 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. For this reason, they might have an effect on the parameters we measured. An analysis including socio-economic factors could highlight air pollution effects in lower socio-economic groups which could not be detected in this study.

CONCLUSIONS

To conclude, the present data support experimental and epidemiological findings according to which ambient air pollution has negative effects on children's respiratory health.

Taking into account the fact that there are cities in Serbia where measured pollutant concentrations were higher in comparison to Niš, it is necessary to perform epidemiological studies in these cities, too.

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REFERENCES

1. Bateman, E.D. 2006. The economic burden of uncontrolled asthma across Europe and Asia-Pacific region: can we afford to not control asthma?. Eur. Respir. Rev. 15, 1-3.
2. Braman, S.S. 2006. The global burden of asthma. Chest.1301 , 4-12S.
3. Dominici, F., Wang, Y., Correia, A.W., Ezzati, M., Pope, C.A. 3rd, Dockery, D.W. 2015.Chemical Composition of Fine Particulate Matter and Life Expectancy: In 95 US Counties Between 2002 and 2007.Epidemiology. 26(4),556-564.
4. Fedortsiv, O., Brozek, G.M., Luchyshyn, N., Kubey, I., Lawson, J.A., Rennie, D.C., Zejda, J.E.2012. Prevalence of childhood asthma, rhinitis, and eczema in the Ternopil region of Ukraine--results of BUPAS study. Adv Med Sci. 57(2), 282-289.
5. Global Initiative for Asthma (GINA). Global strategy for asthma management and prevention [Internet]. Vancouver (WA): Global Initiative for Asthma, 2013. Available from: http://ginasthma.org.
6. Jevtic, Z. [Impact of air pollution on the emergence of chronic bronchitis among school children].[in Serbian] Ph D Thesis, Faculty of medicine, University of Niš,1980.

7. Nikić, D., Bogdanović, D., Stanković, A., Nikolić, M., Milosević, Z. 2008. Impact of air pollution on the rate of hospital admission of children with respiratory diseases.[Article in Serbian] Vojnosanit Pregl. 65(11),814-819.
8. Nikic, D., Bogdanovic, D., Nikolic, M., Stankovic, A., Zivkovic, N., Djordjevic, A. 2009. Air quality monitoring in NIŠ (SERBIA) and health impact assessment. Env. Monit Assess. 158, 499-506
9. Nikolic, M. [Sulphur dioxide and soot as risk factors for the health of children].[in Serbian] Msc thesis, Faculty of medicine, University of Niš, 2000.
10. Nordling, E., Berglind, N., Melen, E., Emenius, G., Hallberg, J., Nyberg, F., Pershagen, G., Svartengren, M., Wickman , M., Bellander, T. 2008.Traffic-related air pollution and childhood respiratory symptoms, function and allergies. Epidemiology.19,401-408.
11. Pope III, A.C., Dockery, D.W. 2006. Health effects of fine particulate air pollution: lines that connect. J. Air. Waste Manag. Assoc. 56, 709-742.
12. Portnov, B.A., Reiser, B., Karkabi, K., Cohen-Kastel, O., Dubnov, J. 2012. High prevalence of childhood asthma in Northern Israel is linked to air pollution by particulate matter: evidence from GIS analysis and Bayesian model averaging. Int. J Environ. Health Res. 22 (3), 1-23.
13. Ronchetti, R., Villa, M.P., Barreto M, Rota R, Pagani J, Martella S, Falasca C, Paggi B, Guglielmi F, Ciofetta G. 2001.Is the increase in childhood asthma coming to an end? Findings from three surveys of schoolchildren in Rome, Italy. Eur Respir J,17,881-886.
14. Samet, J., Maynard, R. Suspectibility of children to air pollution in: Effects of air pollution on children's health and development (A review of the evidence), European centre for environment and health, Bonn Office, WHO,pp 11-13, 2005
15. World Health Organization (WHO). Review of evidence on health aspects of air pollution – REVIHAAP project: final technical report. Copenhagen: WHO, 2013.
16. Wright, RJ. Brunst, KJ. 2013. Programming of respiratory health in childhood: influence of outdoor air pollution. Curr Opin Pediatr.25(2), 232-239.
17. Yogev-Baggio, T., Bibi, H., Dubnov, J., Or-Hen, K., Carel, R., Portnov, B.A. 2010.Who is affected more by air pollution – sick or healthy? Some evidence from a health survey of schoolchildren living in the vicinity of a coal-fired power plant in Northern Israel. Health Place. 16 (2), 399-408.
18. Zivković, Z., Vukašinović, Z., Cerović, S., Radulović, S., Zivanović, S., Panić, E., Hadnadjev, M., Adžović, O. 2010. Prevalence of childhood asthma and allergies in Serbia and Montenegro. World J. Pediatr. 6(4), 331-336.
19. Zuraimi, M.S, Tham, K.W., Chew, F.T, Ooi, P.L, Koh, D .2011. Home air-conditioning, traffic exposure, and asthma and allergic symptoms among preschool children. Pediatr. Allergy. Immunol. 22(1 Pt 2),e112–8.

8.9 EFFECTS OF TOBACCO SMOKE ON PREGNANT WOMEN'S HEALTH AND PREGNANCY OUTCOMES IN NIŠ, SERBIA

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ABSTRACT

The aim of the present study was to determine the effects of tobacco smoke on health and pregnancy outcomes in active and passive smoker pregnant women in Niš. This study was carried out in 812 pregnant women, ages 20-40, who lived in part of the town with low concentrations of outdoor air pollutants and were not professionally exposed to air pollution. The subjects classified as: 497 passive smokers (PS) who did not smoke but either lived with a smoker or worked in an office or ward where smoking was allowed, and 315 active smokers (AS) who smoked three to 50 cigarettes per day. Blood pressure is measured at each trimester of pregnancy. Multivariate methods were used in the analysis with adjustment for potential confounding factors (age, educational level, parity, passive smoking, genetic predisposition). There was no difference in the health and pregnancy outcomes between active and passive smoker pregnant women.

Keywords: passive smoking, active smoking, pregnancy outcomes, women.

INTRODUCTION

Nowadays smoking is a widespread phenomenon. Smoking is considered to be the risk of choice and habit. Exposure to tobacco smoke significantly increases the risk of chronic obstructive pulmonary disease, respiratory symptoms and asthma (Radon et al., 2002; Janson et al., 2001). Also, tobacco smoke has negative effects on cardiovascular diseases (Rigotii, et al., 2006), cerebrovascular diseases (Mandić and Rančić, 2011) and cancer (Sasco et al., 2004). Smoking and pregnancy are terms that should be incompatible. Unfortunately, the reality is different. Smoking during pregnancy and passive exposure to tobacco smoke are a risk for pregnancy because of numerous possible complications. Complications in pregnancy increase proportionally with the number of cigarettes smoked.

The aim of the present study was to determine the effects of tobacco smoke on pregnant women health and pregnancy outcomes in Niš, Serbia.

METHODOLOGY

The present cohort study was carried during 2012. In this study we evaluated data from a sample of 812 pregnant women, ages 20-40, who lived in part of the town with low concentrations of outdoor air pollutants and were not professionally exposed to air pollution. There was no polluting industry within 3 km radius of their place of living. The subjects are of the same ethnicity and are not alcohol consumers. Pregnant women of both groups do not have symptoms of any cardiovascular or pulmonary diseases, anemia, diabetes and pathological conditions of pregnancy.

All of these pregnant women were enrolled in early pregnancy (gestational age <10 weeks). Data on pregnancy were collected on the basis of physical examinations, fetal ultrasounds and hospital registrations in the Gynecological and Obstetrics Clinic, Niš (Serbia). They are informed about the aims of the study, the performance and the expected results of the study. Informed consent was obtained from all subjects.

We classified subjects as: 497 passive smokers (PS) who did not smoke but either lived with a smoker or worked in an office or ward where smoking was allowed, and 315 active smokers (AS) who smoked three to 50 cigarettes per day. All 812 subjects filled out a questionnaire concerning smoking habits and had a private interview with one of the investigators emphasizing the need to be truthful.

Data on age, educational level, parity, exposure of biomass fuels, and genetic predisposition were collected through interviews. Maternal interviews were done by trained workers, and completed forms were checked by field supervisors for errors.

Exposure to biomass smoke was ascertained indirectly by type of fuel used for cooking or heating. Genetic predisposition to high blood pressure and diabetes is defined by positive parental history of these diseases. Blood pressure was measured at each trimester of pregnancy in the Gynecological and Obstetrics Clinic, Niš (Serbia).

Pregnancy-induced hypertension was defined according to criteria described by the International Society for the Study of Hypertension in Pregnancy (ISSHP): development of systolic blood pressure ≥ 140 mmHg and/or diastolic blood pressure ≥ 90 mmHg without proteinuria after 20 weeks of gestation in previously normotensive women (Brown et al., 2001).

Venous blood was analyzed for hemoglobin concentration and hematocrit in the laboratory of the Clinical Care Centre, Niš (Serbia). Anemia in pregnancy has been defined by criteria from the Centers for Disease Control and Prevention (CDC) as a hemoglobin (Hb) level of less than 11 g per dL during the first and third trimesters and less than 10.5 g per dL during the second trimester and values of hematocrit (Ht) <34% (Centers for Disease Control and Prevention, 1989).

The questionnaire about respiratory symptoms and illnesses was adapted from the American Thoracic Society (Ferris, 1978) and validated questionnaires for the Serbian language. Data of the women's prevalence of respiratory symptoms (cough, phlegm, blocked-runny nose, wheezing and shortness of breath) and prevalence of respiratory illnesses (asthma, pneumonia and bronchitis, as diagnosed by their doctors) during the pregnancy were obtained through questionnaires. Training physicians filled out questionnaires during the interview with women. Respiratory symptoms were defined based on yes / no responses to the symptoms questions in the questionnaire. Pregnancy outcome variables were bleeding during the pregnancy, spontaneous abortion, stillbirth (<37 weeks of gestation) and low birth weight (< 2,500g). Birth weight was measured by the midwife that attended the birth. All statistical studies were carried out with SPSS program version 10.0. Testing of correlation of individual characteristics is performed by regression analysis (SPSS), which establishes type and strength of between the tested characteristics. Multiple logistic regression analyses were performed to analyze the relationship between health outcomes (anemia, high blood pressure and respiratory symptoms and respiratory illnesses) and exposure to tobacco smoke, as well as relationship between pregnancy outcomes (bleeding in pregnancy, spontaneous abortion, stillbirth and low birth weight) and exposure to tobacco smoke. Potential confounding factors such as age, educational level, parity, exposure to biomass smoke, genetic predisposition were adjusted for. Results are presented as adjusted odds ratios (OR) with 95% confidence intervals (CI).

Table 1. *Description of the study population included in study (n=812)*

Medical characteristics	No.(%) of women
Anemia	123 (15.14)
High blood pressure	105 (12.93)
Upper respiratory symptoms	199 (24.51)
Lower respiratory symptoms	97 (11.94)
Respiratory illnesses	112 (13.79)
Pregnancy outcomes	
Bleeding	139 (17.12)
Spontaneous abortion	105 (12.93)
Stillbirth	92 (11.33)
Low birth weight	83 (10.22)
Exposure variables	
Active smoking	315 (38.79)
Passive smoking	497 (61.21)
Confounding variables	
Age	

20-30	423 (52.09)
31-40	389 (47.91)
Education	
<12 grades	198 (24.38)
≥12 grades	614 (75.62)
Family history of respiratory illnesses, diabetes and high blood pressure	290 (35.71)
Parity	251 (30.92)
Nulliparous	561 (69.08)
Multiparous	
Use of biomass fuel	214(31.28)

3. RESULTS AND DISCUSSION

A description of the study population is given in table 1. The mean age of the pregnant women was 35 years. Women's education was high (over 75% of women had ≥ grade 12). Over thirty percent of these individual reported exposure to biomass fuel at home.

Out of a total number of studied pregnant women, over 65% were multiparous. The prevalence of medical characteristics for active and passive smoker pregnant women was from 11.94 to 24.51, while the prevalence of pregnancy outcomes was from 10.22 to 17.12.

Results of the multiple logistic regression analyses are presented in table 2 and 3.

There were no significant differences between active smoker and passive smoker pregnant women in terms of anemia, high blood pressure, upper respiratory symptoms, lower respiratory symptoms, respiratory illnesses, bleeding in pregnancy, spontaneous abortion, stillbirth and low birth weight. Only ORs for anemia (0.98 (0.87–1.09)) and bleeding in pregnancy (0.96 (0.59–1.75)) were close to unity.

Most studies which were done around the world proved the connection between the exposure to the environmental tobacco smoke (ETS) and the appearance of the respiratory symptoms and illnesses (Jaakkola et al., 2002, 2003). According to the results of our previous study in Niš which determined the effects of ETS exposure on women's health in pregnancy, we found only significantly higher prevalence of upper respiratory symptoms (χ^2=34.58;p<0.001) among the ETS-exposed pregnant women compared to non-smoking pregnant women (Stanković et al., 2011a). We also studied the respiratory symptoms in relation to ETS exposure in non-smoking women and found significantly higher prevalence of common respiratory symptoms like breathlessness (OR (95% CI): 1.27 (1.04–1.55)) and cough (OR (95% CI): 1.34 (1.11–1.61)) among the ETS exposed individuals (Stanković et al., 2011b).

People passively and actively inhaling tobacco smoke experienced disorders of iron, increase in the blood level of carboxy-hemoglobin (CO-Hb), and red blood cell metabolism, leading to anemia. Subramoney S and Gupta PC (Subramoney et al., 2008) examined whether smokeless tobacco use during pregnancy influenced hemoglobin (Hb) levels in a population-based cohort of 918 pregnant women in Mumbai, India. The results showed that anemia (Hb<10 g/dl) was significantly associated with smokeless tobacco in the univariate analysis (OR = 1.7, 95% CI 1.2-2.5). Passive smokers have significantly higher levels of CO-Hb than non smokers. Mean CO-Hb and 95% confidence intervals were 1.53% (0.78-1.85%) in smokers and 2.59% (1.89-3.29%) in passive smokers (Puente-Maestu et al., 1998).

Tobacco smoke is both prothrombotic and atherogenic, increasing the risks of cardiovascular events. In participants without antihypertensive medication from Ohasama study (Seki et al., 2010), systolic morning blood pressure in exposed ETS was 4 mmHg higher than that in non-exposed ETS (116.8 +/- 1.01 vs. 113.1 +/- 1.08 mmHg, P = 0.02) and systolic evening blood pressure in exposed ETS were 3 mmHg higher than those in non-ETS (115.3 +/- 1.02 vs. 111.9 +/- 1.09 mmHg, P = 0.03).

Table 2. *Multiple logistic regression analysis of associations between health outcomes in pregnant women and exposure to tobacco smoke (OR (95% CI)*

	Health outcomes				
Characteristics	Anemia	High blood pressure	Upper respiratory symptoms	Lower respiratory symptoms	Respiratory illnesses
Exposure to tobacco smoke	0.98 (0.87–1.09)	0.88 (0.81–1.21)	0.86 (0.76–1.54)	0.76 (0.71–1.11)	0.80 (0.70–1.09)
Age	0.80 (0.75–1.10)	0.84 (0.69–1.12)	0.86 (0.72–1.17)	0.67 (0.57–1.93)	0.81 (0.65–1.44)
Educational level	0.35 (0.27–1.43)	0.67 (0.20–1.33)	0.87 (0.63–1.23)	0.78 (0.65–1.43)	0.82 (0.71–1.09)
Use of biomass fuel	0.75 (0.31–1.45)	0.78 (0.77–1.54)	0.78 (0.45–1.41)	0.48 (0.23–1.75)	0.85 (0.47–1.01)
Parity	0.62 (0.46–1.12)	0.81 (0.66–1.11)	0.76 (0.44–1.18)	0.62 (0.77–1.23)	0.44 (0.81–1.09
Genetic predisposition	0.45 (0.77–1.02)	0.86 (0.62–1.61)	0.58 (0.63–1.28)	0.72 (0.75–1.66)	0.81 (0.89–1.79)

Exposure of non-smoking pregnant women to ETS reduces mean birth weight by 33 g or more, and increases the risk of birth weight below 2500 g by 22%, but has no clear effect on gestation or the risk of being small for gestational age (Leonardi-Bee, 2008). High environmental tobacco smoke exposure (> or = 7 hours/day in non-smokers) was moderately associated with preterm birth (AOR 1.6, 95% CL = 0.87, 2.9), and most strongly with very preterm birth (AOR 2.4, 95% CL = 1.0, 5.3) (Fantuzzi et al., 2007). Smoking during pregnancy was strongly associated with preterm delivery with a dose-response effect. ETS exposure in non-smoking women was associated only with early preterm delivery (Windham et al., 2000).

Systematic attention should be paid to socioeconomic determinants in smoking for pregnant women. To better educate the women of health effects of tobacco, anti-tobacco educational strategies and interventions need to be devised.

4. CONCLUSION

Our results suggest that active and passive smoking in pregnancy was not associated with a woman's health and pregnancy outcomes. However, monitoring the influence of tobacco smoke on mother and fetus should be intensively pursued in the future, too.

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Table 3. *Multiple logistic regression analysis of associations between pregnancy outcomes in pregnant women and exposure tobacco smoke (OR (95% CI)*

	Pregnancy outcomes			
Characteristics	Bleeding	Spontaneous abortion	Stillbirth	Low birth weight
Exposure to tobacco smoke	0.96 (0.59–1.75)	0.76 (0.76–1.09)	0.78 (0.84–1.14)	0.65 (0.70–1.58)
Age	0.80 (0.70–1.16)	0.81 (0.71–1.15)	0.84 (0.63–1.48)	0.88 (0.67–1.81)
Educational level	0.78 (0.69–1.12)	0.89 (0.70–1.13)	0.68 (0.68–1.15)	0.86 (0.78–1.37)
Use of biomass fuel	0.60 (0.65–1.25)	0.83 (0.71–1.37)	0.88 (0.63–1.58)	0.83 (0.67–1.84)
Parity	0.58 (0.66–1.11)	0.68 (0.71–1.17)	0.78 (0.79–1.16)	0.86 (0.58–1.24)
Genetic predisposition	0.83 (0.90–1.16)	0.85 (0.91–1.15)	0.66 (0.68–1.48)	0.78 (0.66–1.13)

REFERENCES

1. Brown, M.A., Lindheimer, M.D., Swiet, M., Assche, A., Moutquin, J.M. 2001. The classification and diagnosis of the hypertensive disorders of pregnancy: statement from the International Society for the Study of Hypertension in Pregnancy (ISSHP). Hypertens. Pregnancy., 20, 9-14.
2. Centers for Disease Control and Prevention. 1989. Criteria for anemia in children and childbearing-aged women. MMWR Morb Mortal Wkly Rep, 38, 400–404.
3. Fantuzzi, G., Aggazzotti, G., Righi, E., Facchinetti, F., 2007. Preterm delivery and exposure to active and passive smoking during pregnancy: a case-control study from Italy. Paediatr. Perinat. Epidemiol., 21,194-200.
4. Ferris, B.G. 1978. Epidemiology Standardization Project. II. Recommended respiratory disease questionnaires for use with adults and children in epidemiological research. Am.Rev.Respir. Dis., 118, 7–57.
5. Jaakkola, M.S., Piipari, R., Jaakkola, N., Jaakkola, J.J.K., 2003. Environmental tobacco smoke and adult-onset asthma: a population-based incident case-control study. Am. J. Public. Health., 93, 2055–2060.
6. Jaakkola, M.S., Jaakkola, J.J.K., 2002. Effects of environmental tobacco smoke on the respiratory health of adults. Scand JWork Environ. Health., 28, 52–70.
7. Janson, C., Chinn, S., Jarvis, D., Zock, J.P., Toren, K., Burney, P., 2001. Effect of passive smoking on respiratory symptoms, bronchial responsiveness, lung function, and total serum IgE in the European Community Respiratory Health Survey: a cross-sectional study. Lancet., 358, 2103-2109.
8. Leonardi-Bee, J., Smyth, A., Britton, J., Coleman, T., 2008. Environmental tobacco smoke and fetal health: systematic review and meta-analysis. Arch. Dis. Child. Fetal. Neonatal Ed., 93, 351-356.
9. Mandić, M., Rancić, N. 2011. Risk factors for stroke. Med Pregl., 64, 600-605.
10. Puente-Maestu, L., Bahonza, N., Pérez, M.C., Ruiz de Oña, J.M., Rodriguez Hermosa, J.L., 1998. Relationship between tobacco smoke exposure and the concentrations of carboxyhemoglobin and hemoglobin.. Bronconeumol., 34, 339-343.
11. Radon, K., Busching. K., Heinrich, J., Wichmann, H.E., Jorres, R.A., Magnussen, H., 2002. Passive smoking exposure: a risk factor for chronic bronchitis and asthma in adults? Chest., 122, 1086-1090.
12. Rigotti, N.A., Thorndike, A.N., Regan, S., 2006. Bupropion for smokers hospitalized with acute cardiovascular disease. Am J Med., 119, 1080-1087.
13. Sasco, A.J., Secretan, M.B., Straif, K., 2004. Tobacco smoking and cancer: a brief review of recent epidemiological evidence. Lung Cancer. 45,S3-9.

14. Seki, M., Inoue, R., Ohkubo, T., Kikuya, M., Hara, A., Metoki, H., 2010. Association of environmental tobacco smoke exposure with elevated home blood pressure in Japanese women: the Ohasama study. J .Hypertens., 28, 1814-1820.
15. Stanković, A., Mitrović, V., Živadinović, R., 2011. Uticaj zagadenog vazduha na zdravlje trudnica i ishod trudnoce. Med.Pregl., 64, 279-284.
16. Stanković, A., Nikolić, M., Arandjelović, M., 2011. Effects of indoor air pollution on respiratory symptoms of non-smoking women in Nis, Serbia. Multidisciplinary. Respiratory. Medicine., 6, 351-355.
17. Subramoney, S., Gupta, P.C. 2008. Anemia in pregnant women who use smokeless tobacco. Nicotine. Tob. Res., 10, 917-920.
18. Windham, G.C., Hopkins, B., Fenster, L., Swan, S.H., 2000. Prenatal active or passive tobacco smoke exposure and the risk of preterm delivery or low birth weight. Epidemiology., 11, 427-433.

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