WeBIOPATR2013

Particulate Matter: Research and Management

Proceedings from the
4th WeBIOPATR
Workshop & Conference
Belgrade, Serbia
2.-4.10.2013.

Milena Jovašević-Stojanović
and Alena Bartoňová, eds.

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Publisher
Public Health Institute of Belgrade
Slobodan Tošović, Director
Boulevar Despota Stefana 54 a
Serbia, 11000 Belgrade

Technical assistance
Dušan B. Topalović

ISBN 978-86-83069-40-8

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 air pollution issues.

The 1stWeBIOPATR Workshop "Particulate matter: Research and Management" 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 2ndWeBIOPATR workshop was held in Mecavnik, Serbia, 28.8.-1.9. 2009. It has attracted over 40 participants, notably also participants from the neighbouring countries and EU. The participants discussed air quality issues, research needs and management tools and strategies that are currently used in Serbia. As a new element, 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/publications&folder. Selected extended contributions are published in CHEMICAL INDUSTRY & CHEMICAL ENGINEERING QUARTERLY Vol: 16 No 3 (2010).

The 3rd event, the International WeBIOPATR Workshop and Conference, Particulate Matter Research and Management – WeBIOPATR2011, had a wider international audience, and had 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 biannual meeting, the International WeBIOPATR Workshop and Conference, Particulate Matter Research and Management – WeBIOPATR2013, included 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. From forty-six presentations, the current proceedings contain short papers of about 90% and abstracts of 10% of presentations given at the WeBIOPATR2013. The conference will also contribute to an educational program about air quality by the Serbian national TV. Selected extended contributions will be published in CHEMICAL INDUSTRY & CHEMICAL ENGINEERING Vol 20, No 3/II (2014).

Milena Jovašević-Stojanović and Alena Bartoňová

CONTENTS

1 BACKGROUND

1.1 MEASUREMENTS OF PARTICLES IN URBAN AREAS AROUND THE WORLD, A COMPARASION OF LEVELS AND CAUSES

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ABSTRACT

Airborne particulate matter varies widely in its physical and chemical composition, source and particle size. PM_{10} particles (the fraction of particulates in air of very small size (<10 µm)) and $PM_{2.5}$ particles (<2.5 µm) are of major current concern, as they are small enough to penetrate deep into the lungs and so potentially pose significant health risks. The principal sources of airborne PM_{10} and $PM_{2.5}$ matter in urban areas are mainly from road traffic emissions, particularly from diesel vehicles. However, also, windblown dust, re-suspended dust from the surface, emissions from various industries, power plants, agricultural activities and fires are also causing high particulate matter (PM) concentrations. As presented in this paper the main sources strongly vary from one region to another.

Data from selected urban monitoring programmes were selected, mainly based upon studies performed by NILU. References to other investigations performed in similar urban areas have also been included. The presentation covers a range of PM levels from the relatively clean capital of Norway, Oslo, to the highly polluted cities such as Dhaka, Bangladesh and Ulaanbaatar, Mongolia. Some of the causes to the high PM concentrations may be easy to track, while other are based on rather complicated compositions. In data collected from the Middle East cities such as Abu Dhabi and Cairo, windblown dust from the desert areas is causing the highest PM_{10} concentrations, while brick factories in Dhaka seem to be the main source for PM_{10} in Dhaka. In some areas there is also a clear regional component of smaller particles as demonstrated from satellite images. In European urban areas traffic seems to be the main source for PM.

1. INTRODUCTION

In terms of potential to harm human health, PM is one of the most important pollutants. PM in the air has many sources and is a complex heterogeneous mixture whose size and chemical composition change in time and space, depending on emission sources and atmospheric and weather conditions. Measurements of particles is usually done in two broad categories, coarse and fine fraction (less than 10 respectively less than 2.5 μ/m^3in diameter), but other metrics can also be found.

2. A “CLEAN” CITY - OSLO, NORWAY

Air quality monitoring in Oslo is carried out in a cooperation of the Norwegian Agency for Urban Environment and the Public Roads Administration. A network of 11 monitoring stations across the city monitor pollutants such as nitrogen dioxide (NO_2), particulates (PM_{10}, $PM_{2.5}$), ozone (O_3), benzene, sulphur dioxide and carbon monoxide. Nine of these sites cover PM_{10} (1).Typical daily average PM_{10} concentrations in Oslo during the year 2012 werebetween 15 and 37µg/m^3. The annual average $PM_{2.5}$ concentrations were between 8 and 14 µg/m^3(2). The main sources for the PM levels in Oslo are traffic emissions and in cold periods,with surface inversions, wood burning (3).

3. PARTICULATE MATTER IN EUROPE

The total number of monitoring stations in Europe (EU and non EU countries) reporting PM_{10} was 3040 stations in 2012. 997 stations reported$PM_{2.5}$concentrations (4).In 2010, the PM_{10}24-hour limit value (to be met by 2005) was exceeded at 33% of traffic sites, 29 % of urban background sites, and 17% of 'other' sites (mostly industrial) and even at 14% of rural sites within the EU (5). The annual average concentrations of PM_{10} in European cities varied from 25 to 80 µg/m^3, while the average $PM_{2.5}$concentrations observed in 2010 was between 8 and 30 µg/m^3.

Emissions of primary $PM_{10}$and $PM_{2.5}$decreased by 14% and 15% respectively in the EU and in the EEA-32 countries between 2001 and 2010 (6). The small reduction observed in ambient PM concentrations reflects the slowly declining emissions of primary PM and NH_3.

Twenty one per cent of the EU urban population lives in areas where the EU air quality 24-hour limit value for particulate matter (PM_{10}) was exceeded in 2010. For EEA-32 countries the estimate is 41%.EU urban population exposure to PM_{10} levels exceeding the WHO Air Quality Guideline (AQG)(7) is significantly higher, comprising 81% of the total urban population in 2010.

4. AFRICA

Large differences in reported PM_{10} concentrations are found in Africa. Well-developed cities such as Cape Town and Johannesburg in South Africa report rather low annual average PM_{10} concentrations of around 30–40 µg/m^3. In the greater Cairo area, however, the typical annual average concentrations in urban and residential areas ranged from 60 µg/m^{3}to 200 µg/m^3. In industrial areas concentrations measured were between 200 µg/m^3 and 500 µg/m^3(8).

Cairo, Egypt

Suspended dust is considered a major air pollution problem in Egypt. PM_{10} concentrations can reach daily average levels of more than 4 to 14 times the Air Quality Limit value for Egyptof 70µg/m^3 (9). The highest concentrations are normally observed in the streets of Cairo, and in industrial areas.

Measurements of PM performed in Cairo from 2000 to 2004 indicated that annual average PM_{10} concentrations in urban areas ranged between 100 and 300 µg/m^3.One type of sources, typical for Egypt, was the open air waste burning, which was observed in several areas of Egypt. This type of burning may have considerable health impact to the population. Especially in the Nile Delta it is anticipated that the toxic compounds associated with the PM concentrations may be deposited in the farming areas giving rise to large exposure to the population consuming vegetable and crops grown in these areas.

Towns in arid areas with surrounding deserts frequently receive a considerable amount of dust consisting of wind-blown fine sand. An early study of suspended dust in Cairo revealed that the typical background PM_{10} concentrations averaged 45 to 65µg/m^3 during average wind speed conditions (10, 11). It has also been found based on continuous measurements over several years that the daily background level seems to be around 70 µg/m^3, which is equivalent to the Air Quality Limit values given by the Law no. 4 of Egypt (9). These levels can be found also in areas where local anthropogenic sources do not impact the measurements (12, 13).

It has also been found based on a source attribution study that a major contribution to the PM_{10} concentrations included geological material, mobile source emissions and open air burning(14).Even inside the urban area of Cairo it was found that large fractions of the PM_{10} might be attributed to fine sand particles. During air pollution episodes, however, the burning of agricultural and other waste also contributed.In the city centre during prevailing wind from north a large fraction of the fine particle mass was produced by oil combustion.

The air pollution episodes of Cairo (later called the “black clouds”) were first identified by measurement data in October 1997 (15). These episodes are characterized by low winds, high pressure conditions and elevated inversions.These elevated inversions were established in the subsiding air mass above the Delta and the greater Cairo area.

Air pollution episodes seem to occur repeatedly every year around the month of October. Satellite pictures have also revealed that during these days fires were observed over the eastern part of the Delta (16). Wind trajectory analyses also indicated transport of air from the northerly directions towards Cairo (17). During these episodes hourly PM_{10} concentrations often were recorded above 500 µg/m^3.

Studies of PM in Cairo and in other areas of Egypt have revealed that there is a need to address garbage burning and industrial emissions. Inside the urban areas also transportation measures are important for future attainment.

Dakar, Senegal

A screening study was performed in October 2005 (18). PM_{10} and $PM_{2.5}$ were monitored in one heavily trafficated street. Some samples of PM_{10} and $PM_{2.5}$were analysed for trace elements, elemental and organic and water-soluble components to provide knowledge on the chemical composition of the particulate matter.

The daily concentrations of PM_{10} exceeded the daily EU limit value (19) every day of the sampling period. The PM_{10}levels ranged from 52 to 338 µg/m^3, with an average value of 133 µg/m^3. The $PM_{2.5}$ levels in Dakar were also high compared to concentration levels observed in other urban areas in the world (20). The average $PM_{2.5}$ concentration in the 4 weeks sampling period was 38 µg/m^3.

The elemental carbon/total carbon (EC/TC)ratios indicate that the fine particles in Dakar originate mainly from combustion sources. The average percentage of water-soluble components was 18% for PM_{10} and 15% for $PM_{2.5}$. The measured daily averages of PM_{10}concentration were 2 to 7 times higher than the EU limit values and the daily averages of $PM_{2.5}$ were also high (18). A large fraction of the $PM_{2.5}$ originates from combustion sources, while a large part of the PM_{10} coarse fraction is soil dust and sea salts. This screening study shows that the major air pollution source in Dakar is traffic, although industry is also an important source in some areas. The car fleet is old, not well maintained and contain a number of micro buses run on bad quality diesel.

5. MIDDLE EAST

Abu Dhabi, United Arab Emirates

A number of air quality monitoring stations, owned by the Environment Agency – Abu Dhabi (EAD), are being operated throughout the Abu Dhabi Emirate (21).

The air quality in the Emirate of Abu Dhabi is generally good. However, it experiences occasional exceedances for some air pollutants especially PM. One of the main sources is linked to dust from the desert areas and to the occurrence of sand storms. These “natural” sources normally give rise to the highest concentrations of suspended particles. Also particulate matter from combustion sources such as traffic and industries can be identified in the data based on chemical analyses.

The PM_{10} daily average limit value of 150 µg/m^3 was regularly exceeded every year since 2010 at all monitoring stations in Abu Dhabi. Exceedances of the PM_{10} limit value varied between 33% and 47% of the measurement time in 2012. In the urban area of Abu Dhabi, exceedances occurred between 33% and 39% of the time at the different monitoring sites (22).

While the monthly average concentrations of PM_{10} normally ranged between 100 and 200 µg/m^3 at the different monitoring stations it has been seen every year that the concentrations of PM_{10} raised to hourly averages of between 800 and 1200 µg/m^3(daily up to 800 µg/m^3) during periods with sand storms (dust clouds) sweeping over the area. This phenomenon is similar to what is observed over Cairo.

6. ASIA

Dhaka, Bangladesh

Air pollution and health have been a major focus in Bangladesh in recent years. In Dhaka air quality monitoring since April 2002 has shown that concentrations of $PM_{2.5}$ and PM_{10} represent problems (23). The highest 24-hour average PM_{10} concentration in Dhaka from 2002 to 2007, ranged between 400 and 940 µg/m^3, while the highest $PM_{2,5}$ concentrations were observed between 200 and 400 µg/m^3. The PM_{10} average concentrations for the whole period in Dhaka were between 80 and 180 µg/m^3.

Although local sourcesof air pollution in Dhaka city are quite strong, there are also high PM concentrations originating from distant sources especially during the dry season. Source receptor modelling (24) indicatesthatapart from local contribution of pollution sources, there are also regional influences on fine PM levels in Dhaka.

Two screening studies were performed during the winter season (25, 26) because this is the dry period where air pollutant concentrations will be at their peak. The range of average PM concentrations from the rainy summer season till the dry winter season varies with a factor of ten (average PM_{10} summer: 20 to 100 µg/m^3, winter: 200 to 1000 µg/m^3) (26). The winter season is also the time of the year in which thousands of brick kilns are being operated in the areas surrounding Dhaka. Emissions from these kilns are suspected to be the single greatest local contribution to the air quality problems in Dhaka. Other possible sources of air pollution include re-suspension of road dust from traffic, open air burning, residential cooking, and industrial sources such as cement manufacturing and metal smelting. Regional haze south of the base of Himalaya in India including agricultural burning as well as the use ofhigh-sulphur coal also contributesignificantlyto local concentrations of fine particles.

A total of 23 grab samples of $PM_{10}$and $PM_{2.5}$ (30 minute averages) were taken at different hours of the day and at different locations over the city of Dhaka during the month of February2011 (27). The average 30-minute concentration values ranged from 258 µg/m^3 to 2039 µg/m^3, with an average concentration of 613 µg/m^3 for all sites. The average $PM_{2.5}$ concentration from the 23 grab samples taken was 439 µg/m^3 for all sites. Measurements were also collected at one site over a 24 h period, indicating that the average concentrations of PM in Dhaka exceeded national and international air quality limit values both day and night during the winter season.

Simultaneous measurements of $PM_{2.5}$ and PM_{10} made it possible to study the ratio of the size fractions. The $PM_{2.5}/PM_{10}$ ratio of the concentrations for the samples ranges from 0.4 to 0.9, and the average for all sites was 0.8. This indicates that during the winter season PM levels in the atmospheric air are dominated by $PM_{2.5}$ fraction and smaller, and combustion sources are major contributors to the particulate air pollution in Dhaka city. It also indicated that the regional component of aerosols may play an important role.

Ulaanbaatar, Mongolia

Ulaanbaatar is affected by serious air pollution caused by coal and wood burning stoves used for heating and cooking. The new market economy of the country and its very cold winter seasons has led to the formation of Ger districts, where 60% of the coldest capital city in the world's population resides. The resulting air pollution problem is characterized by very high concentrations of airborne particles.

Daily concentrations in Ulaanbataar are much higher than Mongolian or international standards. The extremely episodic nature of the PM pollution, which is caused by the combination of Ger heating practices and the meteorological situation, causes extremely high short-term PM concentrations. The highest hourly and daily concentrations may represent the highest urban scale PM levels anywhere, with hourly PM_{10} concentrations approaching 2500 µg/m^3 or higher and daily averages above 1000 µg/m^3 in the most polluted parts of the city, i.e. the Ger districts (28). The seasonal average particulate matter concentrations have been recorded as high as 279µg/m^3 during the winter. To put this in perspective, the World Health Organization's recommended that the annual average PM_{10} level should not exceed20µg/m^3. This means that Ulaanbaatar's seasonal PM_{10}levels have been recorded 14 times higher than what is recommended as an annual mean.

Ulaanbaatar’s air pollution comes from many sources; dust from the desert, unpaved roads and open soil surfaces, lack of vegetation, ash and emissions from coal stoves, power plants, boilers, and vehicles. However, coal and wood burning for cooking and heating by the 175,000 households inGer areas contributes to the severity of air pollution in wintertime. A source receptor study for 2007 showed that 40% of the $PM_{2.5}$ concentrations came from combustion (29).The PM concentrations during the summer season are much lower than in winter (30).

Ho Chi Minh City, Vietnam

Ho Chi Minh City (HCMC), Vietnam is not the most polluted city in Asia when PM is concerned. Still the investigations performed by NILU from 2002 to 2005 showed annual average PM_{10} concentrations at the different monitoring sites ranging between 60 and 180 µg/m^3. The highest concentrations were recorded at a road side station in 2002 (31).

The main sources for PM concentrations in HCMC are the traffic, and in particular the thousands of motor bikes and small trucks (32). HCMC seems to be different from the most polluted Asian urban areas, where industries and open air waste burning seem to play a larger role.

7. PM AROUND THE WORLD

A survey of air pollution around the world was performed as part of the WHO air quality Guidelines update 2005 (33). In that study it was reported that the annual average PM_{10} concentrations in the selected Asian cities ranged from about 35 µg/m^3 to 220 µg/m^3 and in Latin America from about 30 µg/m^3 to 129 µg/m^3, while in Europe and North America the typical range of annual average PM_{10} concentrations was 15–60 µg/m^3. About 70% of the cities selected from these regions had annual average PM_{10} concentrations above 50 µg/m^3.

In general, the highest concentrations of PM_{10} were reported from Asia. This statement is also supported by more recent studies (34). This region also experience relatively high background concentrations owing to forest fires and local emissions of particles from the use of poor-quality fuels. A well-known meteorological phenomenon,associated with the winter monsoon, covering large regions of East Asia is causing the Asian brown cloud. Airborne particles originate from windblown dust in the deserts of Mongolia and China and add to the general level of PM in the region (35).

Chinese cities experience very high airborne particle concentrations due to primary particles emitted from coal and biomass combustion and motor vehicle exhaust, as well as secondary sulphates formed by atmospheric chemical reaction from the sulphur dioxide emitted when coal is burned. Typical annual average PM_{10} concentrations in Beijing have decreased from 160 µg/m^3 in 2000 to 120 µg/m^3in 2010 (36). However, the PM concentrations in Chinese cities are still extreme in shorter periods, especially during the winter season. On January 12, 2013 the PM_{10} concentration level reached “an all-time high” in Beijing of 993 µg/m^3 (37).

A selection of typical annual maximum concentrations of PM_{10} measured around the world is presented in Figure 1.

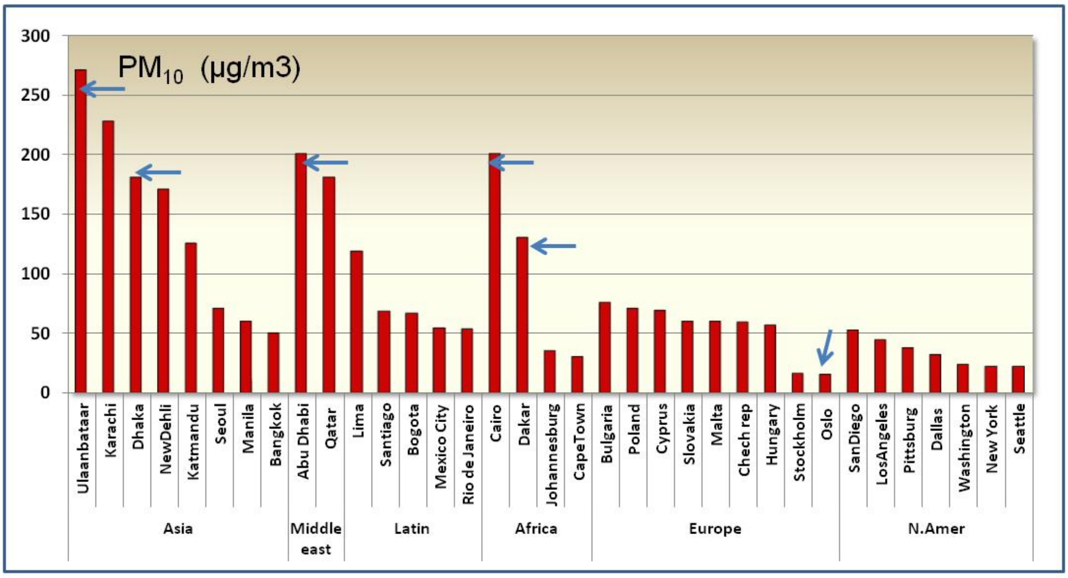

Figure 1: Selected annual PM_{10} concentrations reported around the world.
Six of the cities that were reported in this paper are marked.

The overview based on annual average concentrations does not always give a complete picture of the situation in a city. We have seen that in some urban areas there are very large differences in daily maxima from one season to another, caused by changes in sources and emission rates, meteorological conditions and naturally occurring dust from desert areas. When comparing levels and the reasons for high impact one will have to understand the complete picture. The use of source receptor modelling together with the use of satellite images has been supporting this research.

8. SUMMARY AND CONCLUSIONS

The levels of suspended particles in the air might vary considerably from one region to another, from one city to another and from one season to another. In developed countries, such as in large parts of Europe, the PM concentrations inside the urban areas seem to be mainly caused by traffic emissions.

The highest concentrations reported in developing countries are influenced by weather and burning of bad fuels, like in Ulaanbaatar and in Dhaka. In other areas like in the Middle East, windblown dust from desert areas are the main cause for the highest concentrations measured (both PM_{10} and $PM_{2.5.}$).

The smallest particles, less than 2.5 micrometers, often originates from combustion sources leading to long range transported pollution and regional air pollution, while the larger particle fraction could come from local sources, local waste burning and re-suspended particles from the surface.

Measurement data collected in urban areas, aimed at assessing potential health impact, often show large temporal and spatial variations. When assessing the sources and the relative importance of different sources as a basis for regulations and mitigation measures, it is important to understand the complete picture. Annual average concentrations do normally NOT give the complete pictureand the right answer.

9. ACKNOWLEDGEMENTS

The author would like to thank co-workers at NILU for their excellent contribution to this paper. This concerns Scott Randall for his work in Bangladesh, Claudia Hak for PM studies in Abu Dhabi, Li Liu for the contribution from Mongolia, Philipp Schneider for performing satellite analyses in Bangladesh and Cristina Guerreiro for contribution data from Senegal and the data from the EU annual report.

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1.2 PARTICULATE MATTER: EFCA VIEWS ON POSSIBLE METRICS AND THE ‘ONE ATMOSPHERE’ APPROACH

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ABSTRACT

Air pollution and climate change share the Earth atmosphere to exert their unwanted impacts on our planet and its inhabitants. The dominating causal sources for both problems are essentially the same. While these and other common factors would suppose an integrated approach institutional barriers have, apart from a few exceptions, prevented this at all political levels.

In this article we summarise EFCA’s activities during the last five years aimed at connecting the two problems at the policy level in the European Union and at improving cost-effectiveness of related policies. Recommending Black Carbon as additional metric for particulate matter in air quality legislation may correct its present imperfections while contributing to climate objectives. We also point to the connection between the formation of the toxic PM fraction of Secondary Organic Aerosols and that of the short-lived climate pollutant Ozone as another example with potential for increased cost-effectiveness of legislation in the EU and elsewhere.

1. INTRODUCTION

The European Federation of Clean Air and Environmental Protection Associations (EFCA) was founded by European associations in the 90-ies in reaction to the decision to harmonise environmental policies in Europe. EFCA stimulates scientific and professional activity in Europe and, during the last ten years, developed a strategy with priority topics, in line with its mission to connect science and policy[4].In this paper we report on two interrelated priority topics on which we advised the European Commission:

- “Particulate matter”: improving the PM-regulation
- “One atmosphere”: the need for integrated policies on clean air and climate

2. EFCA’s APPROACH

With 15 Member associations in Europe EFCA is in a position to sponsor a continuous programme of conferences and conference series on atmospheric topics and have specific topics selected. Apart from proceedings also conference reports for policymakers are published. When conferences generate new insights which seem relevant for policy EFCA may take a *Policy Initiative* in which progress is reviewed, deficiencies in European policies are identified and recommendations for improvement are given. Through Forum discussions at its website possible remaining questions may be addressed in order to improve the quality of the advice before it is sent to the European Commission.

3. ONE ATMOSPHERE

The Earth has only one atmosphere which provides an impressive number of eco-services, functions essential for life. However, our atmosphere is facing two causally related problems with high impacts for men and ecosystems: air pollution and climate change.

In 2008 EFCA’s French Member APPA, in cooperation with IUAPPA, organised a first conference on this topic[1].Its conclusions were subsequently tested at a workshop on ‘Intermediate policies for climate and clean air’, organised at the initiative of the Swedish presidency of the EU in 2009and formed the basis of a Policy Initiative[3].

An integrated policy approach may generate co-benefits and also help to avoid trade-offs which result from present separate policies and increase overall cost-effectiveness of policies. EFCA’s assessment of then existing EU legislation revealed that the Climate and Energy package of 2008[7]generates considerable reductions of the emissions of major air pollutants. Also in vehicle regulations it is attempted to balance limit values for exhaust emissions with fuel-efficiency requirements.

In 2010 the existing legislation which is relevant for air quality, however, did not refer to the climate problem. The *Environmental Impact Assessment Directive* has ample scope to include energy-efficiency as a requirement for consideration in new activities. In the recent revision[11]energy-efficiency is referred to, though not as a requirement. In the *Industrial Emissions Directive*[10]energy-efficiency is not either a criterion. Here the Bref’s, reference documents on Best Available Technology, provide an easy way to minimise trade-offs by selecting technologies requiring least energy. It is uncertain whether this road will be taken. The present *National Emissions Ceilings Directive* and the *Ambient Air Quality Directive*[8] do not refer to the challenge to consider climate objectives; proposals for their revision, announced for this year, are being awaited.

4. PARTICULATE MATTER

With respect to air pollution, particulate matter is presently regulated by the metrics PM_{10} and $PM_{2.5}$, in Europe and elsewhere. The legitimation for this is their correlation with a number of short term and long term health endpoints as recently confirmed by WHO Europe[19]. Such ‘container metrics’ ignore the complexity of the atmospheric mixture of particulate matter which varies with respect to source, size, shape, colour, chemical composition, atmospheric behaviour, interaction with gaseous pollutants and are inadequate, therefore, to reduce impacts on health, environment, climate and weather. The implementation of $PM_{10}/PM_{2.5}$ regulation will not necessarily result in measures with maximal health protection.

5. EFCA POLICY INITIATIVE ON METRICS

In 2007 EFCA’s German Member GUS, in cooperation with the Karlsruhe Institute of Technology and EFCA, started a bi-annual series of symposia on ultrafine particles. At UFP-3 in 2011 a group of scientists proposed Black Carbon Particles (BCP) as additional metric to improve health protection, next to $PM_{10}/PM_{2.5}$. The idea was also recognised as a valuable instrument for air quality management at local scale[16] and a scientific assessment in support of the proposal was published in 2012 by WHO[18].Because questions on other aspects remained EFCA organised a Forum discussion at its website (2011/2012) at which the alternative metric of particle numbers (PN) was well addressed. The outcome was the basis for an EFCA Policy Initiative in 2012 in which the position of present and possible metrics was assessed with respect to their usefulness in air quality policy and in climate policy, and in which EFCA concluded to support the proposal of BCP as additional metric as explained in the next paragraph[5].

6. ASSESSMENT OF METRICS

In the political discussion cost/benefits analysis of policy options plays an important role. Integrated assessment modelling, primarily a combination of an air quality model with an economic module, is the basis for such analysis; in Europe IIASA’s GAINS model is being used to assess present health risks in monetised terms and to comparebenefitsofreducedexcessmortality with the costs of the required policy measures. Reliable modelling, however, requires the availability of input data of sufficient quality.

In table 1 the availability of input data for three metrics, $PM_{2.5}$, BCP and PN is compared; these include:

- Dose-response relationsfromepidemiologicalstudies, in particularforlongtermexcessmortality
- EU-wideemissioninventory
- Validatedmodel: emissions vs. monitoringdata

To these we added two additional criteria because of their relevance upon implementation of regulation: source specificity and co-benefits with climate objectives.

Table 1. Comparison of the infrastructure for integrated assessment estimates for three metrics of particulate matter

	$PM_{2.5}$	**BCP**	**PN**
Dose-effect relation (short-term effects)	+	+	(+/-)
Dose-effect relation (long-term effects)	+	+/-	-
Emission inventory	+	+/-	(+/-)
Monitoring data (network-based)	+	+/-	-
Source specificity	-	+	-
Co-benefits with climate objectives	?	+[1)]	?____

+ available/positive +/- incomplete (+/-) scarce data only - data absent/negative

[1)] BC is one of the Short-LivedClimatePollutants [SLCPs; otherareOzoneandMethane[17]. BC isthesecondlargestclimate forcer[2]andheldresponsiblefor 0.5-1.1°C warming in NH; contrary to long-lived climate forcers (CO_2, F-gases), emission reductions of BC have an immediate negative effect on global warming

Not surprisingly, the basic modelling database is complete for $PM_{2.5}$, in contrast with those for BCP and PN.When comparing the latter two, however, the situation is much better for BCP than for PN because completing the emission inventory and further roll-out of operational monitoring capacity for BCP in Europe seems feasible within a few years. For PN our estimate is that this could take 5 to 10 years.

For neither of the metrics a dose-effect relation for long-term health effects (excess mortality) is available. For BCP the outcome of studies is inconclusive; for PN such studies have not been reported yet.
Short-term effects have been reported for both metrics and provide conclusive evidence for BCP with higher RR values than those for $PM_{2.5}$[18]. for PN there are strong indications for a correlation[12].

The differences with respect to infrastructure for assessment modelling plead for BCP as additional metric when compared with PN. Its source-specificity and its potential for creating co-benefits with climate objectives would enable Member States and local authorities to select more cost-effective measures to reach compliance with air quality requirements while contributing to climate targets and makes it the preferred additional metric.

7. EU VEHICLES REGULATION

The preference for BCP may seem at odds with the existing regulation for emissions limit values for PN in the type approval phase of new vehicles[6, 9]. The risk for inconsistencies is small, however, because combustion-generated nanoparticles are likely to be black for a major part. Nevertheless, it is presently impossible to make an estimate of the impact of the regulation on excess mortality, other health end-points or its co-benefits for climate objectives. Establishing robust relations between BC- and PN-emissions for specific sources could diminish this knowledge gap.

8. BLACK CARBON AND ORGANIC CARBON

Black carbon is a major fraction of $PM_{2.5}$ which has a robust correlation with short and long term health effects. It seems logical, therefore, that reducing emissions of black carbon will also reduce health effects, including excess mortality. However, reducing all black carbon emissions to zero is no guarantee for elimination of all PM health effects, because also other fractions of PM may be responsible for these.

One of these is the fraction of organic carbon (OC) which is co-emitted from combustion processes in engines, heating and cooking devices, incinerators and open fires due to incomplete combustion of the fuels. The OC-fraction contains the semi-volatile polycyclic aromatics (PCA). Part of these may be emitted adsorbed on particles; elevated temperatures at combustion conditions cause that a substantial amount is emitted in gaseous state. At the recent EFCA-symposium on Ultrafine particles in May this year in Brussels and the ETH Conference on Combustion Generated Nanoparticles in June in Zurich new findings on the fraction of organic carbon(OC) were presented.

In recent years advanced monitoring techniques have become available which provide information on the two sub-fractions of OC, Primary and Secondary Organic Aerosol (POA and SOA)[14]. Observations made in California made clear that the SOA fraction develops during the day in summer conditions; from a dual approach of cellular and chemical assay of ambient air it could be concluded that this ’aged smog’ is more active in genotoxic tests than the POA-fraction and has a higher oxidative capacity [15]. The SOA fraction primarily consists of ultrafine particles which enhances the risk of causing oxidative stress in humans.

SOA production is part of the process of photochemical smog formation which produces ozone via reaction of NO_x and organics under influence of sunlight. It was confirmed that SOA were formed when irradiating diluted exhaust gas under simulated atmospheric conditions in a smog chamber[13]. Exhaust gases from petrol fuelled cars appeared to be much more productive in SOA production than those from diesel fuelled cars. Diesel particle filters effectively suppress POA emissions; this is important because diesel exhaust contains more PCAs than petrol exhaust. The filters do not reduce SOA formation, however, because gaseous PCA emissions may pass the filters.

Tropospheric ozone and SOA are the most relevant pollutants resulting from photochemical smog formation; addressing them together provides another option to protect public health and simultaneously having the co-benefit of reducing atmospheric levels of the SLCP ozone.

9. CONCLUSIONS

1. Integrated policy approaches on airquality and climate in the EU and elsewhere may further cost-effectiveness and require urgent attention

2. Black Carbon is preferred as additional metric for particulate matter above Particle Numbers: its contribution to global warming and its source specificity furthers theimplementation of airquality legislation

3. Specific regulation for Black Carbon and Particle Numbers are no-regret options

4. Protection of public health requires that also Organic Carbon emissions are being addressed; this may be best achieved in combination with policies aiming at reducing tropospheric ozone levels

5. Knowledge gaps for sound AQ policies on particulate matter include:
    - Dose-response relations forlong-term health effects of BCP and for short-term and long-term health effects of PN
    - Databases of emissions and monitoring data of BCP and PN
    - Robust relations between BC-emissions and PN-emissions from vehicles
    - More detailed data on PCA behaviour and SOA formation
    - Technologies for simultaneous removal of solid particles, NO_x and (semi)-volatile organics from combustion sources

ACKNOWLEDGEMENT

The views presented in the present paper have been discussed within EFCA and have the support of its Member associations.

The authors would like to thank Flemming Cassee, Sef van den Elshout, Andrew Ferrone, Gaëlle Guillossou, Nicole Janssen, Menno Keuken, Andreas Mayer, Manfred Neuberger, Xavier Querol and Martin Williams for helpful discussions.

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1.3 DAILY VARIATIONS OF PARTICULATE MATTER PM_{10} CONCENTRATIONS DURING WINTER AND SUMMER PERIOD IN BELGRADE, SERBIA

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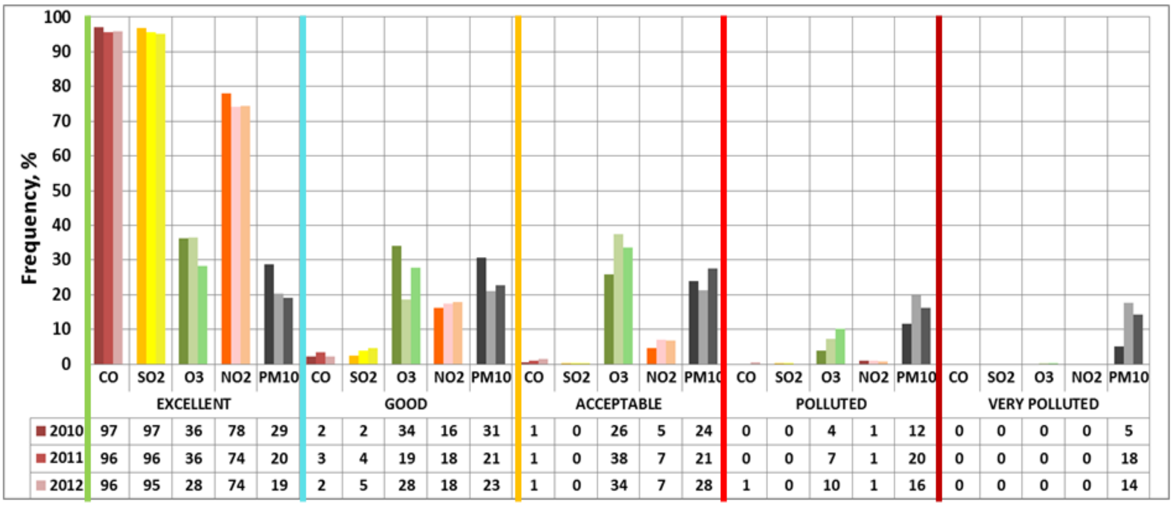
ABSTRACT

The newly established automatic air quality monitoring in the Republic of Serbia, within the national network for air quality monitoring, for the first time provided larger amount of valid data on ambient concentrations of particulate matter PM_{10} in Serbia. The analysis of impact of some pollutants on air quality indicates that the influence of suspended particles PM_{10} on air quality in urban areas in Serbia is dominant. This paper analyzes the daily variations of PM_{10} at two locations in Belgrade: Beograd Stari grad (B-SG) and Beograd Novi Beograd (B-NB). For both sites were available data obtained by gravimetric and automatic method. At both urban sites during winter and summer concentrations of PM_{10} during the day have two maximums.

Key words: air quality, particulate matter, PM_{10}, daily variations

1. INTRODUCTION

Until the adoption of the EU Directive 2008/50 (DIRECTIVE 2008/50/EC on ambient air quality and cleaner air for Europe) in domestic legislation (2009) and its implementation, soot (black soot) was most often used for the quantification of air pollution with particulate matter (PM). Establishing of the national network for automatic air quality monitoring in the Republic of Serbia, AAQMN, enabled generation the information about PM air pollution in accordance with EU legislative. In the previous years, 2010 -2013, special attention was paid to monitoring PM_{10} fraction. A large amount of data indicated that air pollution with PM was very high in some urban areas in the Republic of Serbia.



	EXCELLENT					GOOD					ACCEPTABLE					POLLUTED					VERY POLLUTED				
	CO	SO2	O3	NO2	PM10	CO	SO2	O3	NO2	PM10	CO	SO2	O3	NO2	PM1	CO	SO2	O3	NO2	PM10	CO	SO2	O3	NO2	PM10
■ 2010	97	97	36	78	29	2	2	34	16	31	1	0	26	5	24	0	0	4	1	12	0	0	0	0	5
■ 2011	96	96	36	74	20	3	4	19	18	21	1	0	38	7	21	0	0	7	1	20	0	0	0	0	18
■ 2012	96	95	28	74	19	2	5	28	18	23	1	0	34	7	28	1	0	10	1	16	0	0	0	0	14

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Figure 1. Average daily concentrations of CO, SO_2, NO_2, PM_{10} and maximum 8h O_3 expressed through air quality index classes - SAQI; AAQMS Beograd_Stari grad, 2010-2012

According to the several reports on the state of air quality in the Republic of Serbia [1, 2] and papers [3, 4], air pollution with the PM_{10} have a dominant influence on air quality in the urban areas in the Republic of Serbia. As a good illustration of this fact, the frequency of daily concentrations of air pollutants in the urban agglomeration of Belgrade is shown in Figure 1. The analysis was done by using the Air Quality Index SAQI_11 [5], based on the Regulation for air quality monitoring and air quality requirements ("Off. Gazette of RS" No .11/10, 75/10, 63/13). For calculation of daily averages, minimum 90% of valid hourly averages were required; otherwise the value is considered as missing. Any suspicious data in original ‘row’ data set, such as large spikes or spurious high concentrations were fully investigated. As shown in Figure 1, average daily concentrations of CO, in the dominant number of cases (96- 97%) in the time interval 2010- 2012 were in the class "excellent" according to air quality criteria SAQI_11. Similarly, average daily concentrations of SO_2, in the dominant number of cases (95- 97%) in the time interval 2010- 2012 were in the class "excellent" also. The impact of each particular air pollutant on air quality can be considered on the same way. Concerning the NO_2 small decrease in frequency of class "excellent" and increase in frequency of classes that represent the worse air quality can be observed in the recent years. In the class "polluted”, class that represents exceeding limit value (LV), daily concentrations of NO_2 occur in 1% of cases per year. The average daily concentrations of O_3, actually 8h max O_3 concentrations, have even lower frequency of class "excellent," 28 -36%. They appear more often in classes of poorer air quality than it the case of CO, SO_2 and NO_2 concentrations. In 4 -10% of cases a year the air was polluted due to the maximum 8h concentrations of ground-level O_3 in the area around AAQMN Beograd_Stari grad.

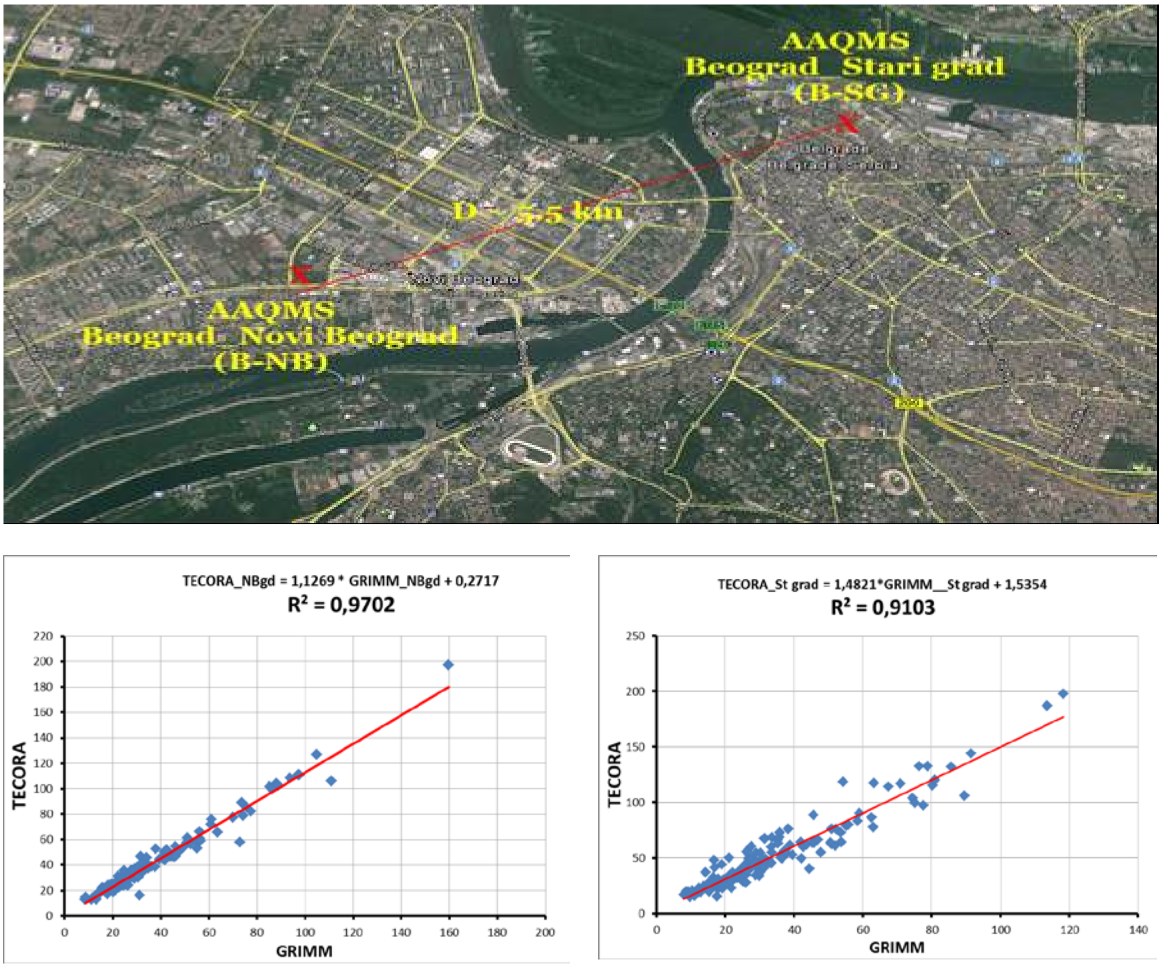

Figure 2. a) Map of Belgrade with the location of measuring points Beograd_Stari grad (B-SG) and Beograd_Novi Beograd (B-NB) marked; b) Graphical presentation of correlations between the PM_{10} levels determined by gravimetric method and by the automatic method

Average daily concentrations of PM_{10}, in only 19 - 29% of days per year were in the class "excellent" in the time interval 2010- 2012 were in the class "excellent" also. They cause class "polluted" in 12-20% cases. The Average daily values of PM_{10} exceeded the tolerant value (TV) and caused class "very polluted" in 5 - 18% of days per year. If we evaluate the air quality only with exceeding of LV (in the presented analysis, it is the sum of the cases in class "polluted" and "very polluted"), then for the area covered by AAQMN Beograd_Stari grad can be concluded that in the period 2010 – 2012 frequency of exceeding the LV was in 17-38% of days per year. The aim of this paper is to present the changes in the average hourly concentrations of PM_{10} in summer and winter. Those variations in average hourly values of PM_{10} mass concentrations during the day may be of use to indicate the major sources of PM_{10} particle fraction. Two different urban locations in Belgrade were selected (Beograd_Stari grad (B-SG) and Beograd_Novi Beograd (B-NB)).

2. METHODOLOGY

In the AAQMN in the operational use are two different methods for PM_{10} concentrations measurement: automatic method of determining the PM_{10} (Optical Light Scattering) and reference gravimetric method (with the TECORA Skypost samplers).

This measuring point Beograd_Stari grad (B-SG) was located in the central part of the city, at hilly terrain (shown in Figure 2). There is a number of local combustions sources in heating season in the area. Also, there is a number of narrow streets of canyon type in the area. This measuring point Beograd_Novi Beograd (B-NB) is located at the left bank of Sava river, where terrain is flat and streets are wide. Thus, this site is well-ventilated and free of local domestic heating combustion sources.

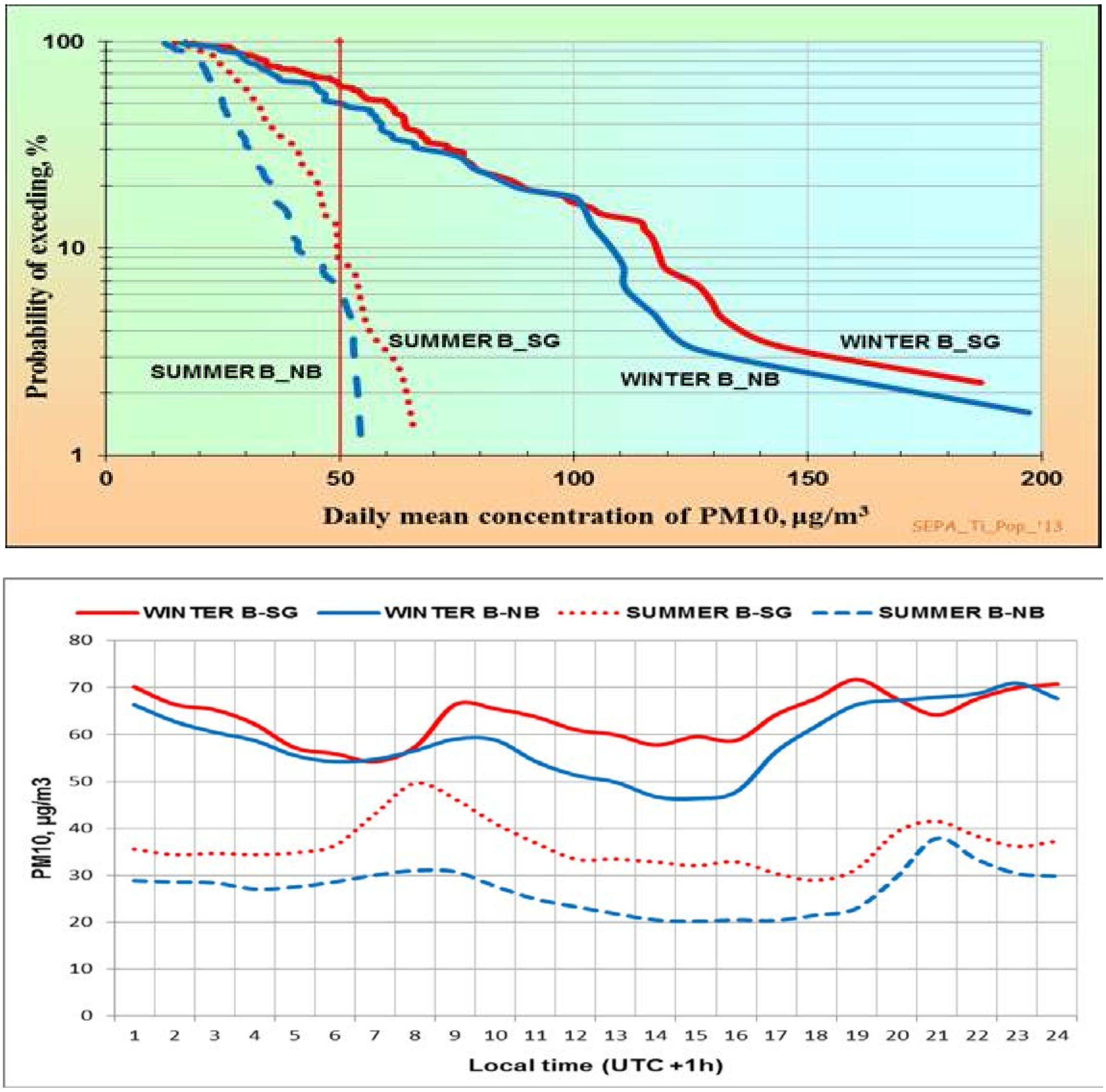

Figure 3. a) Cumulative distribution of average daily PM_{10} concentrations during the summer and winter at measuring points B-SG and B-NB; b) Diurnal variations in PM_{10} concentrations in Belgrade, measuring points B-SG and B-NB

For both sites available data were obtained by gravimetric and automatic method. Gravimetric data were obtained by analysis of samples from the TECORA Skypost sampler. Automated measurements were performed with the GRIMM EDM180. The correlation between average daily concentrations of PM_{10} obtained by reference gravimetric method, and with the EDM180 automatic monitor were calculated for both sites (0.91 for B-SG and 0.97 for B-NB, as shown in Figure 2). Data were analysed to detect both additive and multiplicative bias, and to assess the overall agreement between PM_{10} levels obtained with different sampling techniques. Ordinary least squares (OLS) regressions were performed on PM_{10} concentrations measured with different samplers. Obtained functional relationships were used to correct data obtained by automatic monitor. Automatic data were taken to the reference level. Analyzed data were for the winter 2011/12 (November, December 2011, January 2012) and summer 2012. (June, July, August 2012.).

3. RESULTS AND DISCUSSION

At both urban sites during winter and summer mass concentrations of PM_{10} during the day have two maximums, as shown in Figure 3. At the location B-SG average concentration of PM_{10} in winter is 63.6 $\mu m/m^3$. Frequency of exceeding the daily LV in winter is 60.7 %. Hourly average PM_{10} concentrations have maximums of 66.47 $\mu m/m^3$ (at 9 AM) and 71.7 $\mu m/m^3$ (at 7 PM). At the location B-SG average concentration of PM_{10} in summer is 36.5 $\mu m/m^3$. Hourly average PM_{10} concentrations have maximums of 49.7 $\mu m/m^3$ (at 7 AM) and 41.6 $\mu m/m^3$ (at 9 PM). Frequency of exceeding the daily LV in summer is 9.1 %.
At the location B-NB average concentration of PM_{10} in winter is 58.8 $\mu m/m^3$. Frequency of exceeding the daily LV in winter is 50.0 %. Hourly average PM_{10} concentrations have maximums of 59.1 $\mu m/m^3$ (at 9 AM) and 70.9 $\mu m/m^3$ (at 11 PM). At the location B-NB average concentration of PM_{10} in summer is 26.9 $\mu m/m^3$. Hourly average PM_{10} concentrations have maximums of 31.0 $\mu m/m^3$ (at 8 AM) and 37.9 $\mu m/m^3$ (at 9 PM). Frequency of exceeding the daily LV in summer is 6.5 %.

4. CONCLUSIONS

In winter, morning minimum in PM_{10} concentrations occurs around 7 AM at both locations. It is primary minimum for B-SG, and for B-NB it is secondary minimum. At B-SG PM_{10} levels after reaching the morning minimum increases rapidly. This can be attributed to the local emissions from furnaces and traffic. A small increase in PM_{10} levels after the morning minimum is also registered at B-NB. It can be attributed primarily to traffic. During the midday and afternoon PM_{10} concentrations decrease. This is mostly because the better conditions for diffusion of atmospheric pollutants. Faster decrease of PM_{10} levels in B-NB is a consequence of the orography, type of settlement and better ventilation conditions. At both locations evening increase in PM_{10} concentration begins with the sundown. It lasts until the late evening hours, when PM_{10} levels reach the maximum. Based on our results, pattern of PM_{10} levels in the summer and winter seasons is basically the similar for both selected sites.

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2 POLLUTION SOURCES

2.1 PARTICLE EMISSIONS FROM DIESEL ENGINES - LOOKING BEYOND CARBON SOOT EMISSIONS

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ABSTRACT

Particulate matter (PM) emissions involve a complex mixture of solid and liquid particles suspended in a gas. Whilst epidemiological studies have shown a link between increased ambient PM emissions and respiratory morbidity and mortality, studies of this design are not able to identify the PM constituents responsible for driving adverse respiratory health effects. There is strong evidence that organic compounds are most responsible for the toxicity of airborne particles. Some recent toxicological studies indicate that PM related reactive oxygen species (ROS) and the resulting oxidative stress they engender may be implicated in the instigation of the adverse health effects. Taking this into account we have explored the correlation between particulate organic material and the potential of diesel PM, as a major contributor to the ambient air pollution, to cause oxidative stress. We find that the oxidative potential of diesel PM although proportional to the total organic content in certain cases shows a much higher correlation with the oxygenated organic fraction. This highlights the importance of knowing the surface chemistry of particles for assessing their health impacts. It also sheds a light onto new aspects of combustion particulate emissions that should be taken into account when establishing relevant metrics for health implications of emissions from various future fuels.

Keywords: diesel engines, particles, soot

1. INTRODUCTION

The importance of diesel engine emissions has been recently highlighted by the WHO’s International Agency for Research on Cancer (IARC) [1] when it classified diesel engine exhaust as carcinogenic to humans (Group 1). This was based on sufficient evidence that exposure to diesel engine exhaust increases risk for lung cancer. To develop methods that could help to mitigate the adverse health outcomes induced by PM, it is important to know the PM properties and the mechanism(s) that are responsible for PM toxicity. Identification of the PM properties that are the most relevant for promoting adverse health effects is crucial not only for our mechanistic understanding but also for the implementation of strategies for improving air quality. Such strategies could be specific engineering measures that could be implemented, consequently improving the PM constituent mixture emitted from a given source (engine). As such knowledge of the diesel engine PM physical and chemical properties is critical for the development of understanding of the health effects.

2. THE NATURE OF DIESEL PARTICULATE MATTER EMISSIONS

Complete combustion of a fuel containing hydrocarbons in an internal combustion engine yields only CO_2 and H_2O as combustion products. Whilst CI engines offer a relatively high combustion efficiency (≥ 98 %), in terms of the percentage of fuel that is burnt, the small fraction of unburnt fuel and lubricating oil yield a great number of incomplete combustion products that affect urban air quality and consequently human respiratory health. Diesel exhaust is a complex mixture of gaseous compounds and fine particles that are emitted by CI engines. Not only concentration but also the physical and chemical characteristics of diesel exhaust are dependent on the type of the engine, the fuel used, operating conditions, additives as well as the presence of after-treatment devices (such as a Diesel Particle Filter). DPM is a very dynamical physical and chemical system and its composition is under the strong influence of spatial and temporal factors [2]. It has been estimated that the diesel exhaust consists of about 20000 different chemical compounds [3]. These include gaseous precursors such as sulphuric acid, SO_2, SO_3, H_2O, low-volatile organic compounds, soot particles and metallic ash.

DPM usuallyexhibitsbimodal size distribution with a nucleation mode, that range in diameter from 0.003 to 0.03 µm, and the accumulation mode, in the range between 0.03 and 0.5 µm.Nucleation mode is composed of condensed volatile compounds and comprises very little solid material [4]. It is estimated that 0.1-10% of the particle mass and around 90% of the particle number is found inthenucleation mode.

Besides the physico-chemical composition of DPM, another important feature relates to the physical mixing status of the various DPM constituents. A carbonaceous agglomerate with other adsorbed or condensed species (such as organics, sulphates or metal oxides) refers to a situation termed internal mixing. In internal mixing, the various DPM constituents mix together to form a single, incorporated particle. When the DPM constituents are physically separated into distinct particle types, this situation is referred to as external mixing. The structure, or mixing state, of DPM is another important aspect to consider for assessing the respiratory health effects of this pollutant.

Taking into account its complex nature, the chemical composition of diesel exhaust PM (and PM in general) is often expressed in terms of the organic carbon/elemental carbon ratio (OC/EC). The majority of the diesel PM mass is in the form of elemental carbon, which presents a core onto which various organic compounds may be adsorbed. Organic compounds in diesel PM originate from unburned fuel and lubricating oil, partial combustion and pyrolysis products and include alkanes, cycloalkanes, alkylbenzenes and polycyclic aromatic hydrocarbons (PAHs) and their derivatives [5].

Part of the OC condensed onto the soot particles compromises of the so called semivolatile organic carbon (SVOC). The SVOC can partition between the gas and particle phase depending on the dilution levels to which the diesel exhaust is exposed. Dilution leads to reduced concentrations of both semi-volatile and sorptive species. In that case, semi-volatile species are transferred from particles to the gas phase to maintain equilibrium. Furthermore, as the dilution increases gradually, temperature and concentration of these semivolatile and sorptive materials will reach the background levels and then background conditions should strongly influence the ultimate partitioning of the emissions. This new insight into partitioning theory has to be considered in health effect studies and toxicity studies as well, as the changes in partitioning alter both the mass and the concentration of the aerosol. In a extensive study, Robinson et al. [6] show that the OC/EC ratio and therefore the amount of organic compounds present, is dilution dependent, meaning that the fuel-based emission factors of OC decrease with increasing dilution and decreasing concentration, due to evaporation of the semivolatile fraction. These findings point out that the PM emission factors will vary depending on the dillution conditions due to semivolatile character of OC. In regards to the health effects the results imply that the majority of population in urban environments, that are far away from major local sources (major roads), are mainly exposued to secondary organic aerosols (SOA) as the primary components will partition to the gas phase due to significant dillution. The SVOC's that partitioned to the gas phase can be oxidiesed in the environment and recondense back to the particle phase contributing now as the SOA. Consequently, a relatively local urban emissions problem becomes regional source of oxidised and presumably hydrophilic OA.

3. HEALTH EFFECTS OF DPM

Many cohort studies have demonstrated that airborne particulate matter, of which DPM is a major contributor, is responsible for causing respiratory mortality and morbidity [7]. Despite a substantial body of research addressing this topic, the underlying toxicological mechanisms by which DPM induces adverse health effects are not yet entirely understood. However, in recent years there have been a number of studies indicating that inflammation mediated via oxidative stress through reactive oxygen species (ROS) is the mechanism by which DPM may exert toxicity [8] as the induction of oxidative stress is characteristic of exposure to DPM. Oxidative stress develops when there is an imbalance between the production of reactive oxygen species (ROS) and the availability of anti-oxidant defences. ROS is a collective term that refers to free radicals such as hydroxyl ($HO^{\cdot}$) and peroxyl ($HOO^{\cdot}$, $ROO^{\cdot}$), ions such as superoxide ($O_2^{-\cdot}$) and peroxynitrite ($ONOO^{-}$), and molecules such as hydrogen peroxide (H_2O_2) and hydroperoxides (ROOH). The term “reactive” is used to indicate the higher reactivity of ROS relative to molecular oxygen due to the presence of unpaired electrons. Precursors of ROS such as carbon-centred radicals can also be considered as ROS.

ROS can be formed endogenously, by the lung tissue cells, during the phagocytic processes initiated by the presence of PM in the lungs, or by particle-related chemical species that have the potential to generate ROS. In addition to the particle-induced generation of ROS, several recent studies have shown that particles may also contain ROS (so called, exogenous ROS).

It is a reasonable assumption that exogenous ROS can cause the same responses (oxidative stress) in the cell as endogenously formed ROS. As such, they present a direct cause of oxidative stress and related adverse health effects. Therefore, a rapid screening assay able to evaluate PM oxidative potential in terms of their inherent ROS would be beneficial.

2.1 Methods for evaluating PM oxidative potential (OP)

Cellular responses to oxidative stress have been widely investigated using various cell exposure assays [9, 10]. However, in order to provide a rapid screening test for the oxidative potential of PM, less time-consuming and cheaper, cell-free (or acellular) assays are necessary.

The advantage of acellular assays is that they are much cheaper and less time-consuming than cell and animal exposure studies and they can easily be applied in the field. Moreover, they do not need the ethical approval required for *in vivo* studies. Several cell-free approaches have been used to explore oxidative potential of PM in a quantitative manner. They all have certain limitations, do not provide directly comparable results and, to date, none of these assays has been acknowledged as the best acellular assay and none have yet been widely adopted for investigation of potential PM toxicity.

Recently, a new profluorescentnitroxide (PFN) molecular probe developed at QUT was applied in an entirely novel, rapid and non-cell based assay for assessing the oxidative potential of particles produced by several combustion sources [11-14]. Profluorescentnitroxides are a type of compound consisting of a fluorophore linked to a nitroxide-containing moiety. They have a very low fluorescence emission due to inherent quenching of fluorophore's natural fluorescence by the nitroxide group, but upon radical trapping or redox activity, the quenching effect of the nitroxide group is eliminated and a strong fluorescence is observed. The intensity of the fluorescence emission presents a measure of the number of radicals trapped by the nitroxide, or redox reactions that have occurred. Due to their non-fluorescent nature, these nitroxides are described as profluorescent because a simple chemical transformation converts them to the fluorescent form. This feature makes PFNs powerful optical sensors applicable as detectors of radicals and redox active agents.

A number of profluorescentnitroxide probes were evaluated for their ability to detect and quantify ROS associated with combustion generated particles. Out of all of the evaluated probes 9,10-bis(phenylethynyl)anthracene-nitroxide (BPEAnit) was chosen as the most appropriate for use with combustion generated particles [11]. The excitation and emission wavelength of the BPEAnit are long enough to avoid overlapping with the background fluorescence coming from optically active compounds which may be present in diesel PM (e.g. polycyclic aromatic hydrocarbons and their derivatives).

2.2 Physico-chemical properties of diesel particulate matter that influence inflammation, immune response and oxidative stress

To investigate the use of the profluorescent nitroxide BPEAnit to detect ROS present in combustion-generated particles using fluorescence spectroscopy initial experiments were conducted with cigarette smoke[11]. The BPEAnit was used to further study the potential toxicological impact of particles produced during biomass combustion by an automatic pellet boiler and a traditional logwood stove under various combustion conditions [12]. The fluorescence of BPEAnit was measured for particles produced during various combustion phases, at the beginning of burning (cold start), stable combustion after refilling with the fuel (warm start) and poor burning conditions. For particles produced by the logwood stove under cold-start conditions significantly higher amounts of reactive species per unit of particulate mass were observed compared to emissions produced during a warm start. In addition, sampling of logwood burning emissions after removing all the semivolatile species resulted in an 80-100% reduction of the fluorescence signal of BPEAnit probe, indicating that the majority of reactive species were semivolatile. A significant reduction in PM oxidative potential after thermal conditioning was also observed by Biswas and co-workers [15] who used a dithiothreitol (DTT) assay to measure the oxidative potential of particulate matter produced by heavy–duty vehicles. As a further support of the role of organic species in particle induced oxidative stress, we observed strong correlations ($r = 0.85$ and 0.99) between the amount of ROS and the mass fraction of organic species in the PM during cold-start stable combustion and warm-start combustion (Figure 2).

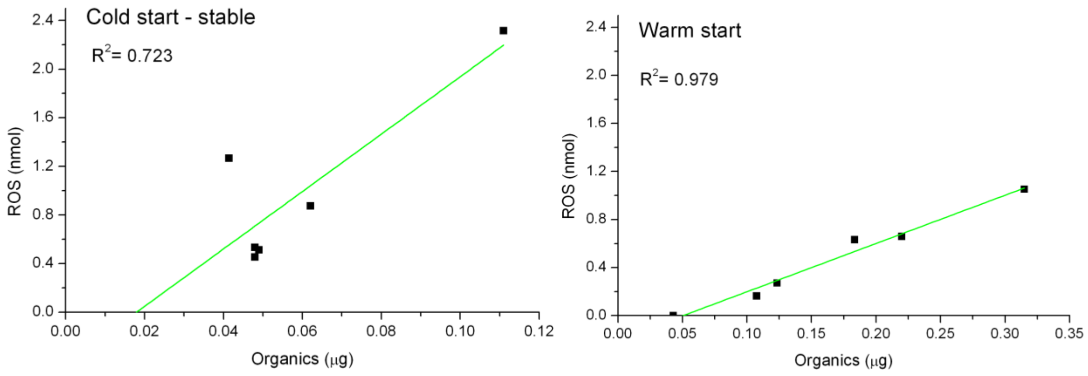

Figure 1. Correlation between the amount of ROS and the amount of organics for stable phase of cold-start (top), and warm-start (bottom) logwood burning.

The role of organic content in the particle OP was further explored in the studies that included diesel particulate matter (DPM) and various alternative fuels. In the study by Surawski et al. [16], we reported OP of PMs generated by a diesel engine using ethanol substitution. This study found that with increasing amount of fumigated ethanol in the fuel, the PM mass is decresing and ROS concentrations incresing accordingly. The obtained values for ROS concentrations were almost 40 times higher for E40 test than for neat diesel. ROS concentrations exhibited an increase with decersing engine load. Suggested explanation for increased redox potential of ethanol fumigate diesel was the occurence of nucleation mode particles. PMs in this mode are composed of organic species and contribute very little to the PM mass. In addition, this study showed that the toxicological potential of particulate emissions is affected by operational practiceandresultingcombustion.

The role of organic content in the particle OP was further explored in the studies that included diesel PM and various alternative fuels. Fuels investigated included Fischer-Tropsch diesel (gas to liquid) and various biodiesel feedstocks (soy, canola, tallow) in various blend percentages and also employing to injections technologies [17, 18]. All of the previous studies have shown that the semi-volatile component of PM is the most important factor influencing the oxidative potential of these particles.

Although a clear link exists between the OP and the organic fraction of PM in the case of biodiesel PM [17] and wood smoke [12] no correlation was observed when reactive oxygen species (ROS) concentration was plotted against organic volume percentage for a variety of different fuels (ethanol fumigated, various biodiesel blends, petro diesel, etc.). Although studies looking at wood smoke [12] showed a good linear correlation between the OP and organic matter it was only for the same burning conditions. This indicates that the relationship between these two parameters is complex and more detailed investigation needs to be undertaken.

To explore the role different organic fractions play in the measured oxidative potential Stevanovic et al [19] analysed, in more detail the organic PM fraction emitted from a diesel engine running on various fuels versus their OP (as measured using the BPEAnit probe). Using a compact Time of Flight Aerosol Mass Spectrometer (c-ToF AMS) enabled a better identification of the different organic fractions that contribute to the overall measured oxidative potentials. Two markers were used, f44 and f57, which reflect the contribution of the particular organic fragment at each molecular ion (*m/z* = 44 or 57) to the total organic mass. Alkyl fragments dominate the hydrocarbon-like OA (HOA) mass profile. As a representative from the C_nH_{2n+1} series, the m/z 57 ($C_4H_9^+$) was chosen as a HOA tracer peak. Oxygenated OA (OOA) species are represented by its prominent *m*/z 44 (CO_2^+) peak. HOA levels are usually in accordance with primary tracers such as EC, NOx and CO ([20]). OOA are however mainly considered as surrogate for secondary organic aerosols (SOA) and are in a good correlation with sulphates, O_3 levels and/or nitrates. OOA can thus represent heterogeneous products of primary organic aerosols (POA) and/or oxidation products of semi-volatile organic compounds (SVOCs) that volatilised from POA and oxidised in a gas phase [20, 21].

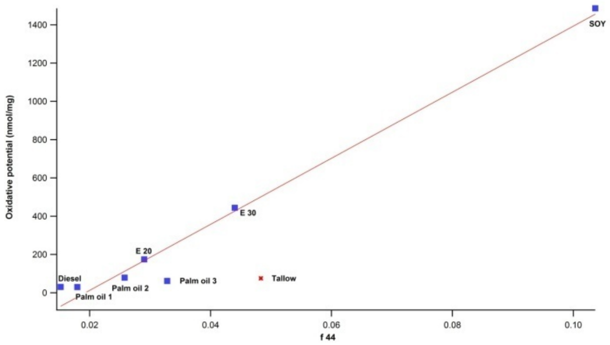

Figure 2. Correlation between oxidative potential, measured as the ROS concentration, and f44 used as a marker for the content of oxygenated organic fraction. A line of linear fit is also shown. A label for the fuel type is next to each data point.

The linear correlation between the organic content of diesel particles, for all the fuels tested, and their OP as measured in this study, showed a very small correlation with $R^2= 0.164$. On the other side when the OAA fraction, through the f44 marker calculated for each fuel type, was plotted against the OP a strong linear correlation ($R^2=0.97$) was observed (see Figure 3). From these results it can be concluded however that in general the oxidative potential of the PM, as measured through the levels of ROS production, although proportional to the total volatile organic volume percentage, shows a much stronger correlation to the oxygenated organic fraction. This highlights the importance of a specific fraction of OA on the particle toxicity.

4. CONCLUSION

Our studies also provided an opportunity to look into the correlation between the physical properties of DPM and oxidative capacity of particles measured as the concentration of ROS. Toxicological studies, such as [22], have pointed to the particle surface area as a potential metric for assessing the health effects of PM. The surface area of a particle provides a measure of the ability of toxic compounds (such as PAHs or ROS) to adsorb or condense upon it. Polycyclic Hydrocarbons (PAHs) are the principal pollutants from incomplete combustion, and are of special interest due to their toxicity, carcinogenicity, and ubiquitous presence in the environment . Therefore, a particle’s surface area can be viewed as a “transport vector” for many compounds deleterious to human health and requires more detailed analysis.

We also highlight the importance of the surface chemistry of particles for assessing the health impacts, as these surfaces are likely to be rich with oxygenated species and structures. Our results also shed new light on previously unrecognised aspects of the nature of particulate emissions that should be taken into account when establishing relevant metrics for health implications of various emissions.

We specifically indicate that the relationship between organic content of PM and related OP has to be explored into more detail and thus provide a better platform for understanding of the processes behind their toxicity. The documented role of semi-volatile compounds in the OP of PM has far reaching consequences on the regulations of particulate emissions from combustion sources.

For instance, the introduction of particle number standards as opposed to mass based regulations, were introduced for diesel vehicle engine emissions (EURO5/6). The new standards better reflect the nanoparticle component of DPM when compared to mass based measurements. However, to achieve reproducible particle number measurements, thermal conditioning of the exhaust is necessary. This causes the removal of semi-volatile components. This brings up the question on the validity of the new diesel vehicle emission standards if the fact that semi-volatile organic component drives the toxicity of PM is taken into account.

5. ACKNOWLEDGMENTS

Parts of this paper were presented at the 4thWeBIOPATR workshop, Belgrade 2-4. October 2013. This work was supported by the Australian Research Council Discovery grant (DP120100126) and Queensland University of Technology

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2.2 THE INFLUENCE OF DIFFERENT BIODIESEL FEEDSTOCKS ON THE OXIDATIVE POTENTIAL OF DIESEL PARTICULATE MATER

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ABSTRACT

Generally, the magnitude of pollutant emission from diesel engines running on biodiesel fuel is ultimately coupled to the structure of respective molecules that constitute the fuel. The presence of oxygen inside the biodiesel molecules leads to significant levels of oxygenated toxic species. In addition, the carbon chain length and the degree of unsaturation influence the biofuel combustion chemistry and these are all dependent on the feedstock. To gain an insight into the relationship between the molecular structure of the esters present in different biodiesel stocks and their respective oxidative potentials, measurements were conducted on a modern common rail diesel engine. Tests were designed to present emissions differences due to changes in fuel, speed and load settings, which included usage of three blends for every biodiesel feedstock (B20, B50 and B100). To establish the oxidative potential of diesel particles the concentration of reactive oxygen species (ROS) was measured using the profluorescent nitroxide probes developed at QUT. The results indicate that there is a strong correlation between the measured concentration of reactive oxygen species (ROS) and carbon chain length as well as the degree of saturation and to a smaller extent engine operating conditions.

Volatility measurements indicating the overall organic coating on particles correlated well with measured oxidative potential. This indicated that ROS content is a function of organic particle composition. However, it does not always exhibit a simple linear trend with volatility data and depending on a particular combustion source may show a much higher correlation with the oxygenated organic fraction.
This highlights the importance of knowing the surface chemistry of particles for assessing their health impacts and reinforces the further investigations to explore this correlation.

BACKGROUND

There is an increasing need for the adoption of biofuels as alternatives to petroleum-based fuels in order to reduce green house gas emissions and improve the long-term availability of fuel resources. To achieve this, biofuels need to meet a number of criteria such as high energy content, low production costs, sustainability of food supply. In addition, health and environmental aspects of biofuels need to be assessed before their implementation is put in place.

Biodiesels currently present on the market are mainly methyl and ethyl esters of fatty acids from plant and animal provenance. Biodiesel can be used as a neat fuel in current automotive engines or it can be blended with petroleum diesel. Generally, there is a consensus that the combustion of biodiesel results in the reduction of the total mass of particulate matter (PM), reduced soot emissions and a substantial decrease in CO [1, 2]. In addition, biodiesels have low sulphur and aromatic content.

However, some studies have shown that biodiesel combustion usually produces increased levels of NOx (a known ozone precursor) [3], increased particle-bound organic carbon [4] and decreased particle diameter [5, 6]. It has also been reported that biodiesel increases emissions of some carbonyl species [8-10]. As vehicles are already the major source of carbonyl compounds in urban air, this aspect needs to be explored in more detail. Greater biodiesel use could lead to higher levels of carbonyl compounds and these compounds can be significant precursors for secondary pollutants.[10]

The presence of oxygen atoms in the molecular structure of the substances present in biodiesel could ultimately give rise to significant levels of oxygenated toxic species (including typically formaldehyde and acetaldehyde) [11].

The most challenging task that remains is to identify the specific PM fraction that represents the most important causal pollutant component (14, 15). This is very complex issue due to composition continuum, as well as the dynamic continuum between carbon particulates and both volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs). More than 200 species have been identified, many of which can undergo chemical modifications and alter their reactivity and toxicity. It was previously indicated in the literature [4, 13] that SVOCs are components of airborne PM that contribute the most to the measured oxidative potential of particles in question. These components undergo partitioning between particulates and the gaseous phase. Upon heating in a thermodenuder however they are transferred predominantly to the gas phase. By using this approach it is possible to attain information on the volatility of the particles. In our previous studies [4, 12], the relationship between the organic fraction of particles and the oxidative potential measured by the BPEAnit assay was clearly established. This correlation highlights the importance of organic species in particle-induced toxicity and reinforces the need for further investigations to explore this relationship.

CORRELATION BETWEEN OXIDATIVE POTENTIAL AND PARTICLE VOLATILITY AND THE LINK WITH CHEMICAL COMPOSITION OF FUELS

Four methyl-ester palm-oil biodiesel fuels with controlled chemical compositions were tested on a modern, common-rail, high injection pressure compression ignition engine. Each test was repeated for four blends on idle and quarter load at 1200 (for idling), 1500 and 2000 rpm. Assuming the organic fraction of diesel particulate matter to be responsible for the majority of the oxidative capacity of particles, the amount of volatile matter in particles was measured in six selected sizes; and then combining the volatility of particles in each size with the corresponding number concentration and the total number concentration, the overall volatility (OV) of particulate matter in each mode was estimated. Also, the oxidative potency of diesel particulate matter was measured by BPEA nitroxide probe for all modes.

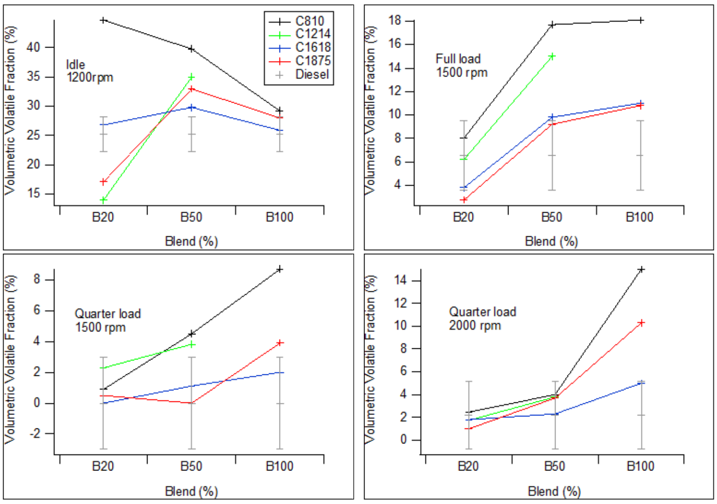

Figure 1. Volatility versus blend

Figure 1 shows the correlation between OV and different blends. As expected, and except at idle, volatility increases with increasing biodiesel percentage in blends, with the lowest values observed for B20. Volatility of particles in idle mode does not follow this trend since the volatility originates from the condensation of heavy hydrocarbons contained in the lubricating oil. Nevertheless, the effect of biodiesel is evident when it comes to B50 and B100 blends since they result in more volatile matter than neat diesel even when it is run in idle mode.

In all modes, particles produced by C810 blends were more volatile than particles from other fuels and blends. At full load and 1500 rpm, C810, which has the shortest carbon chain length and highest saturation number, produced emissions with the highest volatility of PM; while C1214, C1618 and C1875, with longer carbon chain lengths and more c-c double bonds have produced less and less volatile particles respectively (16).

OXIDATIVE POTENTIAL MEASUREMENTS

Figure 2 illustrates the oxidative potential of particles for the same loads and blends as for the volatility measurements. In idle mode, the ROS concentration is much higher than in other cases. This is a result of the additional combustion of lubricating oil which subsequently increases the overall organic content. Also, results do not show blend dependency in this mode. Yet, it is clearly visible that combustion of C810 fuel generates the largest amount of ROS for all 3 blends. This is a consequence of the way the oxidative potential is presented as the concentration of ROS per mass of emitted particles. As the fuels with the highest oxygen content have the lowest mass emission even for the same (or similar) ROS concentration they will exhibit the highest oxidative potential.

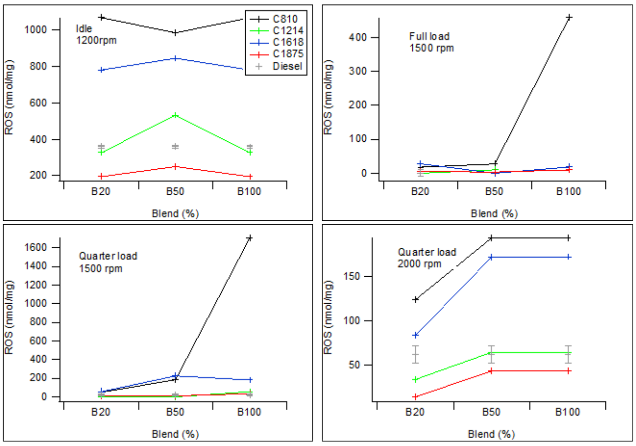

Figure 2. ROS VS blends for idle (top); quarter load, 1500 rpm (middle); full load, 1500 rpm (bottom).

Again, the same goes with C810 in quarter load and full load. Overall biodiesel blends caused more ROS even in 20 percent blends. In 50 and 100 percent blends the ROS increases, but the increase for C810 is, almost, of two orders of magnitude. This is a reasonable result as C810 fuel molecules are of shortest chain, fully saturated and with the largest oxygen content. These three parameters have synergetic effect in terms of prediction of resulting oxidative potential.

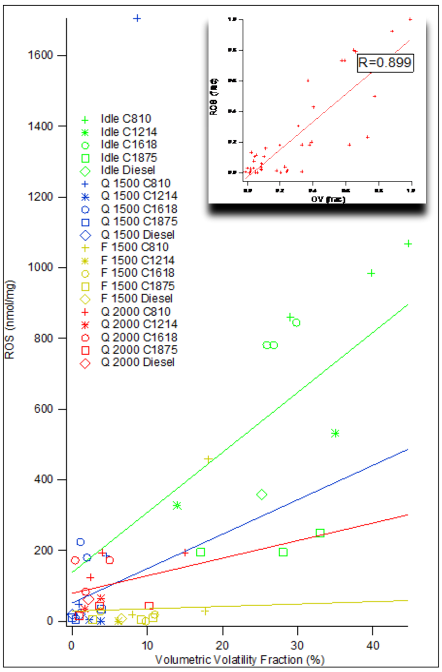

Figure 3. Volatility versus ROS

Figure 3 shows that the organic component is a carrier of oxidative potential. It also highlights the fact that this relationship is dependent on the chemical composition of volatile matter. Although complete combustion can yield volatile paraffins, their oxidative potential is very low compared to oxygenated organic aerosols. The conclusion that follows the investigation of the fuel type on the OV and related oxidative potential is that generally, the oxidative potential is ultimately coupled to the structure of fuel molecules, especially its oxygen content, chain length and level of unsaturation.it was concluded that in idle mode most of the organics and consequently most of the oxidative capacity of the particles come from lubricating oil and incomplete combustion. Nonetheless, the carbon chain length effect can still be seen: The smaller the chain length, the more volatile content, and the higher the ROS and therefore the oxidative potential. Also unsaturation level of fuels causes a decreasing trend of both volatility and ROS in all blends. Importantly, we have also shown that the amount of reactive oxygenated species emitted while idling is, indeed, significant and should not be neglected. This is of great importance given the fact that diesel engines run at idle for considerable amount of time (e.g. while queuing for loading and unloading, in urban traffic, during warm up, etc.).

Particles generated during quarter load in both 1500 and 2000 rpm were very similar in terms of volatility and ROS. It seems that chemical composition of volatile matter, which contributes to high levels of ROS, is different in partial and full load, and thus more detailed chemical analysis of the organic content of DPM is required to shed more light on the toxicity of DPM. The findings of this research show that more saturated fuels caused more potentially toxic substances in the exhaust; although more oxygenated fuels decreased PM, they led to higher levels of ROS in the particles. It was established that the majority of the redox activity is due to the amount of organics in the PM. This highlights the fact that "less particulate matter" does not necessarily mean less harmful for the environment and/or less toxic for human and that new metrics taking into account the potentially toxic parts of DPM should be considered.

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2.3 COMPARISION OF SOURCE APPPORTIONMENT OF URBAN AMBIENT PARTICLE BOUND PAH BETWEEN 2009 AND 2012 MESAUREMENT CAMPAINGS IN BELGRADE, SERBIA

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ABSTRACT

Concentrations of polycyclic aromatic hydrocarbons (PAHs) are associated with adverse health problems and specifically with carcinogenic and mutagenic effects. The major PAH sources outdoors are: stationary sources (industry, residential heating, power plants, and incineration), mobile sources (diesel and petrol engines), biomass burning and agricultural activities (e.g., open burning of brushwood, straw, stubble). PAH concentrations in summer are also influenced by higher degrees of atmospheric photo degradation and evaporation when semi-volatile PAHs change state to gas phase. The aim of this study is to assess differences in particle-bound PAH levels and source contribution between 2009 and 2012 sampling campaigns done at one sampling site. The sampling location is considered representative for a mix of residential, business and industrial areas of New Belgrade, an urban area under rapid development.

Key words: PM_{10}; urban air pollution; monitoring; polycyclic aromatic hydrocarbons; positive matrix factorization

1. INTRODUCTION

PAHs are products of incomplete combustion during the process of pyrolysis of organic materials such as coal, oil, biomass, petrol and diesel fuel (EC, 2001), organic compounds at high temperatures, and fires in the forests and prairies, volcanic activity (Rogge at al. 1993; Wilcke at al. 2000), and fires caused by human activity. The largest contributions originate from burning of fossil fuels. PAHs can also be synthesized naturally, by the activity of some bacteria (Wilcke at al. 2000) and plants (Rogge at al. 1993). The largest amount in the environment comes from burning of coal (Kim 2003), because fossil fuels contain significant quantities of aromatic hydrocarbons which have arisen during their formation by incubation of organic matter under specific conditions without the presence of oxygen. Anthropogenic PAHs arise mostly as products of various pyrolytic processes, especially incomplete combustion of organic matter during industrial activities, energy production (heat and electricity), combustion of waste, and as emissions from motor vehicles (Wild at al. 1995).

2. MATERIALS AND METHODS

2.1 Air sampling

The sampling site, a background urban monitoring station, Omladinskih Brigada Street (44°49'7" N, 20°28'5" E, 116 A), is located in a residential area of New Belgrade. In the vicinity of this monitoring site, in the radius of 5 km, there are the following pollution sources: Belgrade district heating plants; business trade centers, mega markets; high traffic density arterial road (140 000 cars/per day pass a bridge over the Sava river); kindergartens, schools; residential area central heating facilities using gas and oil; agricultural activities. The monitoring site is placed on the roof of the Medical Institute at a height of about 15 meters.

The sampling campaigns were performed in the framework of the WeBIOPATR Project, in two sampling periods: winter (February 18th - March 3th 2009; November 13th - December 14th 2009) and summer (May 25th - July 20th 2009). Follow-up campaigns were conducted during winter and summer in 2011 and 2012, in the framework of regular monitoring program of Institute of Public Health of Belgrade.

Aerosol sampling was conducted using European reference low-volume samplers (Sven/Leckel LVS3) with inlet for PM_{10} fraction, with flow rates 2.3 $m^3 h^{-1}$. Particles were collected onto 47 mm Whatman QM-A quartz fiber filters. The PM_{10} was sampled on a daily basis (24 hours, beginning at 7.a.m.) with one 'field blank' per week, in compliance with the EU Directive (EEC, 1999).

2.2 Analysis

Gravimetric measurements were conducted according to EN 12341 for PM_{10} (CEN, 1998). PAHs were extracted in microwave with mixture of solvents (12.5 ml n-hexane: 12.5 ml acetone) according to an EPA Method (Compendium Method TO 13A).

As internal standard we used the Ultra Scientific Semi-Volatiles Internal Standard Mixture ISM-560 with deuterated compounds: Acenaphtene-d_{10}, Chrysene-d_{10}, 1,4-dichlorobenzene, Naphthalene-d_8, Perylen-d_{12}, Phenanthrene-d_{10}. MQL for PAHs was 0.02 ng/m^3.

2.3 Positive matrix factorization

Receptor modeling aims to obtain information on contaminant sources and to assess the contribution of each type of source in the collected samples. Receptor models include a range of multivariate analysis using results of chemical analysis of samples of certain types of aerosols to determine the type, location and contribution of pollution sources (Hopke at al. 2006, Watson at. al. 2004). Receptor models focus on the pollutants in the point of sampling; this is the opposite of dispersion models, which use information on pollutants emitted by the sources (i.e., they assume that the emissions are known) and predict atmospheric concentrations of pollutants taking into account atmospheric dispersion, chemical transformations and other physical-chemical processes.

For PMF analysis, appropriate uncertainty estimates associated with the concentrations are necessary. PMF programs allow the user to generate matrix using the detection limit of each method and the uncertainty in the chemical analysis. Missing data can be replaced prior to analysis e.g., with median value of the species (Paatero 1999). PMF model reduces the effect of very large values by treating them as outliers (Hopke 2001). Identification of factors and their allocation to source (or source combinations) is subjective, based on knowledge of markers for individual emission sources.

3. RESULTS AND DISCUSSION

3.1 PM and PAH concentration

Mean daily PM_{10} mass concentrations measured during winter and summer in 2009 and 2011/2012 are shown in Table 1. The concentration levels of PM vary substantially within a year, with higher means and peak concentrations in winter in both sampling periods. The concentrations are slightly increased in 2011/12.

The PM-bound PAH have shown the same trend as the PM, with higher concentrations in winter and lower in summer.

Total PAH (mean) concentration was higher in 2011/12 (74.27 ng/m^3 in winter and 3.83 ng/m^3 in summer) than in 2009 (30.01 ng/m^3 in winter and 2.50 ng/m^3 in summer). Maximum daily value of individual PAH was 85.2 ng/m^3 for Chrysene in 2011/12.

The lower PAHs concentrations in summer are likely due to not using fossil fuels for heating, washout effects, and to a lesser extent, photo-degradation and higher percentage of PAHs in the gas phase. The concentration of individual PAH with high molecular weight: Fla, Pyr, Baa, Chr, Bbf, Bkf, BaP, Inp i Bpe were significantly higher in winter in 2012 than in 2009. These PAHs could be markers for traffic as emission source.

The traffic contributes significantly to concentrations of PAHs in the air. The average concentrations for sum of 16 priority PAHs in PM_{10} fractions were more than 10 and 20 times higher in winter (29.3 ng/m^3 in 2009 and 74.1 ng/m^3 in 2012) than in summer (2.4 ng/m^3 in 2009 and 3.5 ng/m^3 in 2012). Concentration of B(a)P was highest in PM_{10} in the heating season (17.4 ng/m^3 in 2009 and 55.8 ng/m^3 in 2012). In 2009, during the non-heating season, all values for B(a)P were below the annual target value. In in 2012, only one value (1.01 ng/m^3). was above the annual target value of one ng/m^3.

Table 1. Statistical parameters of PM concentrations

	PM_{10} (μg/m^3)			
	Winter 2009	**Winter 2011/12**	**Summer 2009**	**Summer 2011/12**
N. of samples	62	55	53	56
Average	69.7	75.8	23.1	29.8
St. deviation	42.7	69.5	9.9	12.0
Median	58.2	53.8	21.5	28.8
Maximum	210.2	380.8	54.9	69.6
Minimum	17.1	13.2	6.8	9.2
98-percentile	153.3	258.9	50.4	58.9
95-percentile	134.1	235.5	43.9	50.9

3.2 Benzo(a)Pyrene concentration

The largest contribution to the cancerogenic activity of PAHs is benzo(a)pyrene (B(a)P) (51-82%) (Akyüz at al. 2008). B(a)P is also used as an indicator of risk to human health. The percentage of B(a)P to total PAHs in summer and winter as well as B(a)P concentrations are given in Table 2.

Table 2. Average daily mean concentration of ∑ PAH and B(a)P (both ng/m^3) and their ratio in PM_{10}

Campaign 2009						**Campaign 2011/12**					
Winter			**Summer**			**Winter**			**Summer**		
∑ PAH	B(a)P	%	∑ PAH	B(a)P	%	∑PAH	B(a)P	%	∑PAH	B(a)P	%
29.04	3.55	**12.2**	2.36	0.09	**3.8**	74.09	8.17	**11.0**	3.48	0.27	**7.6**

Concentration of B(a)P was about 12% of the total concentration of PAHs in PM_{10} during winter (12.2% in 2009 and 11.02 % in 2012). In summer, the percentage of B(a)P was higher in 2012 (7.3%) than in 2009 (3.8%). For comparison, Akyüz at al. (2008) report from a Turkish city of Zonguldak a ratio of total PAHs in the winter and summer 46.2 for $PM_{2.5}$ and 15.0 for $PM_{2.5-10}$.

3.3 Emission sources

Major sources of PAHs, especially in large urban areas, are gasoline and diesel vehicles (Khalili et al. 1995, Simick et al. 1999). Other significant sources are coal and oil combustion as well as biomass combustion. (Simick at al. 1999, Zencak at al. 2007, Yunker at al. 2002). The ratios of some particle-bound PAHs are suggested to be characteristic of certain sources. Table 3 shows selected PAHs ratios used for source identification. These ratios have been calculated for PAH bound on PM_{10}.

3.4 PMF results

The contribution of sources of PAHs to the PAH mass in PM_{10} were identified by Positive Matrix Factorization analysis – PMF (Hopke 2001, Bruinen de Bruin 2006). As input data we used 16 species of PAHs, 53 samples in heating and 61 in non-heating season. Each PMF factor profile was compared with several profiles reported in literature.

Compounds Pyr, Fla, B(b)f and Bpe are released by fossil fuels combustion (Kavouras at al. 2001). Phe, Pyr, Fla are emitted by coal burning (Papageorgopoulou 1999) and a B(a)P, Fla are emitted by wood burning (Papageorgopoulou 1999).

Table 3. Comparison of the ratios of selected particle-bound PAHs in the four campaigns

Ratio	Source and value	Ratios determined			
		Winter 2009	Winter 2012	Summer 2009	Summer 2012
IdP/(BghiP+IdP)	Diesel: 0.35-0.70 (Rogge at. al., 1993, Khalili,at al 1995)	0.52	0.47	0.52	0.36
BaA/Chry	Gasoline: 0.28-1.2 (Khalili,at al 1995, Simick at al., 1999, Tang at al., 2005)	0.66	0.74	0.43	0.51
BaP/BghiP	Coal: 0.9-6.6 (Simick at al., 1999) Vehicles: 0.3-0.78 (Simick at al., 1999)	1.15	1.17	0.42	0.41
Fla/(Fla+Pyr)	Coal: 0.53 (Kim at al., 2003) and >0.5 (Zencak at al., 2007, Yunker at al., 2002) Gasoline: 0.40-0.5 (Yunker at al., 2002)	0.54	0.46	0.50	0.52
BghiP/IdP	Diesel: 1.1 (Zencak at al., 2007)	0.91	1.12	0.92	1.77
BkF/IdP	Diesel: 0.5 (Li at al., 1993)	0.68	1.29	0.80	1.07
Ant/(Ant+Phe)	Wood combustion: >0.1 (Pio at al., 2001, Yunker at al., 2002)	0.17	0.19	0.34	0.21

Pyr, Fla and Bbf are present in exhaust gasses from the cars without catalyst (Kavouras at al. 2001). Phe, Baa i B(a)P also come from emissions from motor vehicles (Fraser at al. 1997). Baa is formed during combustion of diesel fuel and natural gas, while B(a)P comes from automobile emissions with and without catalyst (Rogge at al. 1993). Phe, Chr, Baa i Pyr are released by traffic (Budzenski at al. 1997) as well as Bpe, Dba, B(a)P, Bbf, Bkf, Inp (Papageorgopoulou at al. 1999). Typical markers for diesel combustion are Phe, Pyr, Fla, Chr (Smith at al. 1996). Bpe and Inp also originate from traffic (Papageorgopoulou at al., 1999).

PAHs typical for stationary sources (industry, cement production, power plants) are B(a)P, Baa, Bep (Papageorgopoulou at al. 1999) and also Ant (Akyüz at al. 2008) .

Between three and five factors were considered and optimal solution (with 20 initial random starting points). Three factors were extracted for both season: (1) stationary sources (combustion of oil, coal, residential heating, thermal power plant) (2) traffic (diesel and gasoline vehicle exhaust), (3) biomass burning.

Factor 1: This source accounts for 29.6 % (8.6 ng/m^3) in 2009 and 37.1 % (27.4 ng/m^3) of total PAHs in 2012 in winter, in summer 31.3% (0.7 ng/m^3) in 2009 and 38.7 % (1.3 ng/m^3) of total PAHs in 2012. Factor 1 represents stationary sources such as coal and oil combustion, residential and domestic heating. Residential heating with coal and oil give large contributions to PAH pollution in winter. Main congeners are Fla, Baa, Ant, Pyr, Chr.

Factor 2: The percentage contribution of this source to the PAHs is 59.3 % (17.2 ng/m^3) in 2009 and 55.3 % (41.0 ng/m^3) in 2012, in summer 30.7 % (0.7 ng/m^3) in 2009 and 49.1% (1.6 ng/m^3) in 2012.

PAHs in Factor 2 are tracers for diesel and gasoline vehicle exhaust emissions. BbF and BkF are the highest loaded PAHs on this factor but Ane, Phe, BbF, BkF, B(a)P, Inp and Bpe are also present. Tracers that represent diesel exhaust emission are Nap, Flu, Phe, Ant, Flt, Pyr and Chr. BbF and BgP represent petrol exhaust emission.

Factor 3: The percentage contribution of this factor to total PAH levels is 11.1% (3.2 ng/m^3) in 2009 and 7.6% (5.6 ng/m^3) in 2012 in winter. In summer, 38.8% (0.9 ng/m^3) in 2009 and 12.2% (0.4 ng/m^3) in 2012 is coming from this source. The main markers are Nap, Ane, Any, Fle, Phe, Ant, present biomass including wood burning.

4. CONCLUSION

Mean daily PM$_{10}$ mass concentrations were higher in winter than in summer campaigns. The concentration levels of PAHs fluctuated significantly within a year and followed the trend of PM concentrations. During winter, the higher means and peak concentrations were due to residential fuel combustion for heating (individual stoves coal burning and central heating). The lower PAHs concentrations in summer are likely due to not using fossil fuels for heating, washout effects, and to a lesser extent, photo-degradation and higher percentage of PAHs in the gas phase. Traffic has a large contribution to emission of PAHs in air both in winter and summer periods.

The identified sources, factors, were: (1) stationary sources (2) traffic (diesel and gasoline vehicle exhaust), (3) biomass burning. Taking into account the whole sampling period, percentage contribution of emission sources to the total PAH was increased for the stationary sources and traffic in summer. Traffic was more intensive in summer in 2012 than three years earlier. This may be due to overall rapid urban development, resuspended dust and traffic jam as well as to the existence of individual domestic heating in cold, heating period. During winter, source contribution of traffic was higher in 2009. Lower contribution of wood and biomass burning in 2012 during winter may be due to removing Gypsy camp that was nearby the sampling location in 2009. Stationary sources were slightly increased in 2012 than 2009. Relative contribution of the different factors is shown in Figure 1.

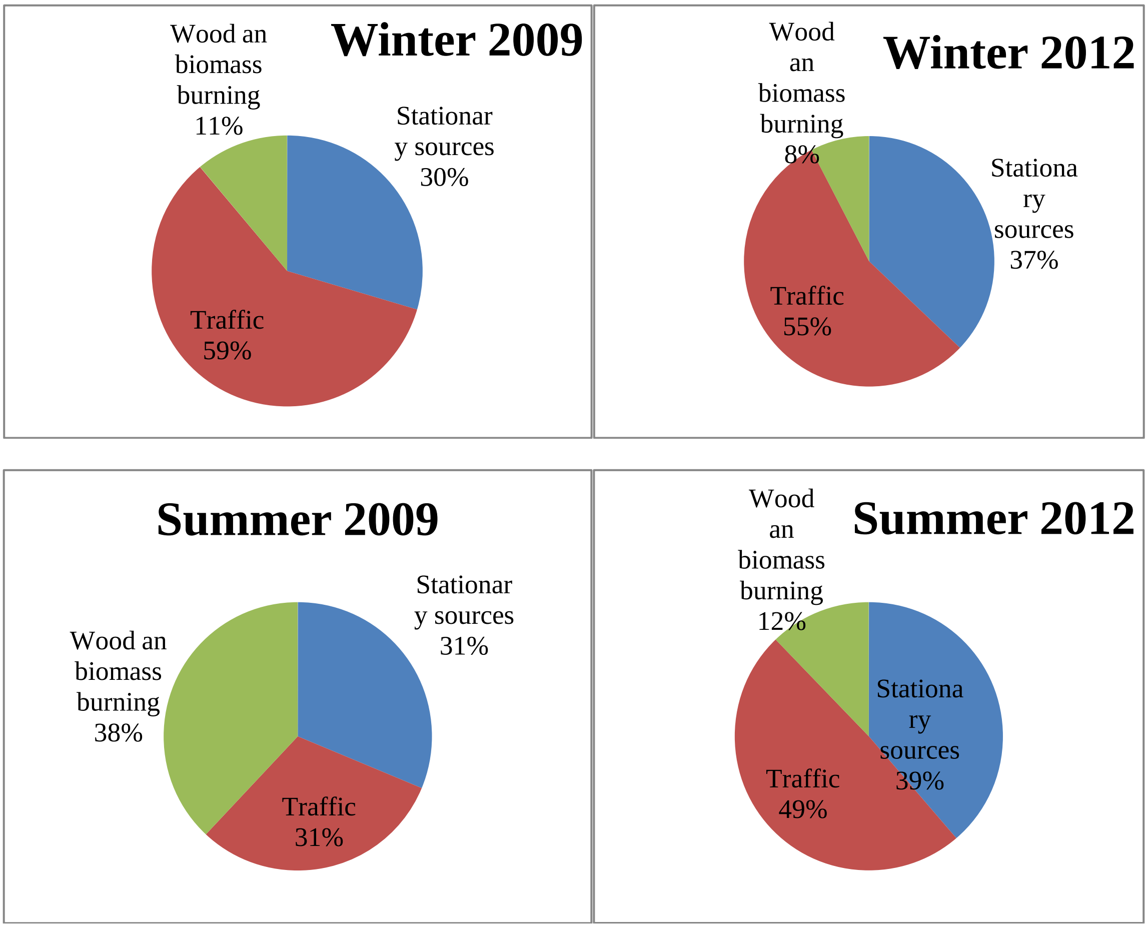

Figure 1 : Percentage contribution of identified emission sources to the total PAHs

Traffic and stationary sources were more intensive in 2012 than three years earlier. This may be due to overall rapid urban development. Lower contribution of wood and biomass burning in 2012 may be due to removing a Gypsy camp that was nearby the sampling location in 2009.

5. ACKNOWLEDGEMENTS

This work was supported by the following projects and sponsors: WeBIOPATR (2006-2009) funded by the Research Council of Norway; III41028, INGEMAS (2011-2014) funded by the Ministry of Education, Science and Technological Development of Serbia (2011-2014) ; Municipality of Belgrade, Secretary of Environmental Protection.

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2.4 THE INFLUENCE OF AIR MASS ORIGIN AND POTENTIAL SOURCE CONTRIBUTIONS ON PM10 IN BELGRADE

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ABSTRACT

Together with ozone, coarse particulate matter (PM_{10}) is the pollutant of most concern in terms of risk it may impose to health. Besides various local sources, remote pollution sources through the long-range transport have a significant impact on the air quality in large cities. Therefore, various factors such as the area characteristics, meteorological conditions, as well as local and remote anthropogenic activities and natural phenomena can affect seasonal variations of PM_{10} source contributions. In order to examine the influence of synoptic air masses and long-range transport on local pollution levels, as well as to assess the contribution of potential local and remote sources to the observed PM_{10} concentrations and their seasonal variations in Belgrade, Potential Source Contribution Function (PSCF), Concentration Weighted Trajectory (CWT), Trajectory Cluster (TCA) and Trajectory Sector Analysis (TSA) were applied.

1. INTRODUCTION

Coarse particulate matter with aerodynamic diameter less than 10 μm (PM_{10}) is emitted from various sources of both natural (marine aerosol, wind resuspension of soil, biomass burning, Saharan dust events) and anthropogenic (motor vehicle exhaust, industry sectors, heat and power generation plants) origin [Huang *et al.*, 2011; Gonzales-Santiago *et al.*, 2011, Panis *et al.*, 2010; Zanobetti and Schwartz, 2009; Liu *et al.*, 2010; Unal *et al.*, 2011]. Thereby, for most of the locations, the impact of PM_{10} long-range transport on pollution levels cannot be neglected [Kallos *et al.*, 2007; Yuval, 2006; Yoshimoto *et al.*, 2011] as meteorological conditions play a substantial role in distribution, accumulation and deposition processes [Wang *et al.*, 2010; Dayan *et al.*, 2011; Stephens *et al.*, 2008]. Determination of a quantitative relationship between ambient air quality and pollutant sources is one of the most significant tasks in air pollution management. With reference to this, various mathematical models have been developed for source identification of atmospheric pollutants, estimation of their source contributions and identification of potential source regions. Thereby, contributions of different pollution sources to the total PM_{10} concentrations in both urban and rural area, exhibit seasonal variation depending on anthropogenic activities or natural phenomena [Marenco *et al.*, 2006; Ducret-Stich *et al.*, 2013]. Regarding this, several studies have observed the highest PM_{10} concentrations during African dust outbreak or soil resuspension during summer season [Rodriguez *et al.*, 2002; Hedberg *et al.*, 2005; Artinano *et al.*, 2003; Salvador *et al.*, 2012], while traffic emission, wood and coal burning are found to be main sources of PM_{10} pollution during winter months [Huang *et al.*, 2010]. According to Annual Air Quality Report issued by National Environmental Protection Agency of Serbia [Annual Air Quality Report, NEPA, 2011], the current PM_{10} concentrations at several traffic hot points in Belgrade exceed air quality limit, with the major pollution sources being coal combustion in heating plants and motor vehicle exhaust emission which has been elevated within the past decade. In this paper we examined the influence of synoptic air masses and long-range transport on local pollution levels and made assessment of the contribution of potential local and remote sources to the observed PM_{10} concentrations and their seasonal variations in Belgrade.

2. METHODOLOGY

In order to estimate the likely source locations for regional aerosol transport, Potential Source Contribution Function (PSCF) and Concentration Weighted Trajectory (CWT) [Wang *et al.*, 2008] models were applied on 1-h PM_{10} particle data obtained from the automatic monitoring station of the Institute of Public Health during 2012 in Belgrade. The PSCF values can be interpreted as a conditional probability describing the spatial distribution of probable geographical source locations by analysis of trajectories arriving at the sampling site. Since the method is known to have difficulties in distinguishing strong from moderate sources, the CWT model that determines the relative significance of potential sources has been additionally performed. Weighted concentration fields show concentration gradients across potential sources improving the determination of the relative significance of potential sources.

Air mass back trajectories were computed by the HYSPLIT (HYbrid Single Particle Lagrangian Integrated Trajectory) model through interactive READY system. Daily 72-h back trajectories, started from Belgrade (44°49' N, 20°28' E) every hour UTC each day, were evaluated for three different heights above the starting point at ground level (500 m, 1000 m, and 2000 m). In addition, to reveal the major pathways of air masses, a study of airflow characteristics was performed using Trajectory Cluster (TCA) [Wang *et al.*, 2008] and Trajectory Sector Analysis (TSA) [Husain *et al.*, 1990; Baria *et al.*, 2003].

3. RESULTS AND DISCUSSION

Statistical parameters for 1-h PM_{10} mass concentrations are shown in Table 1 indicating elevated concentrations during the winter and autumn seasons.

Table 1. Descriptive statistics of measured PM_{10} concentrations [µg m^{-3}]

	Valid Number	Mean	Median	Perc 10th	Perc 95th	Std Dev
2012	8345	55.4	37.3	11.9	155.2	80.6
Winter	2106	82.1	61.4	24.0	195.4	99.8
Spring	2184	33.9	28.5	8.2	78.3	27.9
Summer	2207	40.8	28.4	7.0	80.8	96.3
Autumn	1848	67.8	47.0	16.6	193.8	65.1

The results of PSCF (Figure 1) and CWT (data not shown) analyses indicate that the main sources of PM_{10} pollution are located in bordering countries, as well as in Central Europe. Investigated sources contribution differed for summer and winter season (Figure 1). In the winter months, dominant PM_{10} sources affecting receptor site were located in the northeast, south and southwest, while moderate ones were located in the northwest. In contrast to this, modeling results during the summer season indicated there is a large emission source area located in the south, and moderate one in the east. Overall, relatively low concentrations were observed during spring and summer (Table 1).

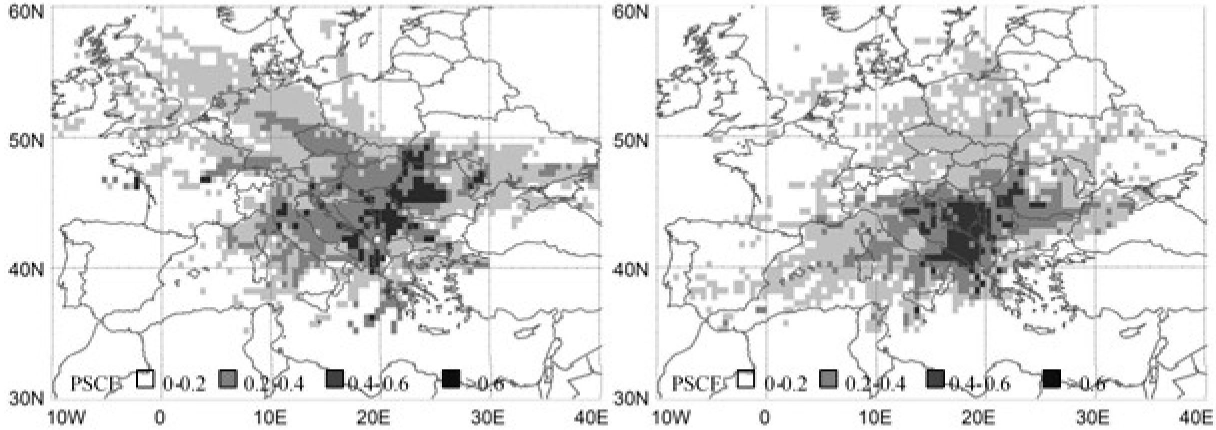

Figure 1. PSCF derived maps: winter (left) and summer (right)

Trajectory clustering for whole monitoring period (data not shown) generated six clusters: two long-range trajectory clusters, representing the flow from northwest and north directions, and four short-range clusters. The major arriving air masses originated from southwest (23%) and northwest (23%), while the less frequent ones were associated with northeastern (7%) trajectory cluster. These results suggest that the largest contributions to PM_{10} concentrations at Belgrade were observed for the two short-range clusters: the northeastern (PM_{10} mean value 52.23 µg m^{-3}) and the southern (PM_{10} mean value 45.37 µg m^{-3}). Taking into consideration the low flows of air masses arriving from these sectors, this indicates the areas with strong emission sources.

As shown in Figure 2, the analysis of air masses main pathways in the summer and winter season emphasizes not only the differences in the position and length of trajectories and their contribution to the local pollution levels, but also in the number of clusters. After comparing the results of PSCF and CWT analyses, a clear relationship between the potential PM_{10} sources and air mass flows during the summer season can be observed. It should be also noted that, for the winter months, TCA did not result in satisfactory explanation due to the lack of clusters from south where the dominant emission sources are shown to be located.

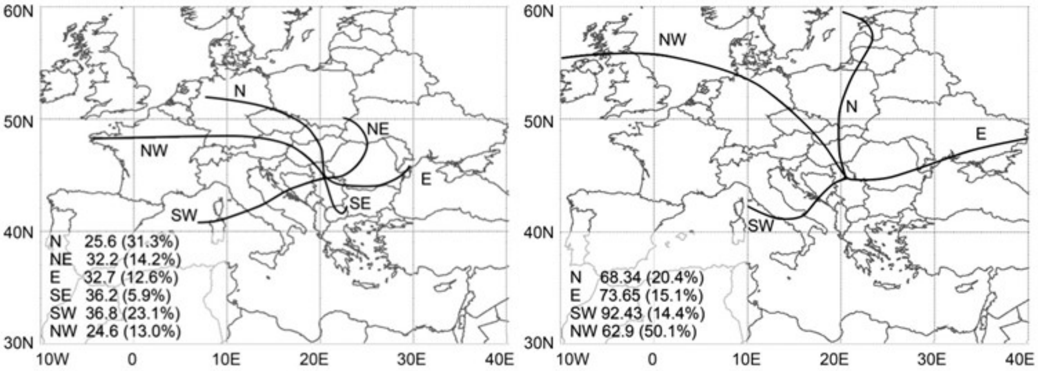

Figure 2. Representative trajectories mean PM_{10} concentrations [µg m^{-3}] and trajectory frequencies within clusters for winter (left) and summer (right) seasons

On the basis of the trajectories coming from the north (Figure 3) which are associated with relatively low PM_{10} concentrations, TSA analysis was used for determination of the local background [Zhu *et al.*, 2011], and subsequently by combining the frequency of arriving air masses with transported concentrations, the contribution of long-range transport to measured PM_{10} concentrations for all seasons was estimated. As can be seen in the Figure 4, the impact of the long-range transport on the observed PM_{10} levels in Belgrade is significant and ranges from a low of 5 µg m^{-3} during spring time to a high of 13 µg m^{-3} during autumn and winter season. Thereby, the contribution of the remote pollution sources has proved to be highest during summer (22%) and lowest during spring time (17%).

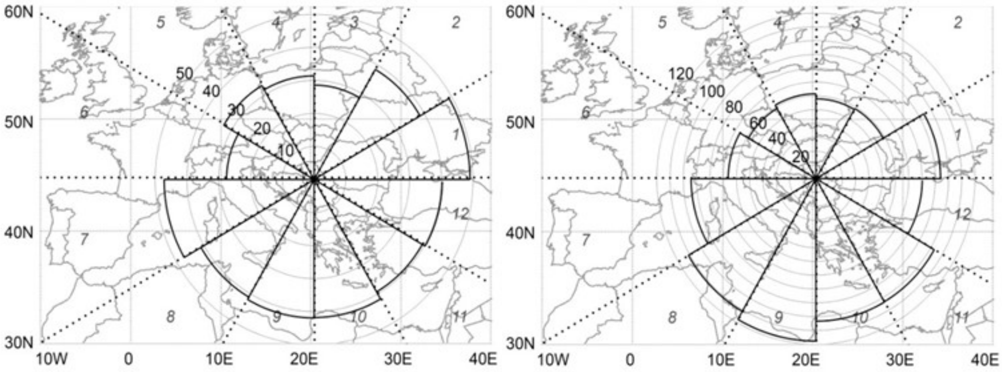

Figure 3. TSA analysis: angular PM_{10} concentrations in winter (left) and summer (right) season [µg/m^3]

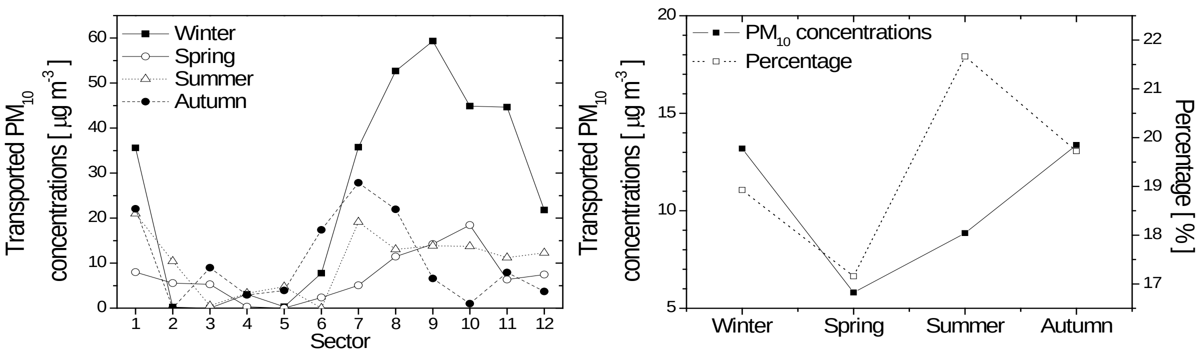

Figure 4. Seasonal variations of transported angular PM_{10} concentrations (left) and seasonal contribution of long-range transport to measured PM_{10} concentrations (right)

4. CONCLUSIONS

The aim of this study was to assess the impact of long-range transport on local PM_{10} concentrations in Belgrade urban area during all seasons in 2012. According to the results of PSCF and CWT analyses the main emission sources are located in bordering countries and Central Europe. The TCA results suggest that the largest contributions to PM_{10} concentrations were observed for the northeastern and the southern cluster, which, taking into consideration the small flows of air masses arriving from these sectors, indicates the areas with strong emission sources. While the impact of the long-range transport on the observed PM_{10} levels in Belgrade ranged from 5 μg m^{-3} during spring time to 13 μg m^{-3} during autumn and winter season, the contribution has proved to be highest during summer (22%). Gaining better understanding of the mechanisms controlling PM_{10} concentrations is mandatory for predicting concentrations of air pollutants, as well as for improving of the effectiveness of future emissions reduction measures.

5. ACKNOWLEDGEMENTS

This paper was realized as a part of the project No III43007 financed by the Ministry of Education and Science of the Republic of Serbia within the framework of integrated and interdisciplinary research for the period 2011-2014. The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model and READY website (http://www.arl.noaa.gov/ready.php) used in this publication, and to the Institute of Public Health of Belgrade, Serbia for providing data to utilize air quality data for this study.

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2.5 CHEMICAL CHARACTERISATION OF RESPIRABLE PARTICULATE MATTER IN AMBIENT AIR OF THE TOWN OF BOR

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Hazardous air pollutants released from industrial sources may have a serious impact on the population as well as on the surrounding area. In order to assess the relationship between outdoor and indoor air pollution in the vicinity of Copper Smelter Complex in the town of Bor the simultaneous sampling of both particulate matter fraction, PM_{10} and $PM_{2.5}$, indoor and outdoor, were conducted during heating and non-heating seasons in 2009. and 2010. In the town of Bor, there have been historically measured concentrations of SO_2 and arsenic concentrations in excess of the National Ambient Air Quality Standard (NAAQS) for TSP at monitoring locations.

This study showed that the average outdoor PM_{10} and $PM_{2.5}$ concentrations were 34 % and 45 % higher during heating season in comparison to non-heating season. Similar results were recorded for particulate fraction in indoor microenvironment, the average indoor PM_{10} concentrations were 33.8 µg/m^3 and 44.0 µg/m^3 during non-heating and heating seasons, respectively. The average indoor $PM_{2.5}$ concentrations were 25.8 µg/m^3 and 36.6 µg/m^3 during non-heating and heating seasons, respectively.

The concentrations of 21 target elements were determined using ICP AES and GF AAS. The percentage ratio of all analyzed elements in outdoor ambient were higher during non-heating season for both fractions, while the percentage ratio of trace elements measured outdoors (that are presented at ng/m^3) were higher during heating season, 1.63 % of PM_{10}, and 1.56 % of $PM_{2.5}$. The same situation were observed for concentrations in indoor microenvironment.

Calculated EF values varied widely between 0.7 and 25627.3 during non-heating season, and between 1.1 and 1118266.9 during heating season. The EF values for most of the elements of indoor $PM_{2.5}$ were higher than those of the outdoor $PM_{2.5}$.Most of the measured elements have high EF that confirm that they originate from anthropogenic sources.

In addition, 12 different elemental ratios were used as tracer of main pollution sources in the vicinity of copper smelters.

The positive matrix factorization (PMF) was applied to the PM_{10} data sets to identify the diverse sources of pollution of the town of Bor. Source appointment and chemical characterization of outdoor PM_{10} particles in Bor, town located in the vicinity of copper smelter facilities, have been conducted for the first time in this region. For both campaigns, heating and non-heating, seven sources have been identified.

Supported by the projects TR21009(2008-2010) and III41028(2011-2014), Ministry of Education, Science and Technological Development of Serbia

3 ATMOSPHERIC MODELING

3.1 THE ROLE OF AIR QUALITY MODELLING IN PARTICULATE MATTER MANAGEMENT IN CITIES. RESULTS FROM THE AIR IMPLEMENTATION PILOT

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ABSTRACT

In 2011, the European Commission and the EEA agreed to reinforce efforts to improve knowledge on implementation of air quality legislation through a joint pilot project. The Air Implementation Pilot lasted for 15 months and was finished in June 2013. It aimed to better understand the challenges cities faced in implementing air quality policy. Twelve European cities were selected and invited to join the project.

One of the issues addressed in the pilot was to examine the model practices in these cities, to assess the strengths and weaknesses of such applications and to further identify needs for guidance in the use of air quality models. The results of the analysis of model practices for air quality management are presented in this work. More than 20 different models have been used for air quality assessment and management in these cities. Most of the cities have applied a different model depending on the purpose. The main purposes for which cities applied models are air quality assessment, source contribution and long term planning.

The cities have found models helpful and the outputs have been used in urban air quality management, including the evaluation of strategies to reduce PM ambient levels. However, the cities found difficulties in the application of models as for instance the quality and availability of input data or the validation and uncertainty estimation of the model results.

Keywords:air quality models, urban air quality management, particulate matter, EU legislation.

INTRODUCTION

The quality of the environment in urban areas is of vital importance. It is one of the main factors that determine whether a city is a healthy place to live in. Europe is one of the most urbanized continent in the world. Today, more than two thirds of the European population lives in urban areas and this share continues to grow (EC, 2011). At the same time car use in Europe is growing, and a further doubling of traffic is predicted by 2025 (EC DG ENV). Traffic is the dominant urban source per today along with domestic combustion (which has been growing over the last few years) (EEA, 2013b). Persistent air quality exceedances of the limit or target values for particulate matter are observed in urban areas across Europe (ETC/ACM, 2012). Furthermore, in 2011 33% of the urban population in Europe was exposed to concentrations of PM_{10} in excess of the EU daily limit value and 15% was exposed to $PM_{2.5}$ concentrations above the EU target value (EEA, 2013b).

In 2011, the European Commission and the European Environment Agency (EEA) agreed to reinforce efforts to improve knowledge on implementation of air quality legislation through a joint pilot project (EEA, 2013a). The objective of the pilot was to help identifying and addressing the reasons underlying why some pollutants concentrations remain above regulated levels, and find “effective ways of dealing with problems on the ground” that prevent the effective implementation of environmental legislation. The Air Implementation Pilot aimed to better understand the challenges cities faced in implementing air quality policy, identify good practices, encourage cities to share their knowledge and experiences, so they could learn from each other, and also identify areas where further guidance would be helpful. The Pilot brought together 12 cities across the European Union and was jointly run by the cities themselves, the European Commission, and the European Environment Agency (EEA. 2013a).

The Air Implementation Pilot project lasted for 15 months, starting in March 2012. The cities selected to join the pilot are a representative sample of the diversity of European urban areas. The selection aimed at including cities from different parts of Europe, of different population sizes, with different administrative traditions, and with a variety of sources of air pollutants. The cities are: Antwerp (Belgium), Berlin (Germany), Dublin (Ireland), Madrid (Spain), Malmö (Sweden), Milan (Italy), Paris (France), Ploiesti (Romania), Plovdiv (Bulgaria), Prague (Czech Republic), Vienna (Austria) and Vilnius (Lithuania).

The pilot focused on five “workstreams”, where lessons for implementation could most usefully be drawn: (i) emission inventories (ii) air quality modelling activities, (iii) air quality monitoring networks, (iv) management practices and (v) public information.

The results discussed in this manuscript focus exclusively on the workstream related to assessment of air quality modelling activities in the cities. More information about the results and conclusions obtained in the other workstreams can be consulted in the EEA Report No7/2013 (EEA, 2013a).

METHODOLOGY

One of the aims of the Air Implementation Pilot was to examine air quality modelling practices (where they exist) in the context of the air quality directives (EC, 2004 and EC, 2008) in the 12 participating cities, to assess to which extent modelling is used, strengths and weaknesses of model applications, and to identify further guidance needed by the cities. The work presented here does not provide precise recommendations on the application of models, but focuses on the experiences of these cities when applying models for air quality assessment and/or management.

According to the current Air Quality Directives (EC, 2004 and EC, 2008), the main applications of models in relation to air quality legislation are (EEA, 2011):

- Assessment of existing air quality: to supplement, complement, or replace monitoring stations; and to provide adequate information on the spatial distribution of the ambient air quality.
- Management of air quality and providing assistance in the drafting of the following plans:
    - Long-term air quality plans when limit values or target values are exceeded;
    - Short-term action plans in regard to exceedances of alert thresholds;
    - Joint international air quality plans with other Member States when transboundary air pollution is the cause of exceedances.
- Source apportionment: modelling in combination with monitoring to assess the causes of exceedances and the contribution to pollution from different sources.
- To provide supplementary information for the geographical areas not covered by measurement data. This could serve as a basis for calculating the collective exposure to pollution of the population living in an area.

Additionally models can also be used to provide complete spatial coverage of air quality; be used prognostically; and to provide improved understanding of the sources, causes and processes that determine air quality.

In order to examine model practices in the 12 cities a questionnaire was prepared to obtain an overview of the applications for which models are used, gain an insight on how the model has been applied for each of the purposes, and learn about where the modelling competence lies (e.g. authorities, scientific institutions, consultants, etc.)as well as existent cooperative activities with other institutions. The questionnaire was sent to a contact person in each city. The questionnaire aimed to give answers to the following main questions:

a. What types of models have been used?
b. Which particular models?
c. For what purposes are models used?
d. Which input and other data (e.g. emissions, meteorology, observed concentrations, boundary conditions, etc.) have been used and considered?
e. How are models validated?
f. Are the model results considered to be “fit for purpose”?

The questionnaire and the complete analysis can be consulted in the ECT/ACM Technical Paper (ETC/ACM, 2013).

RESULTS AND DISCUSSION

All the cities, with the exception of Dublin, have used models for air quality activities. There are several reasons why Dublin has not used air quality models. These reasons include: administrative issues (the difficulty of bringing together the various stakeholders); the current economic situation; and the perception that air quality modelling is an area where there is a lack of the required skill and experience to operate a model.

All of the other 11 cities replied to the questionnaire on modelling activities, with the exception of Ploiesti which instead of submitting the questionnaire, submitted a document informing that models have only been applied for assessing air quality in general and not for other purposes. Therefore, for the sake of comparability, information from Ploiesti has not always been taken into account.

As mentioned before, air quality models can be used for many different purposes. In the questionnaire, the participating cities were asked about eight specific applications:

1. Assessment of air quality in general (including evaluating the impact on air quality of new infrastructure, such as highways, airports, etc).
2. Reporting of air quality compliance assessments (both under the air quality assessment questionnaire and for time extension notifications).
3. Assessment of source contribution.
4. Long-term planning and scenario calculations.
5. Short-term action plans.
6. Air quality forecasting.
7. Assessment of the exposure of populations to air pollution.
8. Supplementing measurements from monitoring stations.
9.

None of the cities have used models for other applications than the eight mentioned above and which applications the cities use models for varies considerably from city to city. Figure 1 shows the summary of the applications for which the ten cities that have submitted the questionnaire have used air quality models.

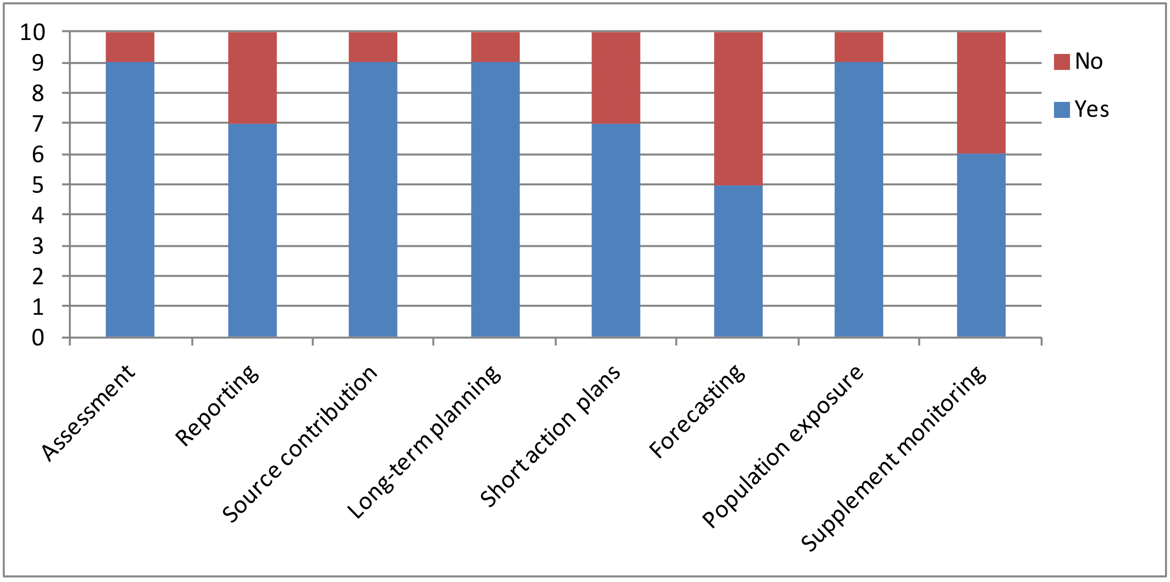

Figure 1. Number of cities, out of the 10 that submitted the questionnaire, that have used models for each particular air quality assessment and management application.

The information about the models and the purpose it was run has been summarized in the Table 1. As it can be seen in the table, the models applied differ from city to city, and only three models have been applied in more than one city. Different types of models have been employed for the same application:

- For assessment of air quality in general the type of models that have been applied are Gaussian (6), Eulerian (4) and Lagrangian (3), street canyon model (1) and also an statistical model based on interpolation (1).
- For reporting of air quality compliance the type of models applied are Street canyon model (1), Eulerian (2), Lagrangian (1) and Gaussian (1).
- For assessment of source contribution Gaussian (5), Lagrangian (4), Eulerian (4) and also a chemical mass balance model (1)have been applied.
- For long term planning and scenario calculations, Street canyon (2), Gaussian (4), Eulerian (3) and Lagrangian (2) models have been employed.

- For short term action plans Gaussian (4), Eulerian (3) and Lagrangian (2) models have been applied.
- For air quality forecasting the cities have employed Eulerian dispersion models (2), a statistical model based on neural networks (1), Lagrangian models (2) and Gaussian models (1).
- For assessing the exposure of the population the models used have been Gaussian (5), Eulerian (3), Lagrangian (3), street canyon (1) and interpolation model (1).
- Finally, to supplement measurements the types of models applied are Street canyon (1), Eulerian (3), Lagrangian (3) and Gaussian (3).

Almost all the models are documented in the Model Documentation System (MDS). The MDS aims to provide guidance to any model user in the selection of the most appropriate air quality model for his application. Only two models do not have public documentation available. A more detailed information about the models and its applications can be found in the ETC/ACM Technical paper (ETC/ACM, 2013) and the references there.

Table 1. Summary of the type of model, applications, and links to documentation of the models used by the cities participating in the Air Implementation Pilot.Applications: 1) Assessment of air quality in general; 2) Reporting of air quality compliance assessment; 3) Assessment of source contributions; 4) Long-term planning and scenario calculations; 5) Short-term action plans; 6) Air quality forecasting ; 7) Assessment of population exposure and 8) Supplement measurements.

Name of the model	Type	Applications	City	Documentation
AERMOD	Gaussian	1;3;4;5;7	Malmö	http://pandora.meng.auth.gr/mds/showlong.php?id=128
OSPM	Street canyon	2;5 1;4;7;8	Malmö, Madrid Antwerp	http://pandora.meng.auth.gr/mds/showlong.php?id=74
FARM	Eulerian	1;2;4;5;7;8	Milan	http://pandora.meng.auth.gr/mds/showshort.php?id=130
SPRAY	Lagrangian	3	Milan	http://pandora.meng.auth.gr/mds/showshort.php?id=87
CALPUFF	Gaussian	3 1	Milan Paris	http://www.epa.gov/ttn/scram/dispersion_prefrec.htm#calpuff
CBM	Chemical mass balance	3	Milan	http://www.epa.gov/scram001/receptor_cmb.htm
GRAL modified	Lagrangian	1; 2; 3; 4; 7; 8	Vienna	http://pandora.meng.auth.gr/mds/showlong.php?id=133
CAMx	Eulerian	5; 6;7	Vienna	http://pandora.meng.auth.gr/mds/showshort.php?id=177
SERENA	Statistical Neural Network	6	Madrid	http://www.mambiente.munimadrid.es/opencms/opencms/calaire/SistIntegral/SistPrediccion.html
CMAQ	Eulerian	2; 3; 4; 5	Madrid	http://www.cmaq-model.org/
WRF-Chem	Eulerian	2; 3; 4; 5	Madrid	[http://www.acd.ucar.edu/wrf-chem/]
ATEM	Gaussian	1; 2; 3; 4; 5; 7	Prague	[http://www.atem.cz/en/atem.html]
SYMOS	Gaussian	5	Prague	http://pandora.meng.auth.gr/mds/showshort.php?id=119
REM_CALGRID_RCG	Eulerian	1,3	Berlin	http://pandora.meng.auth.gr/mds/showshort.php?id=173
IMMISluft (IMMIScpb)	Gaussian	1, 3, 4, 7,8	Berlin	http://pandora.meng.auth.gr/mds/showshort.php?id=178
CHIMERE	Eulerian	1;2;3;4;6;7	Paris	http://pandora.meng.auth.gr/mds/showshort.php?id=144
ADMS urban	Gaussian, Lagrangian	1 1,2,3,5,6,7,8	Paris Vilnius	http://pandora.meng.auth.gr/mds/showshort.php?id=18
PMSS	Eulerian		Paris	http://www.harmo.org/Conferences/Proceedings/_Kos/publishedSections/H14-176.pdf
STREET	Street	2; 4; 7	Paris	NA

Name of the model	Type	Applications	City	Documentation
	canyon			
AUSTAL 2000	Lagrangian	1; 3; 4; 5; 7;8	Plovdiv	http://pandora.meng.auth.gr/mds/showlong.php?id=132
PROKAS_B	Gaussian	1; 3; 4; 5; 7	Plovdiv	http://pandora.meng.auth.gr/mds/showlong.php?id=115
VinMISKAM	Eulerian	1; 3; 4; 5; 7	Plovdiv	http://pandora.meng.auth.gr/mds/showlong.php?id=123
POLTRAN	Eulerian	1; 3; 7; 8	Plovdiv	NA
RIO	Interpolation model	1;4;7;8	Antwerp	http://rma.vito.be/demo/faces/documents/rio/RIO.pdf
AURORA	Eulerian	1;4;7;8	Antwerp	http://pandora.meng.auth.gr/mds/showlong.php?id=167
IFDM	Gaussian	1;4;7;8	Antwerp	http://pandora.meng.auth.gr/mds/showlong.php?id=50

In terms of the input data used for the modelling, emissions, meteorology and boundary conditions, the data employed depend on the type of model, the purpose of application, and on the information available. From the information provided by the cities it was found that:

- **Emission inventories**. Cities have developed a specific *local emission inventory* to run the model, and the *spatial and temporal resolution* of the emission inventories vary according to the model used and the resolution employed in the air quality (AQ) modelling. For instance, spatial resolution goes from 24 m in the AUSTAL 2000 (Plovdiv) or 50m in the OSPM model (Malmö) to 4x4km^2 in the FARM model (Milan); the temporal resolution employed is hourly or annual. *The sources* included in the emissions also vary depending on the purpose, model and information available. For instance, in relation to the traffic emissions, all the cities answered that traffic congestion is a problem in their cities with the exception of Vilnius, however not all the models are capable of reflecting it. For instance, FARM (Milan) or REM_CALGRID (Berlin) do not take into account traffic congestion, and the cities of Paris and Plovdiv also indicate the difficulties in modelling traffic congestions as traffic emissions are based on traffic counts that cannot completely reflect congestion effects. Other traffic emissions that are usually not included are the non-exhaust emissions. For commercial and domestic sources the precise location within the cityis notalways known. A further difficulty is the lack of data on the emission height of these sources.
- **Meteorology**. Meteorological data for air quality modelling are obtained from different sources such as measurement towers (as in the case of Malmö, Prague, Berlin, Plovdiv, Antwerp), high resolution meteorological models (as in the case of Madrid, Vienna and Paris), or model results combined with a local monitoring network (as in the case of Milan).
- **Background concentration**. The background concentration of pollutants is considered in all the cities, but using different sources as for instance: 1) estimation from modelling of regional sources together with several measurement stations (Malmö); 2) estimation from monitoring data from background stations and emission inventories of neighbouring provinces when needed (Vienna, Paris, Plovdiv, Vilnius and Antwerp); 3) provided as boundary conditions under nesting models (Madrid), other regional models (Berlin, Vilnius) and models run at national level for forecasting (Vilnius); and 4) European simulations (Berlin).

To evaluate the results of the model, the cities compare the model output against local measurements and use indicators as for instance bias, root mean square error, mean error correlation, etc. Most of the cities have also estimated the 'uncertainty' (accuracy) of their air quality model, as required by EU legislation (EC, 2008 and EC, 2004).

In the questionnaire sent to the cities it was also asked a personal evaluation of the usefulness of the model and of the challenges found in the application of models for air quality assessment and/or management. The answers showed that all the cities have found their models to be helpful for the purpose for which they were implemented. Furthermore and in general, the model results have been considered in air quality management decisions.

Regarding the challenges encountered when running the models, five points were mentioned by almost all the cities:

- *Input data quality and availability*. For instance emission inventories, estimation of background concentrations at national and international level, or the lack of good quality urban meteorological data.
- Technical difficulties on *representing the physical and chemical processes in the city*. For instance, traffic congestion, hot spots, etc.
- Dealing with the *uncertainties* in the model results, as for instance overestimations and underestimations in the pollutant concentrations.
- The *resources* required, not only in terms of computational time and computing servers, but also in terms of personnel competence. As commented before, this is the main reason most of the cities don’t run the model themselves and collaborate with universities or research institutes.
- *Interpretation of the results*. Linked with the two points mentioned before, the results are complex and their interpretation requires a high degree of competence within air quality modelling.

In view of the results and the comments expressed by the cities, improvement in modelling activities could come from the following areas (EEA, 2013a):

- Training/guidance on how to use a model, how to apply it, and how to validate it. Training is also needed on how to know which model to use.
- Improvement of input data, for instance to take into account the urban topography.
- Production of emission inventories with the better quality/accuracy of the emission data (emission rates and emission conditions (e.g. height) and adequate spatial and temporal resolution for the model application.
- Creation of a service that provides cities with background concentrations as an input for their models.
- Creation of a general framework for modelling, criteria harmonisation, and exchange of experiences. The involvement of cities in FAIRMODE activities (http://fairmode.ew.eea.europa.eu/) can be a way of promoting this exchange of experiences.

CONCLUSION

The questionnaire was sent to 12 European cities: Berlin, Dublin, Madrid, Malmö, Milan, Ploiesti, Prague and Vienna in the year 2012 and Antwerp, Paris, Plovdiv and Vilnius in the year 2013. All the cities applied models for air quality management except the city of Dublin. All the cities expect to learn from the city pilot about how the other cities have applied models and share the difficulties inherent to the application of dispersion models: data input, interpretation of the results, etc.

The models have been used for different purposes, as for instance, reporting of air quality compliance, long term planning, population exposure estimation or source apportionment. Not all the cities have applied models for all the purposes. Moreover, most of the cities have established some collaboration with universities and research institutes, and indeed from the 10 cities that filled in the questionnaire, only two have enough technical and professional resources to run the models themselves.

From the analysis of the questionnaires and the conclusion from the workshops, several points that can help cities in their application of the models were identified. They include training, creation of forums for discussion, or providing better input data for the models.

Despite the challenges in the application of models, all the cities have found models helpful for the applications they were used for, and the outputs have been employed for air quality management decisions.
The Air Implementation Pilot has shown that enabling the different stakeholders and experts to exchange their knowledge will ultimately promote a better understanding of issues related to the implementation of air quality legislation, including within the use of models for air quality assessment and management.

ACKNOWLEDGEMENTS

This work is based on studies prepared by the European Environment Agency's Topic Centre for Air and Climate Change Mitigation (ETC/ACM). The results presented here have been recently published in the EEA Report No 7/2013 and the ETC/ACM Technical Paper 2013/4.

The authors would like to thank the EEA task manager Anke Lükewille for her guidance and discussions on the content of the analysis. Special thanks are also due to the pilot cities' contacts for the modelling activities.

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3.2 THE USE OF HYBRID RECEPTOR MODELS AND GROUND-BASED REMOTE SENSING OF PARTICULATE MATTER FOR IDENTIFICATION OF POTENTIAL SOURCE REGIONS

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ABSTRACT

Suspended particulate matter (PM) in the atmosphere, commonly known as aerosol, plays an important role in air quality, climate change and long-range transport of pollutants. The complexities of aerosol processes in the atmosphere are so great that they lead to large uncertainties in quantitative understanding of their role in many environmental issues. Aerosols originate from a wide variety of natural and anthropogenic sources. Thus determining the quantitative relationship between ambient air quality and pollutant sources is one of the main difficulties in air pollution management, which can be addressed by use of receptor models.Receptor modeling is an application of multivariate statistical methods for identification and quantitative apportionment of air pollutants to their sources. In this work the application of hybrid receptor models to resolve potential source locations is demonstrated. In addition, case studies of LIDAR, an active remote sensing technique, measurements are used for determination of vertical aerosol distribution, thus contributing to further aerosol transport processes analysis.

INTRODUCTION

The atmospheric processes are very complex, and pollutant concentrations are inherently random variables because of their dependence on the fluctuation of a variety of meteorological conditions and emission intensity.Various chemicals are emitted into the air from both, natural and anthropogenic sources. Among them, atmospheric particles – aerosols – represent the key component of the atmosphere since they influence the energy balance of the Earth's surface, visibility, climate and environment as a whole [1]. According to World Health Organization (WHO), ozone, particulate matter (PM), heavy metals and some hydrocarbons present the priority pollutants in the troposphere [2]. A number of epidemiological studies have demonstrated that acute and chronic health effects are related to the inhalable PM_{10} (aerodynamic diameter less than 10 μm) exposure in the urban environment, and some data also seem to indicate possible seasonal effects of the particulate matter on human health [3,4].

One of the main difficulties in air pollution management is to determine the quantitative relationship between ambient air quality and pollutant sources. Source apportionment is the process of identification of aerosol emission sources and quantification of the contributions of these sources to the aerosol mass and composition. Although significant improvements have been made over the past decades in the mathematical modelling of the dispersion of pollutants in the atmosphere, there are still many instances where the models are insufficient to permit the full development of effective and efficient air quality management strategies. These difficulties often arise due to incomplete or inaccurate source inventories for many pollutants. Therefore it is necessary to have alternative methods available to assist in the identification of sources and the source apportionment of the observed pollutant concentrations. These methods are called receptor-oriented or receptor models since they are focused on the behaviour of the ambient environment at the point of impact [5-9].

From a receptor point of view, pollutants can be roughly categorized into three source types: source known, known source tracers (i.e. pollutant is emitted with another well characterized pollutant) and source unknown. The two main extremes of receptor models are chemical mass balance (CMB) and multivariate models. One of the main differences between the models is the required degree of knowledge about the pollution sources prior to the application of receptor models. For sources that have known tracers but do not have complete emission profiles, factor analysis tools such as Principal Component Analysis (PCA), UNMIX, Positive Matrix Factorization (PMF) can be used to identify the source tracers [10-13]. For pollutant sources that are unknown, hybrid models that incorporate wind trajectories (Residence Time Analysis, Potential Source Contribution Function (PSCF), Concentration Weighted Trajectory (CWT) can be used to resolve source locations [14-15].

While for monitoring of the air quality at street level, i.e. where people are in direct contact with aerosols, in situ measurements are most adequate, the attribution of concentrations in receptor areas to emissions from distant sources, as well as the assessment of the role of transport and transformation processes, requires

observations of the aerosol vertical distribution.The requirement for improved observations of the aerosol vertical distribution is related to the fact that practically all long-range transport occurs at elevated layers of the atmosphere. LIDAR (LIght Detection And Ranging) techniques represent state-of-the-art active remote sensing tool which provide aerosol measurements with high spatial and temporal resolution [16,17]. The basic LIDAR system is the elastic-backscatter LIDAR that allows the direct determination of the altitude and thickness of aerosol layers. The laser transmits short-duration light pulses into the receiver field of view. Intensity of the light backscattered by atmospheric molecules and particles is measured versus time by appropriate detector. High vertical resolution profiles measured with a Raman LIDAR allow the optical characterization of atmospheric aerosol layers in the planetary boundary layer, as well as in the free troposphere. The aerosol characterization can be further improved by the use of multi-wavelength Raman LIDAR equipped with depolarization channels. These data can be inverted to provide information about aerosol microphysical properties such as size, shape and refractive index. The information obtained from the LIDAR measurements can be used as input to different aerosol transport models to enhance their predictions.
LIDAR networks are fundamental to study aerosols on large spatial scale and to investigate transport and modification phenomena. EARLINET (European Aerosol Research Lidar Network) is the first such aerosol LIDAR network, with the main goal to provide a comprehensive, quantitative, and statistically significant database for the aerosol distribution on a continental scale [18].

This paper presents the most popular receptor models that have been applied to solve the general aerosol mixture problem and link the ambient PM with their sources, with emphasis on results obtained by applying some of these models on PM_{10} data sets measured in Belgrade. In addition, contemporary LIDAR methodology will be described and case studies of LIDAR observations and complementary prediction of vertical profiles of Saharan dust aerosols at the Bucharest EARLINET site will be also carried out.

METHODOLOGY

Potential Source Contribution Function (PSCF)

Air parcel back trajectories, ending at the receptor site, are represented by segment endpoints. Each endpoint has two coordinates (latitude, longitude) representing the central location of an air parcel at a particulate time. To calculate PSCF, the whole geographic region of interest is divided into an array of grid cells whose size is dependent on the geographical scale of the problem so that PSCF is a function of locations as defined by the cell indices *i* and *j*. If a trajectory end point lies in a cell of address (*i, j*), the trajectory is assumed to collect material emitted in the cell. Once aerosol is incorporated into the air parcel, it can be transported along the trajectory to the receptor site. The PSCF value can be understood as a conditional probability that describes the spatial distribution of probable source locations [19]. The staying time of all trajectories in a single grid cell is n_{ij}, and m_{ij} is the staying time in the same cell that corresponds to the trajectories that arrived at the receptor site with pollutant concentrations higher than a pre-specified criterion value (average PM_{10} and metal concentrations were used in this study). The PSCF value for the *ij*-th cell is then defined as

$$PSCF_{ij} = \frac{m_{ij}}{n_{ij}} \tag{1}$$

Cells related to the high values of potential source contribution function are the potential source areas. However, the potential source contribution function maps do not provide an emission inventory of a pollutant but rather show those source areas whose emissions can be transported to the measurement site.To remove the large uncertainty caused when a grid cell has small staying time and large PSCF values, the PSCF value is usually multiplied by a weight function $W(n_{ij})$ to better reflect the uncertainty in the values for these cells [20]. In this study the grid covers area of interest defined by (35^0- 50^0)N and (10^0- 30^0)E with cells $0.5^0 \times 0.5^0$ latitude and longitude.

Air masses back trajectories were computed using the HYSPLIT (HYbrid Single Particle Lagrangian Integrated Trajectory) model [21] through interactive READY system [22]. Daily 48-h back trajectories, started from the center of Belgrade (44.804^0N 20.478^0E) at 12:00 UTC each day, were evaluated for six different heights above the starting point at ground level (350, 500, 750, 1000, 1500 and 2000 m). The total number of days was 280, therefore, the total number of end points was 80640. On average, there are80640/1200 or about 70 end points per cell. In the present study the weight function $W(n_{ij})$ was defined as:

$$W(n_{ij}) = \begin{cases} 1 & n_{ij} \geq 140 \\ 0.85 & 70 \leq n_{ij} < 140 \\ 0.5 & 40 \leq n_{ij} < 70 \\ 0.25 & n_{ij} < 40 \end{cases} \tag{2}$$

The weighting function reduced the PSCF values when the total number of the endpoints in a particular cell was less than about two times the average value of the end points per each cell.

Concentration Weighted Trajectory (CWT)

In the current PSCF method, grid cells having the same PSCF values can result from samples of slightly higher concentrations than defined by the criterion or extremely high concentrations. As a result, larger sources cannot be distinguished from moderate sources. Therefore, a method of weighting trajectories with associated concentrations (CWT - concentration weighted trajectory) was developed [23]. In this procedure, each grid cell gets a weighted concentration obtained by averaging sample concentrations that have associated trajectories that crossed that grid cell as follows:

$$C_{ij} = \frac{1}{\sum_{l=1}^{M} \tau_{ijl}} \sum_{l=1}^{M} C_l \tau_{ijl} \tag{3}$$

C_{ij} is the average weighted concentration in the grid cell (*i*,*j*), C_l is the measured PM concentration observed on arrival of trajectory l, τ_{ijl} is the number of trajectory endpoints in the grid cell (*i*,*j*) associated with the C_l sample, and M is the total number of trajectories. Similarly to the PSCF method, CWT method also employs the arbitrary weight function to eliminate grid cells with few endpoints. Weighted concentration fields show concentration gradients across potential sources. This method helps to determine the relative significance of potential sources.

PM_{10} sampling and elemental analysis

Sampling of atmospheric particulate matter PM_{10}, on two sites in the very urban area of Belgrade, was conducting from July 2003 to December 2006. The elemental composition of the PM_{10} samples (Al, V, Cr, Mn, Fe, Ni, Cu, Zn, Cd and Pb) was measured by the atomic absorption spectroscopy (AAS) method. Depending on concentration levels, samples were analyzed for a set of elements by flame (FAAS) (Perkin Elmer AA 200) and graphite furnace atomic absorption spectrometry (GFAAS) using the transversely-heated graphite atomizer (THGA; Perkin Elmer AA 600) with Zeeman-effect background correction [24].

LIDAR measurement

Case study of multiwavelength Raman lidar measurement at Bucharest, Romania is presented. The multiwavelength lidar system (RALI) is based on compact, pulsed Nd:YAG laser, emitting simultaneously pulses of 110, 55 and 65 mJ output energy at 1064, 532 and 355 nm, respectively, with a 10 Hz repetition rate [16]. The receiving Cassegrainian telescope has a primary diameter of 400 mm. A complete overlap between the laser beam and the telescope field of view is expected at the range of 700 m. Photomultiplier tubes (PMTs) are used to detect the received lidar signals in the analog and the photon counting mode, with a corresponding spatial resolution of 3.75m. The detection channels include elastic wavelengths (1064, 532p, 532s, and 355 nm) and Raman wavelengths (607, 387 and 408 nm). Averaging time of the lidar profiles was of the order of 1 min for daytime measurements and 5 min during the night. Optical parameters of aerosols were extracted from lidar data using pre-processing and processing algorithms [25] based on Fernald-Klett method [26,27] previously tested and validated in the intercomparison campaign of EARLINET-ASOS project [28].

RESULTS AND DISCUSSION

Some studies have already reported a long – range transport of PM from western countries over Balkan Peninsula which is sporadically (mostly in spring and summer) associated with African dust outbreaks [29,30]. Based on the trace metal data set content in PM_{10} for the period 2003-2006.thepossible transport process over Belgrade was investigated. The PSCF and CWT plots for PM_{10}, V, Al and Mn are presented in Fig.1. It can be seen that PSCF plot for PM_{10} shows high probability area in the northeast and west region.

CWT plot indicated that the high concentrations of PM_{10} are related to the sources located in the west, northwest and northeast direction distinguishing major sources from moderate ones by calculating concentration gradients. The highest PSCF and CWT values for V were similarly distributed in the northeast region. Since V followed Weibull distribution transportation process is expected and this region the most likely influences receptor site. Mn is a metal related to dominant local sources but transportation process can be expected from southeast direction.

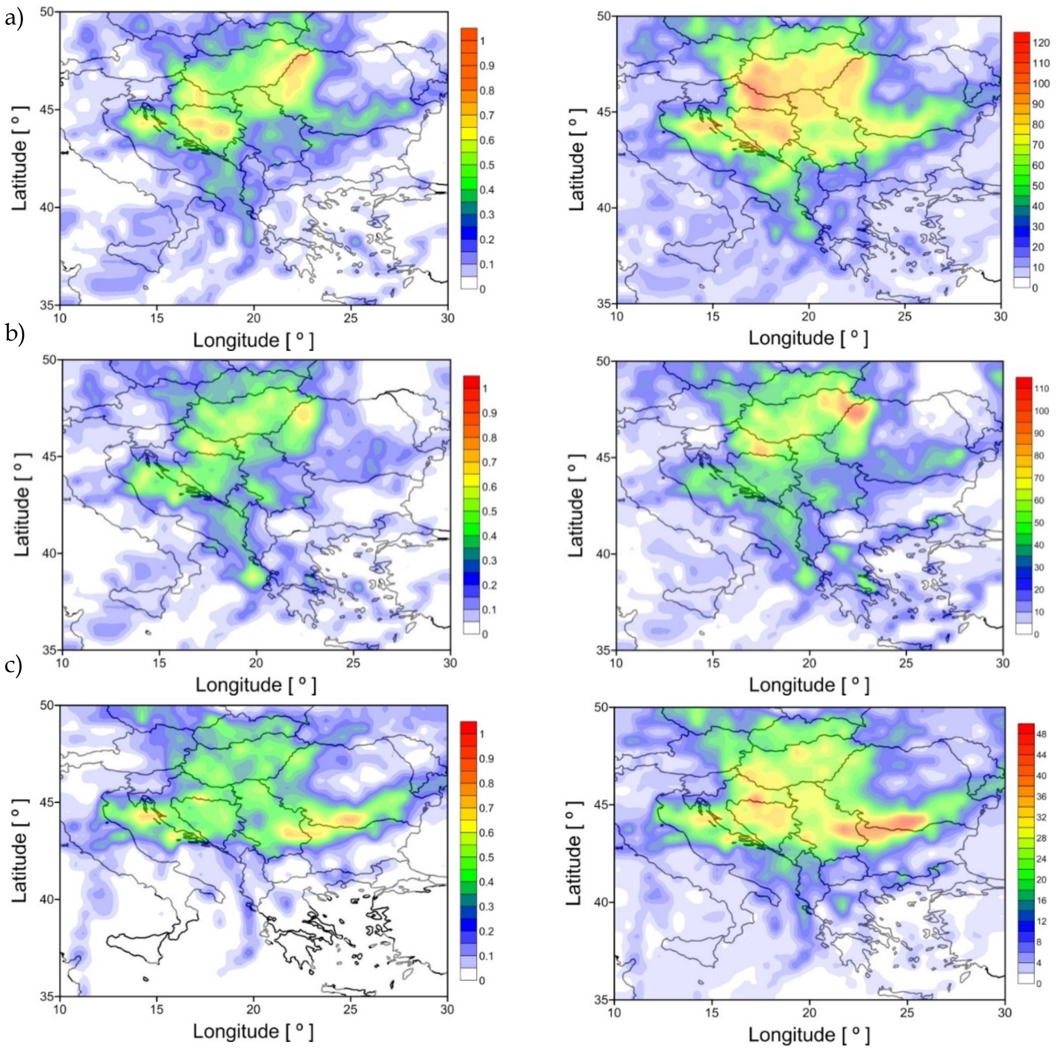

Figure 1. PSCF and CWT maps for a) PM_{10} (μg m^{-3}) and b) V (ng m^{-3}), c) Mn(ng m^{-3}) in PM_{10}.

The PSCF map for fossil fuel combustion sources, resolved using Positive Matrix Factorization receptor model (Fig. 2) indicates that, besides local sources, there is high probability that regional transport has contribution to this factor. The main source areas are Eastern France, Austria, Southern Germany and Central Italy. In addition, significant contribution can be associated to specific south area of Turkey and Greece. Since the PSCF results present a conditional probability describing the spatial distribution of probable geographical source locations it is useful to compare these PSCF results to existing EPER (www.eea.europa.eu) emissions metal-compound data in Europe for 2004.The obtained data were divided into the 0.5×0.5° grid cell and emission of each metal-compound was calculated.

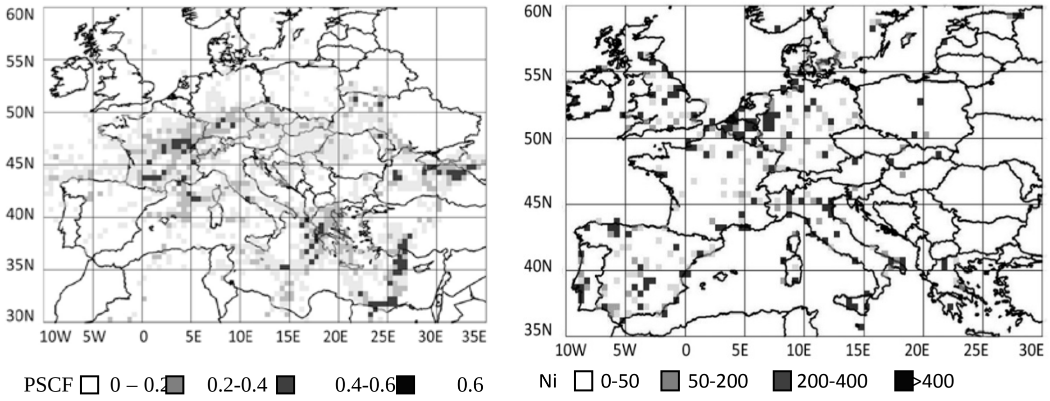

Figure 2.PSCF derived maps for fossil fuel combustion (left) and emissions of Ni metal-compounds (tons/year) into the atmosphere in 2004, Europe (right)

As Ni and Zn are mainly assigned to fossil fuel combustion resolved factor, it is expected that source regions obtained from PSCF analysis should match some of these emission hot spots. It can be seen from Fig 2. that PSCF results have good coincidence with emission regions in Italy, Austria, Germany and western France.

Besides application of receptor models on long-term measurements and identification of possible source regions, real time vertical profiling of aerosols is also important in order to be able to filter dispersion models output and perform comparison between model prediction and observation. This kind of measurements is crucial for understanding processes such as the boundary layer evolution, vertical inhomogeneities of the aerosols and transport.

A case of Saharan dust transport, captured with lidar in Bucharest on June 9, 2012 is discussed here. Figure 3 shows results of the lidar measurements carried out for two hours during the afternoon on this day: time series of range corrected signal and volume depolarization ratio. The volume depolarization ratio shows an increased contribution of non-spherical particles in a layer at the altitude between 3 km and 5 km, indicating the presence of dust. In agreement with this result, the vertical profile of aerosol extinction coefficient shows weaker wavelength dependence in this layer, in comparison with the boundary layer, as shown in Fig. 4. This is indicative of significant contribution of large particles. The presence of dust is confirmed by DREAM (Dust REgional Atmospheric Model)[31,32] and HYSPLIT back trajectories (Fig.5), as well as by sunphotometer measurements at the same site.

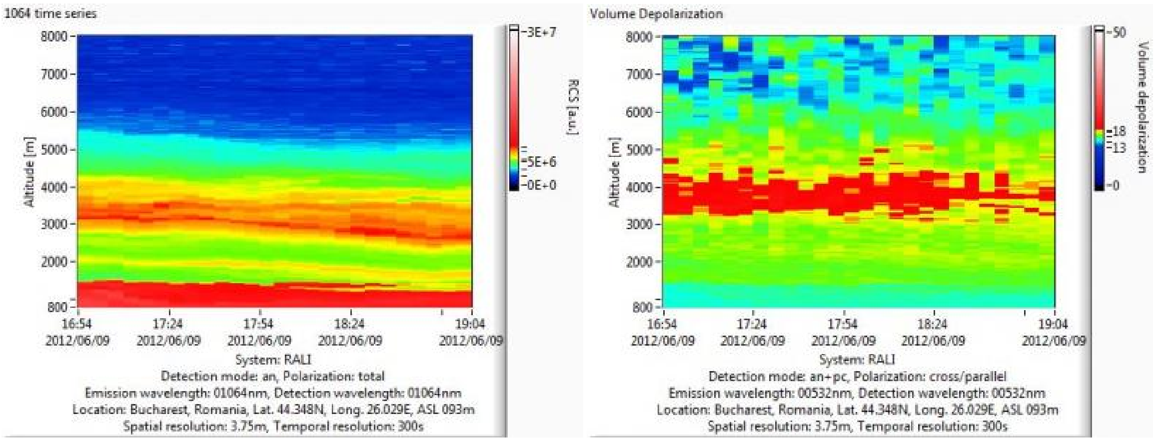

Figure 3. Time series of range corrected signal and volume depolarization ratio.

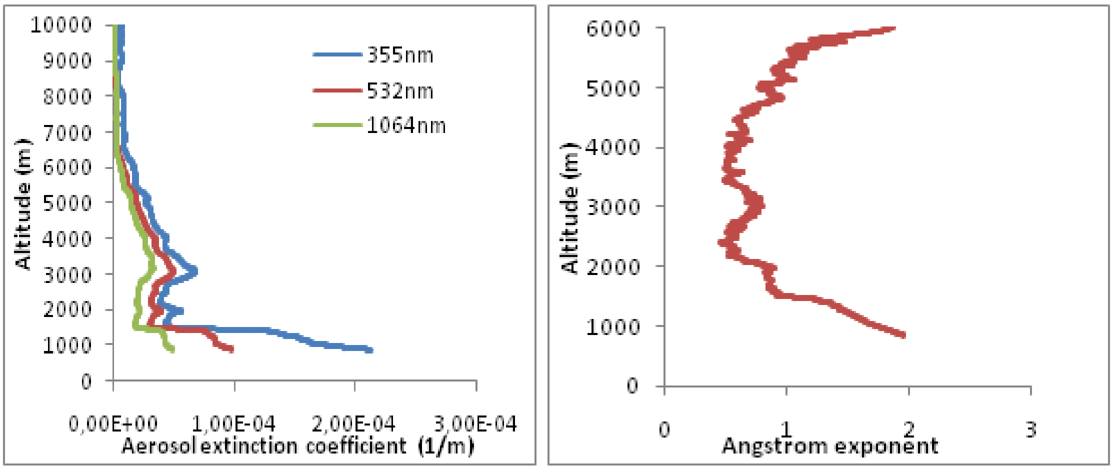

Figure 4. Vertical profile of aerosol extinction coefficients at three wavelengths: 355 nm, 532 nm and 1064 nm (left) and vertical profile of Angstrom exponent calculated from extinction coefficients at 355 nm and 532 nm (right).

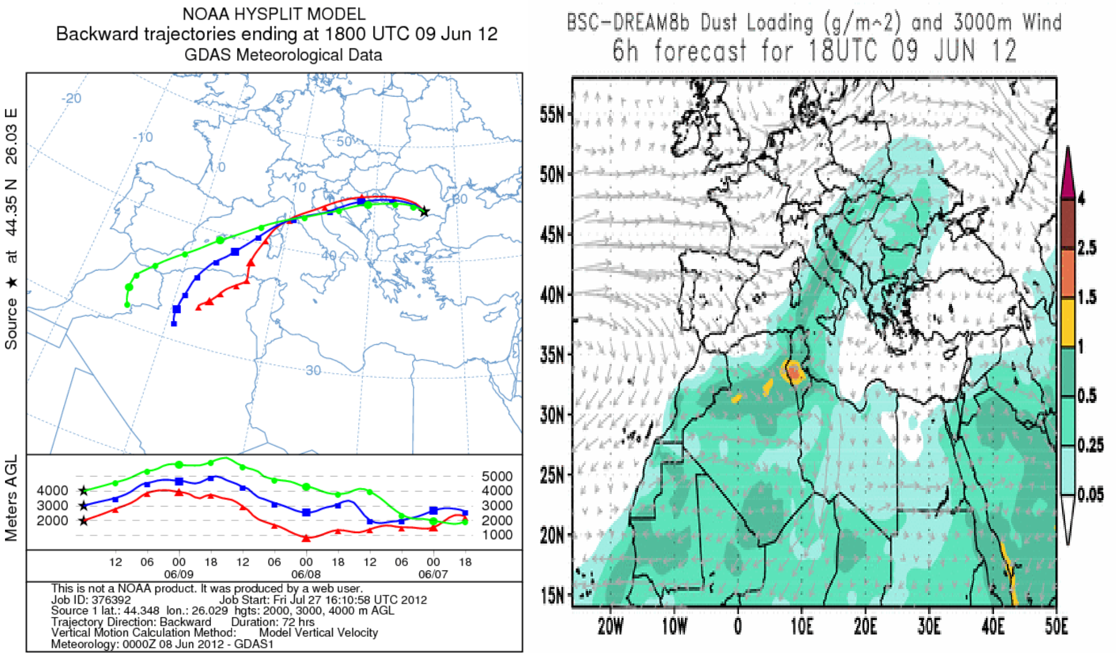

Figure 5. Backward trajectories from NOAA HYSPLIT, indicating the origin of atmospheric layers over Bucharest on June 9, 2012 (left); results of DREAM model for the same date (right).

CONCLUSION

In the field of atmospheric sciences hybrid receptor models aim to re-construct the impacts of emissions from different sources of atmospheric pollutants based on ambient data measured at the monitoring sites.The information provided by receptor models is key to the design of effective mitigation strategies of the pollutant on the local and meso-scale. Many epidemiological and health-related studies used the results obtained by receptor modeling. Short review of most popular hybrid receptor models is presented and some of them are applied on PM_{10} data sets measured in Belgrade. In addition, a case of active ground-based remote LIDAR technique measurement is discussed. Comparison of DREAM model prediction of dust intrusion above Bucharest and lidar measurement is presented as well.

ACKNOWLEDGEMENTS

This paper was realized as a part of the project “Studying climate change and its influence on the environment: impacts, adaptation and mitigation" (III43007) financed by the Ministry of Education and Science of the Republic of Serbia within the framework of integrated and interdisciplinary research for the period 2011-2014. Part of the research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 262254.The authors gratefully acknowledge the Institute of Public Health of Belgrade, Serbia for providing appropriate data set and the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model and READY website (http://www.arl.noaa.gov/ready.php) used in this publication.

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3.3 DATA ASSIMILATION: ADDING VALUE TO THE CITIZEN'S OBSERVATORY

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ABSTRACT

The main objective of the EU-funded CITI-SENSE project is to develop "Citizens' Observatories" to empower citizens and citizens' groups to: (i) contribute to and participate in environmental governance; (ii) support and influence community and policy priorities and associated decision-making; and (iii) contribute to European and global monitoring initiatives. Citizens' Observatories are communities of users that share technological solutions, information products and services, and community participatory governance methods using appropriate communication solutions, and who by these activities complement established environmental data and information systems and improve local decision making about environmental issues.

The main objective of the project involves developing and testing an environmental monitoring and information system based on innovative and novel Earth Observation capabilities and applications such as data assimilation, focused on the citizen's immediate environment. This paper describes the roadmap for the application of data assimilation ideas to the Citizen's Observatories.

INTRODUCTION

Important societal challenges of the 21st Century include climate change, environmental degradation and access to clean water (IPCC, 2013). These challenges have a strong impact on society, incurring social and economic costs (Lahoz *et al.*, 2012), and require an intelligent response. Information is required for making choices on future action. Regardless of the source of information, society needs to be able to use this information to make predictions, test hypotheses and monitor changes in the Earth System. This allows society to take action, according to the information provided, to prepare for the future behaviour of the Earth System (prediction); to test understanding of the Earth System, and adjust this understanding accordingly (hypothesis testing); and record and evaluate changes in the Earth System (monitoring).

We first discuss information, introducing observations and models. Then we indicate how data assimilation can add value to both observational and model information. Finally, we discuss the outlook and challenges for data assimilation when applied to the Citizen's Observatory, including using "crowdsourcing" (i.e., the practice of obtaining needed services, ideas, or content by soliciting contributions from a large group of people, and especially from an online community, rather than from traditional employees or suppliers) as a source of environmental information; and provide conclusions.

INFORMATION

Information is needed to address challenges in society; assess the problems associated with these challenges; understand the causes of the problems; take action to solve or mitigate the problems; and assess if actions taken are working, e.g., by reducing or removing the problems. Examples (not exhaustive) of societal challenges include climate change, environmental degradation, and access to clean water. We have two broad sources of information of the Earth System: measurements of the system ("observations"); and understanding of the spatio-temporal evolution of the system (typically embodied in "models").

Observations sample the system with various spatio-temporal scales. They provide information on the system and contribute to building an understanding of its spatio-temporal evolution. The methods used to observe the Earth System include (Thépaut and Andersson, 2010; Lahoz, 2010): in situ observations from ground-based stations, buoys and aircraft; and satellite observations from low Earth orbit satellites (LEOs) and geostationary satellites (GEOs). Collectively, these observational platforms are termed the Global Observing System (GOS). The in situ and satellite platforms are complementary (USGEO, 2010): in situ platforms have relatively high spatio-temporal resolution, but do not have global coverage; satellite platforms have substantial coverage over the globe, for LEOs this coverage being quasi-global, but have relatively poor spatio-temporal resolution. In situ data are often used to evaluate satellite data (Lahoz *et al.*, 2012).

Observations exhibit two key features. The first is that they contain errors – these can be systematic (also called bias), random, and of representativeness. Random errors have the property that they are reduced by averaging. Systematic errors are not reduced by averaging; if known, they can be subtracted from an observation. The representativeness error is associated with differences in the resolution of observational information and the resolution in the way this information is interpreted. The second is that they have spatio-temporal gaps (see Fig. 1 in Lahoz *et al.*, 2010a). It is desirable to fill gaps in the information provided by observations: (i) to make this information more complete, and hence more useful; and (ii), to provide information at a regular scale to quantify the characteristics of this information. Information at an irregular scale can be quantified, but this procedure is more tractable when done at a regular scale.

To fill in the gaps in the observations we need a model. This model can be simple, e.g., linear interpolation, or take account of the system's behaviour. For example, the model could be a chemistry-transport model (CTM), incorporating a suite of chemical equations and heterogeneous chemistry (Errera *et al.*, 2008); or it could be a general circulation model (GCM), incorporating the discretized Navier-Stokes equations (Lahoz *et al.*, 2007). The model thus extends the observations and fills in the gaps and allows one to organize, summarize and propagate the information from observations. The model, like the observations, also exhibits spatio-temporal gaps.

It is desirable to find methods that allow intelligent filling in of the observational information gaps. By intelligent, we mean an "objective" way, which makes use of concepts for combining information. For example, by finding the minimum or maximum value of a quantity calculated from the information available. In this way, we can think of the model as an intelligent interpolator of the observation information: intelligent because it embodies our understanding of the system; intelligent because the combination of the observational and model information is done in an objective way.

DATA ASSIMILATION METHODOLOGY

Mathematics provides rules for combining information objectively, based on principles which aim to maximize (or minimize) a quantity (e.g., a "penalty function"), or on established statistical concepts which relate prior information (understanding, which comes from prior combination of observations and models) with posterior information (which comes from making an extra observation). It provides a foundation to address the question: "What combination of the observation and model information is optimal?", and provides an estimate of the errors of the "optimum" or "best" estimate. This is "data assimilation", and has strong links to several mathematical disciplines, including control theory and Bayesian estimation (Nichols, 2010; Talagrand, 2010). Data assimilation adds value to the observations by filling in the observational gaps, and adds value to the model by constraining it with observations (see Fig. 2 in Lahoz *et al.*, 2010a). In this way, data assimilation allows one to "make sense" of the observations. The result of data assimilation, where one combines observational and model information and their errors, is termed the "analysis".

Although Bayesian estimation (Rodgers, 2000) defines a systematic and rigorous approach to data assimilation, its full-scale implementation in many areas, including weather forecasting, is impossible, chiefly due to the size of the problem. However, the Bayesian approach is still useful in that it provides general guidelines for developing a data assimilation system and evaluating its results. Two main lines have been followed: (i) statistical linear estimation, and (ii) ensemble assimilation (Lahoz *et al.*, 2007).

Statistical linear estimation achieves Bayesian estimation when the system is linear and the errors are Gaussian. In particular, statistical linear estimation provides a way of estimating the Best Linear Unbiased Estimate, BLUE (Lahoz *et al.*, 2007). There exist two broad classes of numerical algorithms for data assimilation: variational and sequential (Bouttier and Courtier, 1999). In the context of statistical linear estimation, these algorithms take respectively the form of the 4-D variational method (4D-Var), or the Kalman filter (KF). (If the time dimension is omitted, the 4D-Var method becomes the 3-d variational method, 3D-Var.) These are two different algorithms for determining the BLUE, and they are equivalent under the only condition of linearity. The KF can be generalized to account for non-linearity, although in this case neither the optimality of the analysis nor the equivalence with 4D-Var holds. The resulting equations are known as the Extended Kalman filter, EKF.

Ensemble assimilation is a form of Monte-Carlo approximation, which attempts to estimate probability distribution functions (PDFs) from the spread of the ensemble. In present applications (e.g., the Ensemble Kalman filter, EnKF, Evensen, 2003), the size of the analysed ensembles typically lies between a few tens to a few hundreds of model states. Another development in data assimilation using ensemble methods is the particle filter, PF (van Leeuwen, 2009).

Mathematics provides the basis for applying data assimilation to real problems such as weather forecasting, where data assimilation has been very successful. Over the last 25 years, the skill of weather forecasts has increased – for example, the skill of today's 5-day forecast is comparable to the skill of the 3-day forecast 25 years ago (Simmons and Hollingsworth, 2002).

Besides weather forecasting, data assimilation is applied to many areas. These include chemical data assimilation; air quality forecasting; ocean data assimilation; land data assimilation; and the design of the global observing system using observing system simulation experiments, OSSEs (see various chapters in Lahoz *et al.*, 2010b).

OUTLOOK

A key area of data assimilation is the representation of errors, including systematic, random and of representativeness (see various chapters in Lahoz *et al.*, 2010b). For example, Ménard (2010) discusses bias estimation in data assimilation. Recent developments at the weather centres include the combination of ensemble and variational methods to describe the background errors used to represent uncertainty in previous knowledge, commonly obtained from a short-term forecast, and the extension of ensembles to include elements of the Earth System (see presentations at the data assimilation session at IAMAS 2013, http://www.daca-13.org/program/SympB1/index_EN). Furthermore, weather centres are moving towards simulating smaller spatial scales, typically of the order of 100s of metres (Roger Saunders, *pers. comm.*). These smaller spatial scales are closer to the needs of users than those scales used hitherto by the weather centres.

A new and exciting opportunity for providing environmental information is the Citizen's Observatories (see the CITI-SENSE project, http://www.citi-sense.eu). The EU has funded 5 projects (CITCLOPS, CITI-SENSE, Cobweb, Omniscientis and WeSenseIt; see links in http://www.citi-sense.eu) under the aegis of this concept; set up a meeting in Brussels in January 2013 to discuss synergies between these 5 projects; and included a contribution from the CITI-SENSE project in the EC Green Week held during June 2013 (http://ec.europa.eu/environment/greenweek). The Citizen's Observatory concept is associated to the notion of "crowdsourcing", defined to be the practice of obtaining needed services, ideas, or content by soliciting contributions from a large group of people, and especially from an online community, rather than from traditional employees or suppliers.

The Citizen's Observatory concept builds on the fact that mobile phones are becoming increasingly ubiquitous, given growth in mobile use, changes in mobile usage, and the increasing range of features provided to mobile phone users (http://www.smartinsights.com/mobile-marketing/mobile-marketing-analytics/mobile-marketing-statistics/). Through a mobile phone, the citizen can provide and receive information on their immediate environment, e.g., on air quality parameters such as ozone and aerosols; and on meteorological parameters such as temperature and humidity (see Lahoz, 2013, for more details). Ongoing work at the Met Office, UK (Weather Observations Website, WOW; http://wow.metoffice.gov.uk/) makes use of the concept of crowdsourcing to obtain information on, e.g., snow conditions in the UK. Crowdsourcing also provides temperatures in an urban environment (e.g., Overeem *et al.*, 2013). The use of crowdsourcing information for data assimilation brings its own challenges. These include: different spatio-temporal scales (10-100 kms vs street level); model development (need to simulate smaller spatial scales); noisy information from users and from microsensors (Shanley *et al.*, 2013); and representation of uncertainty (Spiegelhalter *et al.*, 2011). These challenges are being addressed in the EU-funded CITI-SENSE project, which will study a number of approaches to provide gridded air quality and meteorological data for users, including data assimilation (Lahoz *et al.*, 2010b), data fusion (Warmer *et al.*, 2013), and land-use regression (Ryan and LeMasters 2007; Wen *et al.*, 2013).

CONCLUSIONS

Data assimilation provides many benefits to users. Examples include providing analyses for studying the Earth System; providing the initial state for weather and air quality forecasts; evaluating observations and instruments; assessing the relative value of elements of the Global Observing System; and assessing the added value of future additions to the Global Observing System (see various chapters in Lahoz *et al.*, 2010b). The new opportunities provided by the concept of the Citizen's Observatory, and the associated use of mobile phones and crowdsourcing as a source of environmental information, and a platform to receive environmental information, have enormous potential benefit, and provide an opportunity to extend data assimilation to areas addressing more directly the needs of users. However, the use of crowdsourcing information in data assimilation has several challenges, including simulating the smaller spatial scales associated with the street level, and the representation of observational and model errors. These opportunities and challenges will be addressed by the EU-funded CITI-SENSE project.

ACNOWLEDGMENTS

The project “Development of sensor-based Citizens’ Observatory Community for improving quality of life in cities” (CITI-SENSE) is funded by the EU, under grant agreement No. 308524.

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3.4 FREQUENCY ANALYSIS OF PM_{10} TIME SERIES AND ASSESSING SOURCE REDUCTION FOR AIR QUALITY COMPLIANCE IN SERBIA

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ABSTRACT

According to World Health Organization, ozone, particulate matter (PM), heavy metals and some organic compounds present the priority pollutants in the troposphere. In this study,PM_{10} mass concentrations measured in Belgrade and Niš during 2011 were investigated.Significant effect of anthropogenic sources of PM_{10} can be seen from statistical weekday-weekend variations, phenomenon known as the “weekend effect”. In order to examine the existence of periodicity, especially weekly cycles of measured variables, spectral analysis of daily PM_{10} mass concentrationswas applied. Results indicated that the mass concentrations of PM_{10} showed seven days periodicity probably due to weekly pattern of human activities.The obtained data for daily average concentrations have been subjected to statistical processing in order to determine the appropriate frequency distribution function. Several distribution functions were tested and based on the fitted results, lognormal distribution was chosen to fit the PM_{10} data for both sampling sites. Required emission reduction in order to meet current Air Quality Standard was then estimated using rollback equation.

1. INTRODUCTION

Numerous studies have shown that acute and chronic health effects are related to the inhalable PM_{10} (aerodynamic diameter less than 10 μm) exposure in the urban environment [Atkinson et al., 2010; Chen et al., 2009; Dockery et al., 1994]. European Union air quality standard [Directive 2008/50/EC] established the PM_{10} annual limit values of 40 $\mu g\ m^{-3}$ and daily average concentration of 50 $\mu g\ m^{-3}$ not to be exceeded more than 35 days per year.Despite the implementation of different emission abatement strategies high PM_{10} concentrations are still frequently occurred. Weekly cycles of mass concentrations of anthropogenic aerosols have already been observed in many urban regions with significant contribution to particle levels of the primary sources, industry, fossil fuel combustion and traffic [Gong et al., 2007]. In order to reveal underlying physical processes and the influence of emission sources on time variability of PM_{10} concentrations spectral analysis was used [Hies et al., 2000]. Similarly to other air pollutants, PM concentrations are random variables influenced by the emission level, meteorological conditions and topography. Each area is specific and the required emission reduction to meet Air Quality Standard (AQS) is different. Information about the frequency distribution of pollutants is useful for developing air pollution control strategies. When the specific probability function of an air pollutant is known, it is easy to predict the required emission reduction and the frequency of exceedance of the AQS. The objective of this paper is examination of the time series of measured variables, determination the function that best fits the data and estimate the reduction of pollution in two large cities in Serbia.

2. METHODOLOGY

In the present study daily average mass concentrations of PM_{10} sampled at two urban sites in Belgrade and Niš during the 2011 were analyzed. Data were obtained from the Air Pollution Measurement Network that operates under the supervision of the Serbian Environmental Protection Agency. Sampling site in Belgrade is not far from the junction of Mostar in the vicinity of highway. In Niš, the location at which the measurement took place is in the center of the town, in the area under the strong influence of traffic.

In order to observe the periodicity of some process, spectral analysis was applied in many fields, including the analysis of aerosol mass concentrations. The periodogram of PM_{10} time series, strength of the signal as a function of frequencies, was calculated using the Fast Fourier Transform algorithm (FFT). The power spectrum contains a background value determined by “red noise” fit to the spectrum. The power spectrum with a red noise background was used because most of the geophysical time series tend to have larger power at lower frequencies [Ghil et al., 2002].

In addition, the available PM_{10} concentration data for both sampling site were fitted to most common probability distributions for PM: lognormal (Eq. 1) [Mage et al., 1984; Kao et al., 1995; Lu et al., 2002;], Weibull(Eq. 2) [Georgopoulos et al., 1982] and gamma distribution (Eq. 3) [Lu et al., 2004].

$$f(x) = \frac{\exp\left(-\frac{1}{2}\left(\frac{\ln x - \mu}{\sigma}\right)^2\right)}{x\,\sigma\sqrt{2\,\pi}} \qquad (1)$$

$$f(x) = \frac{\alpha}{\beta}\left(\frac{x}{\beta}\right)^{\alpha - 1}\exp\left(-\left(\frac{x}{\beta}\right)^{\alpha}\right) \qquad (2)$$

$$f(x) = \frac{x^{\alpha - 1}}{\beta^{\alpha}\,\Gamma(\alpha)}\exp(-x/\beta) \qquad (3)$$

The distributional parameters were estimated by the maximum likelihood method and the goodness of fit was evaluated using non-parametric Kolmogorov-Smirnov (K–S). The K–S statistic is defined as the maximum difference between the sample cumulative probability and the expected cumulative probability:

$$D = \max | f_n(x) - F(x)|$$

Where f_n (x) and F(x) are the expected and observed cumulative frequency functions, respectively, and the smaller values of D means the better goodness of fit.

Assuming unchanged spatial distribution of emission sources, meteorological conditions and nonreactive species, according to the rollback equation [Seinfeld et al., 1998] the emission source reduction R (%) required to meet AQS can be estimated by:

$$R = \frac{\mathrm{E\{Cp\}} - \mathrm{E\{C\}s}}{\mathrm{E\{Cp\}} - \mathrm{Cb}}$$

In this equation $E\{C\}_s$ is the mean (expected) concentration of distribution when the extreme value equals C_s (the concentration of the AQS), $E\{C_p\}$ the mean concentration of the actual distribution and C_b the background concentration. If C_s=50μg m^{-3}, the PM_{10} daily average concentration is not exceeded more than 35 days per year ($P[PM_{10}>C_s]=35/365=0.09589$), then $E\{C\}_s$ is the expected daily PM_{10} average concentration of a distribution where the probability of a concentration exceeding 50μg m^{-3} equals 0.09589.

3. RESULTS AND DISCUSSION

Table 1.Descriptive statistic for PM_{10} mass concentrations [μg m^{-3}] at two sampling sites.

Sampling site	Sample Size	Range	Mean	Std. Deviation	Min	Max	Percentile 10%	Percentile 95%
Belgrade	365	213.90	50.83	36.09	10.05	223.95	21.00	128.72
Niš	365	242.20	66.95	46.89	12.59	254.79	27.28	172.89

In Table 1 the elements of the basic statistics of the measurement results are given. It revealed that the average annual PM_{10} mass concentrations on both sites exceeded the prescribed limit values during the 2011. Even during the stable weather conditions high PM_{10} concentrations are distinguished, which indicates the existence of local sources.

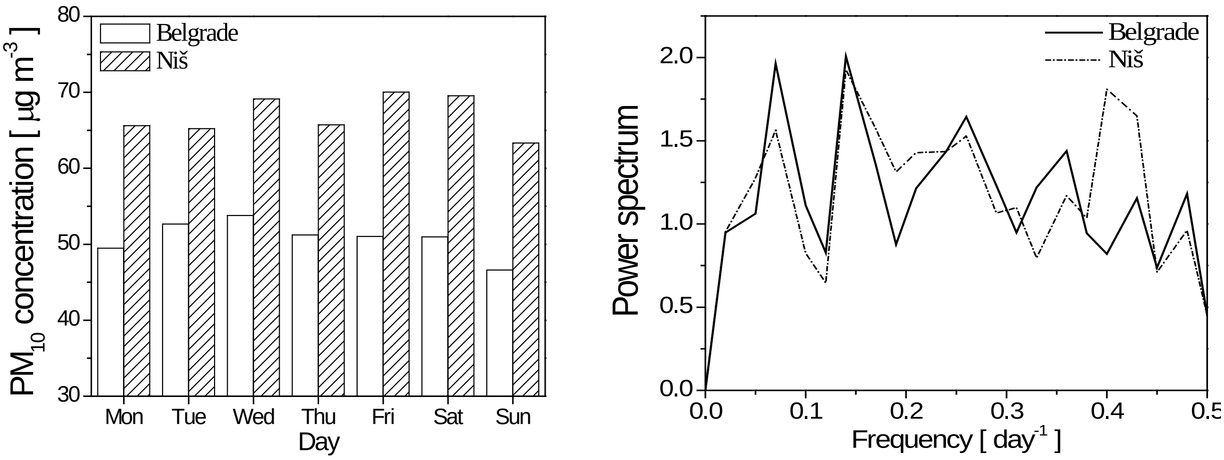

Figure 1. Mean daily concentrations of PM_{10} during the weekdays and weekend (left) and a periodogram of PM_{10} time series(right)

Weekly cycles in PM_{10} time series are observed at both sites located in the urban areas where anthropogenic influences are strongest. Compared to weekdays, decrease of about 20% in the PM_{10} concentrations have been observed during Sunday's as a result of reduced human activity (Fig. 1).At the sampling station in Belgrade this occurrence is also observed with the traffic originated compounds CO, SO_2 and NO_x. Results of spectral analysis applying, for both sites, show existence of the high spectral power peak at the frequency about 0.14 day $^{-1}$which corresponding to 7 days period. At the sampling site Belgrade the peak is noticeable at a frequency at a frequency of 0.7 day $^{-1}$which corresponds to the period of 14 days, while on location Niš peak observed at upper frequency (period of about 2-3 days).

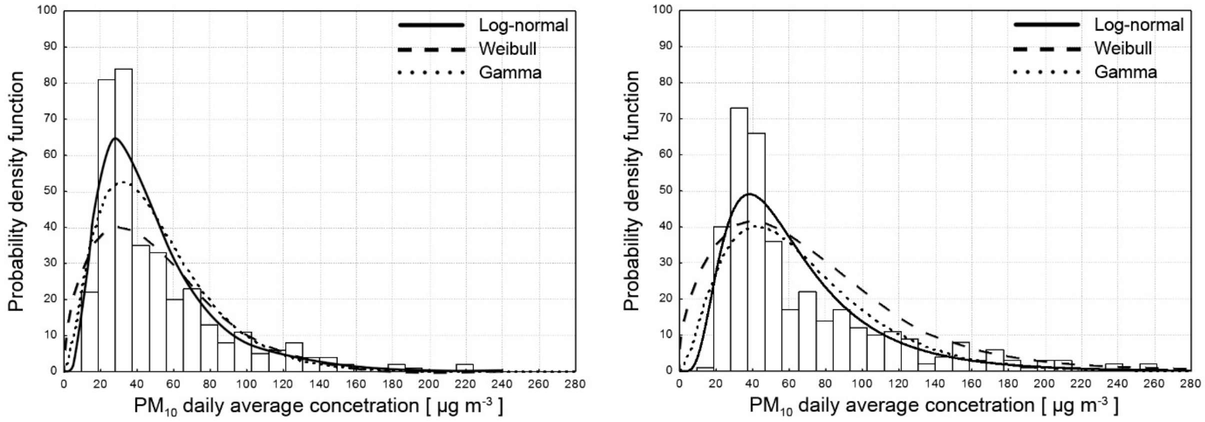

Figure 2.Comparison of the empirical results with the theoretical lognormal, gamma and Weibull probability density function in Belgrade (left) and Niš (right)

The lognormal distribution was found to best fit measured concentrations at both locations (Fig. 2), with values obtained by the K-S test of 0.09 for Belgrade and 0.11 for Niš. The distributional parameters estimated by the maximum likelihood method and the goodness of fit are shown in Table 2.

Table 2.Characteristics of the gamma, lognormal and Weibull distribution fitting thePM_{10}concentrationsat two sampling sites, and goodness of fit criteria.

	Gamma distribution		Lognormal distribution		Weibull distribution	
Belgrade						
Distribution parameters	α=1.98	β=25.62	σ=0.61	μ=3.73	α=1.95	β=55.67
Kolmogorov-Smirnov test	0.11		0.09		0.15	
Niš						
Distribution parameters	α=2.04	β=32.83	σ=0.60	μ=4.01	α=1.92	β=73.76
Kolmogorov-Smirnov test	0.12		0.11		0.17	

With known probability function of PM_{10}mass concentration at Belgrade and Niš sampling location, using rollback equation it is feasible to predict the required emission reduction. The results suggested the need of PM_{10} emission reduction of about 61% in Niš and 49% in Belgrade urban area. Therefore, the source emissions should be controlled much more to reduce PM_{10} concentrations and meet AQS in the future period.

4. CONCLUSIONS

PM_{10} mass concentrations measured in Belgrade and Niš, and analysis of time periodicity and statistical characteristic of measured variables were presented. Annual and daily limit values of PM_{10} mass concentrations were exceeded at both stations during the 2011. Existence of weekly cycle and decries concentrations during the weekends indicate the major contribution anthropogenic sources to PM_{10} mass concentrations. The similar behavior of compounds that have the same origin indicates that the traffic is the most important source of air pollution in urban areas. According to the goodness of fit statistical tests, the lognormal distribution was found to best fit the experimental data. Based on the fitted distribution the minimum reduction required in order to attain the daily AQS was estimated using the rollback equation.

5. ACKNOWLEDGEMENTS

This paper was realized as a part of the project No III43007 financed by the Ministry of Education and Science of the Republic of Serbia within the framework of integrated and interdisciplinary research for the period 2011-2014.The authors would also like to thank the Serbian Environmental Protection Agency for providing PM_{10} data set used in this study.

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3.5 ENVIRONMENTAL IMPACT ASSESSMENT OF THE NUCLEAR REACTOR AT VINCA, BASED ON THE DATA ON EMISSION OF RADIOACTIVITY FROM THE LITERATURE - A MODELING APROACH

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ABSTRACT

In the paper is presented an assessment of impact on the environment, of the assumed emissions of radio nuclides in the boundary layer of the atmosphere, from the ventilation of nuclear reactor in Vinca. This estimation was done taking into account characteristics of the reactor ventilation system, then based on the assumed emission of radioactivity (from the literature), local meteorology of Vinca for the period 2001-2005 and whole 2009 year, terrain topography around nuclear reactor and corresponding dose factors for inventory of radio nuclides. In the paper are also presented average annual activity concentration fields in the air and yearly activity due to dry and wet deposition, as well as annual dose received by the hypothetical resident in the period 2001-2005 and whole 2009 year. Radionuclide emissions from artificial sources should not contribute to the limit values of total dose above 1% of the dose received by an individual from natural background radiation (limit value 10-3Sv for a year). In this way, the limit value of the total dose for the individual is a 10-5 Sv, or 1e-5 Sv to the convention on the recording format of small numbers. Based on the results of mathematical modeling with parameters of the ventilation stack of nuclear reactor "RA", assumed emission of radio nuclides, soil characteristics, meteorological data collected with an automated meteorological station at 40m tall meteorological tower on the representative location at "RA", then on the recommended dose factors for the observed radionuclide's and on the conservative approach that the reactor operates continuously 24 hours throughout the year, only in 2002 and 2005 in two isolated locations, maximum values for the total annual dose were slightly higher than the limit value, amounted to 1.1e-5 Sv. On the basis of the described approach and assuming that the range of appropriate meteorological data for the application of described mathematical model, of five consecutive years 2001-2005 and 2009 is enough for this kind of analysis, we can conclude that the nuclear reactor "RA" in the course of its work from 1959 up to 1984 whatever was unable to influence it's environment above the prescribed limit 10µSv/year.

1. INTRODUCTION

After the accident at nuclear reactor "RB" in 1958, in the Institute "Vinca", as a condition for the operation of the 10 MWt reactor "RA" was to establish a set of the classic meteorological measurements, observations and data processing, which remain to this day. From 1997 began with measurements and data processing at 37m high meteorological tower, using an automatic weather station of the Institute of Physics in Zemun, and in 2008 Slovenian company AMES built an automatic weather station at new 40m tall meteorological tower.

File contains the ten-minute meteorological data received by measurement of the automatic meteorology station, which sensors are appointed on a pillar 37 m high. This database was used for calculation during five years period 2001 - 2005. From 2009 new automatic meteorological station is used to collect data, sensors are placed at several levels in the renewed meteorological tower, 40m high.

Physical characteristics of the ventilation stack of the reactor "RA" was received from technical documentation of ventilation drain, shown in fig.1.

Meteorological data since 2001 to 2005 were collected with an automatic meteorological station of the Institute of Physics, whose sensors are appointed on a meteorological tower 37 m high.
Meteorology station measured:

Top of the tower, 38m above ground (37 m high tower + 1 m cantilever)

- Air temperature
- Wind speed and direction

2 m above ground

- Air temperature

- Relative humidity
- Global solar radiation

1 m above ground

- Precipitation/Rainfall

In 2008 structure of the meteorological tower is rebuild and put into operation a new meteorology station of Slovenian company AMES.

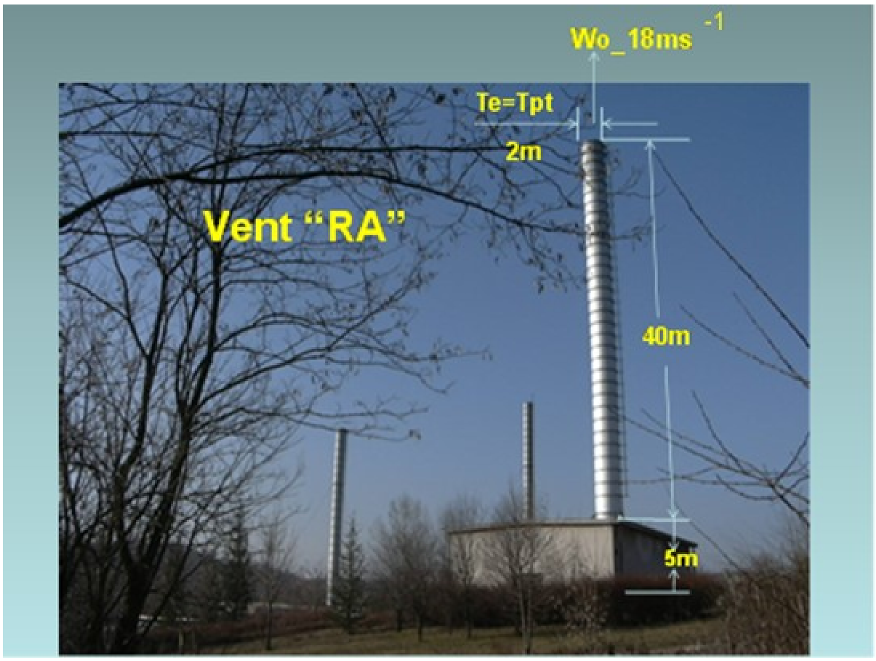
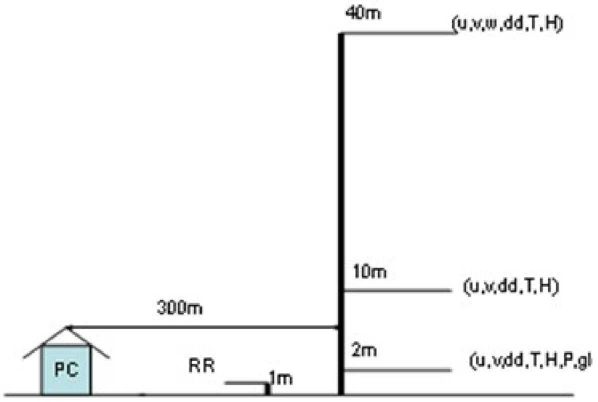


Fig.1. Ventilation stack of the reactor "RA”



u,v,w_components of the wind vector
dd_ wind direction
T_air temperature
H_humidity
P_air pressure
Glo_global sun radiation
Nr_net radiation
RR_precipitation
PC computational room

Fig.2. Scheme of measurements at meteorological tower in NFS in Vinca (AMES Ljubljana)

Data from the station are recorded in a minute or ten-minutes, in a file that is automatically created for each new minute or ten-minute data set in the format like in the example below:

1211080835 15.5 95.5 734 321 7.3 313 3.1 22.1 10.1 323 24.9 15.4 343 1.5 -1.2345E-06 4

Where: **1211080835** date, month, year, hour, minute (two numbers each), **15.5** temperature (2m), **95.5** relative humidity (2m), **734** global solar radiation, **321** NR (net radiation) (2m), **7.3** wind speed (2m), **313** wind direction (2m), **3.1** Rainfall, **22.1** Temperature (10m), **10.1** wind speed (10m), **323** Wind direction (10m), **24.9** Temperature (40m), **15.4** Wind speed (40m), **343** Wind direction (40m), **1.5** Vertical component of wind speed (40m),**-1.2345E-06** Monin Obukhov length, **4** Stability class.

2. MODELING ENVIROMENTAL EFFECTS OF REACTOR „RA”

In Public Company Nuclear Facilities of Serbia (NFS), we have established meteorological program which is subordinate to the requirements of computer codes we have developed for modeling dispersion of pollutants in the boundary layer of atmosphere and it is primarily based on measurements with automatic meteorological station on the meteorological tower. For the computer code for routine work, which is based on the Gaussian model of atmospheric diffusion and on the Pasquill original theory, a program of classical measurements and observations, also was established.

In this work we used our own code based on well-known equation of Gaussian straight line plume model:

$$C(x,y,z)=\frac{Q}{2\pi\sigma_y\sigma_z u}\exp\left(-\frac{1}{2}\frac{y^2}{\sigma_y^2}\right)\left\{\exp\left[-\frac{1}{2}\frac{(z-H)^2}{\sigma_z^2}\right]+\exp\left[-\frac{1}{2}\frac{(z+H)^2}{\sigma_z^2}\right]\right\} \tag{1}$$

Where:

C (x, y, z)	the concentration of pollutants at the point (x, y, z)
Q	strength source (emission rate) (kg / h, Bq / h ...)
σ_z	standard deviation of the Gaussian cloud in the direction of z axis, which define its dimensions in terms of time *t* or distance downwind x =*u t*, (m)
σ_y	standard deviation of the Gaussian plume in the direction of y-axis (m)
H	the effective source height

This program provides the input data: cloudiness in total and by type, height of the base of prevailing cloud, wind speed and direction at a height of 10m above the ground and precipitation, at each hour term of meteorological measurements and observations. Insolation in each hourly term and the beginning of the day and night (sunrise and sunset for any location sources) are determined by the computer code we have developed based on spherical trigonometry equations that define the relationship of the sun between horizon and equatorial coordinate astronomical system. Classic program of meteorological measurements and observations in PC NFS serves as a reserve and used when the automatic weather station is out of service. Basic meteorological program based on measurements of automatic meteorological station, among other benefits, allow direct determination of stability class at Turner's scheme in practically real-time and access to the same rate and to the values of σ_z and σ_y.

Starting information for this type of analysis, in addition to the mentioned meteorological data, is the emission of activity/radionuclides per unit of time (source strength) and duration of releases. Monitoring of activity releases at the exit of chimney ventilation should provide this input data to the mathematical model, but in NI "Vinca" couldn’t receive such data. Because of inability to get adequate data on the inventory of radionuclides during routine operation of the reactor, "RA" in NI "Vinca", we used publicly available data Brook Haven Laboratory U.S. (1997) on the assumed annual emissions of radionuclides into the atmosphere, Table 1.

Table 1. Supposed power source based on Brookhaven national Laboratory (1997).

nuclide	Ar41	Al26	As76	Ba128	Ba140	Br82	Ce141	
Emission	8.2e+13	4.5e+2	1.7e+7	6.9e+6	5.8e+6	3.2e+8	6.7e+3	Bq/god
nuclide	Ce144	Co60	Fe59	Hg203	I124	I131	I133	
Emission	5.3e+4	9.8e+4	1.4e+5	2.2e+6	7.0e+5	1.2e+6	1.3e+7	Bq/god
nuclide	La140	Mo99	Na24	Sb122	Sc46	Se75	Sr91	
Emission	3.0e+7	5.7e+3	8.5e+6	1.8e+4	7.9e+2	7.5e+3	1.2e+7	Bq/god
nuclide	Tc99m	Ti44	Xe133	Xe135	Zn65	Zn69m		
Emission	2.2e+6	4.8e+6	3.8e+6	4.0e+7	7.2e+5	5.3e+4		Bq/god

Along to given emission, we used the available data on the characteristics of the reactor ventilation "RA", data from automatic station whose meteorological sensors placed on pillar near the reactor, "RA", 3D topography of the area around the Institute "Vinca", the physical characteristics of pollutants and dose factors (dose conversion factors) available through international publications, ICRP(1989), ICRP (1990), ICRP (1991a), ICRP (1991b), EPA (1993), IAEA (1996), IAEA (2000), Health Canada (1999), Council Directive 96/29/(1996) , etc.

This paper started from the conservative assumptions, that the emission of radionuclides in the boundary layer of the atmosphere was continuously 24 hours a day, 365 days a year and that the hypothetical resident continuously throughout the year, was exposed to radiation by inhalation, radiation from dry and wet deposition of radionuclides on the ground and that hypothetical resident was in a “radioactive cloud” formed as a result of continuous emission of radionuclides.

3. RESULTS

Results of the mathematical modeling of the dispersion of radionuclides through the boundary layer of the atmosphere are the fields of mean annual activity on 1m above the ground, fields of annual activity of dry and wet deposition and the fields of total annual dose to a hypothetical inhabitant of the selected computational domain.

3.1. Fields of average air activity concentration in the five years series 2001-2005 and 2009

Emitted radionuclides carry activity, which represents the number decays in period of time. The unit of activity is the Becquerels (Bq) and is the number of decays per second. Source activity, depending on the half-life radionuclides, changes with time and with distance from the source. Fields of average annual concentration of activities, gained by the presented emission of radionuclides, taking into account the characteristics of sources, weather conditions and soil characteristics, are shown graphically in fig.3.

The maximum of average annual activity concentration in the air at 2m above the ground, ranged from 3.9 Bqm-3 - 5.6 Bqm-3.

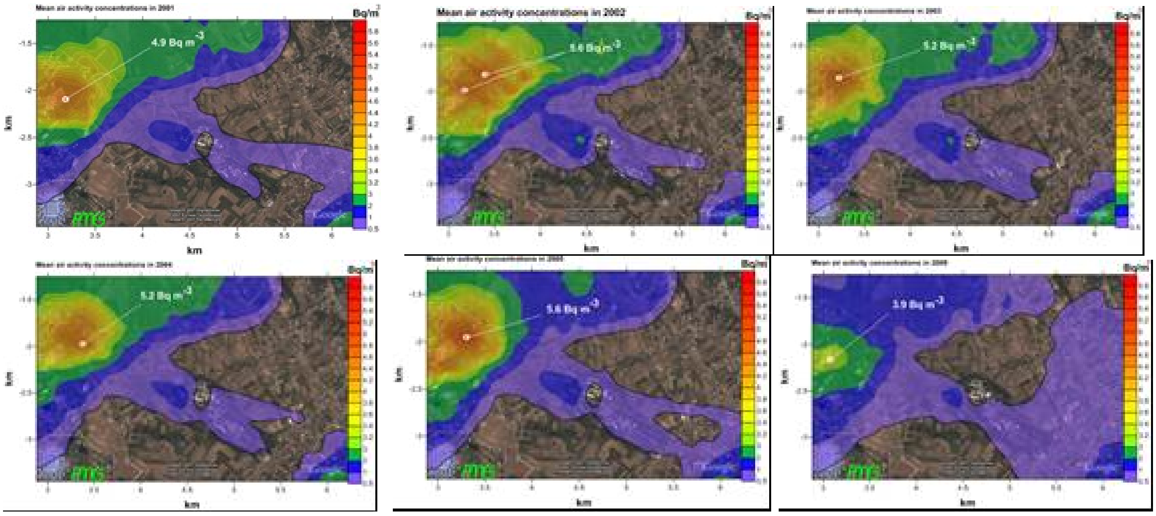


Figure 3. Fields of average annual concentration activity for assumed annual emission of radionuclides in period 2001-2005 and 2009

3.2.Fields of annual dry deposition of activity (2001-2005 and 2009)

Dry deposition was calculated from the activity concentrations in air and deposition rate for the selected terrain and for the radionuclide emission inventory. Speed of dry deposition is taken from the literature, Sehmel (1980) and was based on the recommendations for the deposition rate of 0.008ms^{-1}. Fields of dry deposition correspond to fields of concentration of activities, both in shape and by zones with maximum values. Maximum annual values of dry deposition of activities for the selected period 2001-2005, whatever and 2009 are in the interval 12-17 kBqm^{-2} fig. 4.

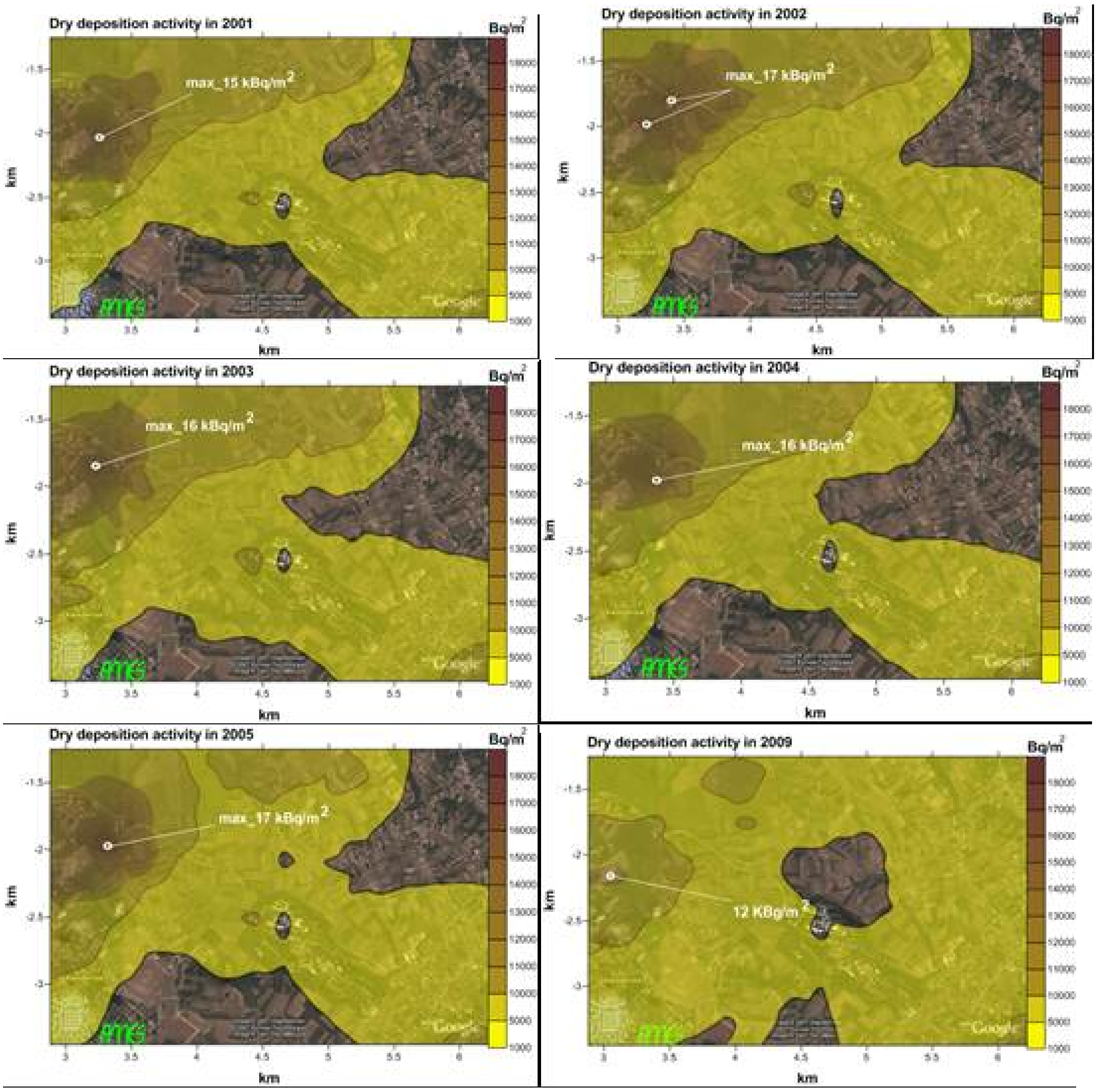


Figure 4. Dry deposition of activity (2001-2005 and 2009)

3.3. Fields of annual wet deposition of activity (2001-2005 and 2009)

Wet deposition is calculated as washing with precipitation. The intensity of rainfall was measured by an automatic station for ten minutes. Fields of annual activities of wet deposition are calculated from the distribution of activity concentrations with the height and intensity of rainfall. Maximum values of wet deposition vary in the interval 120-630 Bqm^{-2}, fig.5.

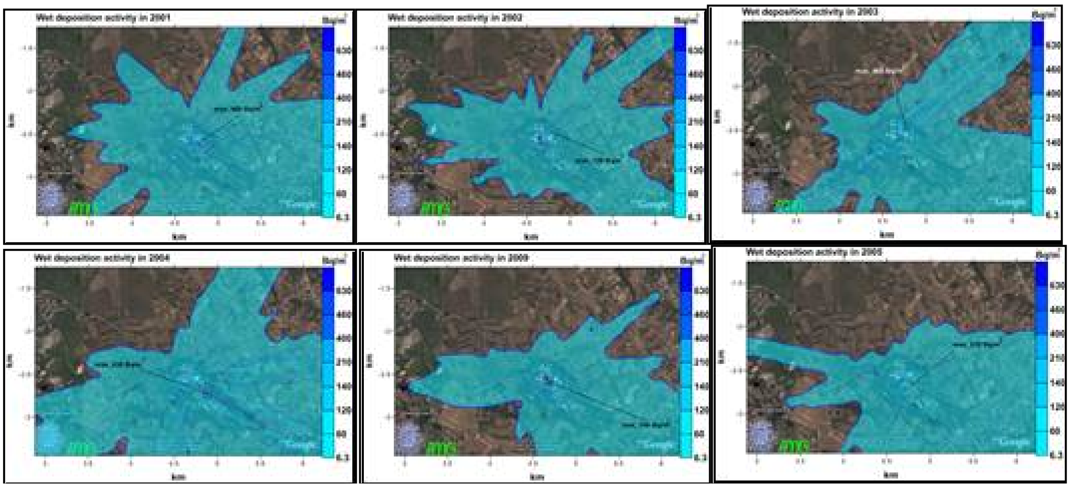


Figure.5. Wet deposition of activity (from upper left to bottom righ, 2001-2005 and 2009)

3.4. Dose

Dose is calculated with algorithm for the calculation of dose in accordance with IAEA recommendations IAEA (2013) based on dose conversion factors:

Table.2. Densities, dose coefficients for the adult population, time constants for radionuclides

radionuclide	density g/cm^{3}	ginh Sv/Bq	guob Sv·m^{3}/(Bq·s)	gdep Sv·m^{2}/(Bq·s)	hli
Ar41	1.784	0	6.13 e^{-14}	0	1.8h
Al26	2.702	1.2e^{-8}	1.28 e^{-13}	2.47 e^{-15}	7.2 e^{5}y
As76	5.72	9.2 e^{-10}	2.06 e^{-14}	5.24 e^{-16}	2.43d
Ba128	3.51	0	2.54 e^{-15}	6.78 e^{-17}	12.8d
Ba140	3.51	0	8.07e^{-15}	1.90 e^{-16}	35h
Br82	3.119	0	1.21 e^{-13}	2.48 e^{-15}	32.5d
Ce141	6.77	3.2 e^{-9}	3.10 e^{-15}	6.93 e^{-17}	284d
Ce144	6.77	3.6 e^{-8}	7.63 e^{-16}	1.84 e^{-17}	5.27y
Co60	8.9	1.0 e^{-8}	1.19 e^{-13}	2.30 e^{-15}	44.5d
Fe59	7.874	3.7 e^{-9}	5.62 e^{-15}	1.10 e^{-15}	46d
Hg203	13.456	2.4 e^{-9}	1.04 e^{-14}	2.22 e^{-16}	4.2d
I124	4.933	0	5.04 e^{-14}	1.04 e^{-15}	8.04d
I131	4.933	0	1.69 e^{-14}	3.64 e^{-16}	20.8h
I133	4.933	0	2.76 e^{-14}	6.17 e^{-16}	1.68d
La140	6.7	0	1.11 e^{-13}	2.16 e^{-15}	40h
Mo99	10.289	8.9e^{-10}	6.99 e^{-15}	1.78 e^{-16}	66h
Na24	0.971	2.7 e^{-10}	2.08 e^{-14}	3.59 e^{-15}	15h
Sb122	6.684	1.0 e^{-9}	2.02 e^{-14}	4.85 e^{-16}	2.7d
Sc46	2.989	0	9.36 e^{-14}	1.88 e^{-15}	83.6d
Se75	4.79	1.1 e^{-9}	1.68 e^{-14}	3.61 e^{-16}	119d
Sr91	2.54	0	3.27 e^{-14}	7.27 e^{-16}	9.5h
Tc99m	11.5	1.9 e^{-11}	5.25 e^{-14}	1.14 e^{-16}	6.02h
Ti44	4.549	0	4.70 e^{-15}	1.18 e^{-16}	47.3y
Xe133	5.897	0	1.39 e^{-15}	0	5.27d
Xe135	5.897	0	1.11 e^{-14}	0	9.1h
Zn65	7.133	1.6 e^{-9}	2.72 e^{-14}	5.41 e^{-16}	244d
Zn69m	7.133		1.84 e^{-14}	3.98 e^{-16}	13.8h

3.4.1.Inhalation dose

Inhalation dose is calculated from speed of breathing, activity concentrations in air and appropriate inhalation dose conversion coefficients:

$$D_{inh} = g_{inh} \cdot C(x,y,z,t) \cdot V_{br} \qquad (2)$$

where:

g_{inh}	coefficient inhalation dose for radionuclide observed (Sv/Bq)
$C(x,y,z,t)$	activity concentration in the air (Bq/m^3)
V_{br}	speed of breathing air (1.2 m^3/h)

3.4.2.Dose of the cloud (immersion)

The dose from external radiation of observer wrapped with radioactive cloud, which is formed in accidental situations, is calculated according to the relationship:

$$D_{obl} = g_{obl,r} \cdot C(x,y,z,t) \qquad (3)$$

where :

$g_{obl,r}$	coefficient of dose from external radiation from radionuclides clouds r, (Sv·m^3/(Bq·s))

3.4.3.A dose of dry and wet deposition

External radiation dose from the total radioactivity deposited on the ground, that hypothetical inhabitant receives from its 18 to 70 age is calculated according to the model:

$$D_{dtot} = \left[(1-\vartheta)\cdot g_{b,r}^{>17a} + \left(1-\vartheta^{52}\right)\cdot b \cdot g_{b,r}^{>17a}\right]\cdot \frac{1}{\lambda_r}\cdot\left(Dry_{dep,r} + Wet_{dep,r}\right) \qquad (4)$$

$$\vartheta = \exp(-\lambda_r \cdot t_1) \qquad (5)$$

where:

t_1	time period 1 year (s)
λ_r	coefficient for radionuclide dissolution r (1/s)
$g_{b,r}^{\rangle 17a}$	dose deposition coefficient for the resident older than 17 years for the radionuclide r (Sv·m^2/(Bq·s))
$Dry_{dep,r}$	dry radionuclide deposition r, (Bq/m^2)
$Wet_{dep,r}$	wet radionuclide deposition r, (Bq/m^2)
b	dimensionless coefficient

Fields of annual dose from external radiation for a hypothetical resident are calculated as inhalation, dose of staying in radioactive cloud (dose of immersion) and a dose of radioactive material deposited on the ground in the form of dry and wet deposition. Total annual dose is calculated as sum of the doses listed above according to conservative assumptions. The model is started for each year separately. Limit value of total annual dose coming from artificial sources shall not exceed 1% of the annual dose limit received by a resident from natural background sources, which is annually 1mSv. This way, the contribution of artificial sources to total annual dose should not be greater than 1e- 5Sv or 10μSv. The total annual dose to a hypothetical resident around nuclear reactor "RA" for the hypothetical radionuclides emission were in the range of 9.4e $^{-6}$ to 1.1e $^{-5}$Sv. On two occasions, 2002 and 2005, these values were 10 % larger than the limit values for artificial sources (1e^{-5}Sv), i.e. they were 1.1e $^{-5}$Sv.

Inhalation doses were calculated as the product of breathing rate, exposure time, inhalation dose coefficients (dose conversion factor from) and activity concentration of each radionuclide from the emissions inventory. Exposure time was equivalent of the annual or monthly period for which the dose are calculated, at the speed breathing air for a grown man to 1.2 m^3 / h.

External radiation dose received by the observer at the ground, which is wrapped in cloud of radionuclide/activities for observed monthly and annual periods, it is proportional to the activity concentration in the air near ground, the exposure time and the corresponding dose coefficients for radionuclide present in the cloud.

3.4.5.The total annual dose.

The total annual doses are received as the sum of the inhalation dose, dose from clouds and dose of dry and wet deposition fig.6.

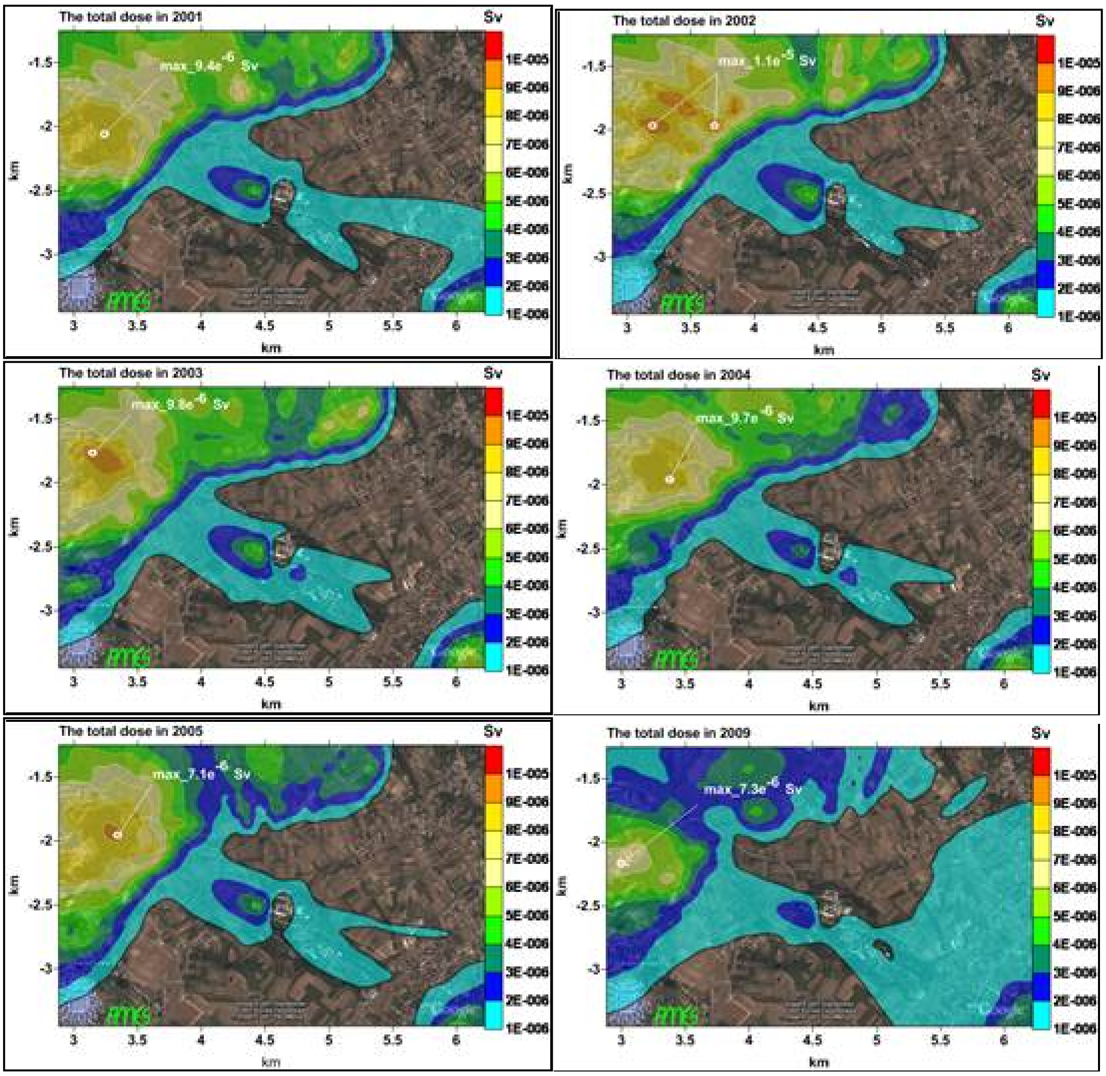


Figure 6. Fields of total annual dose of internal (inhalation) and external radiation (immersion and groundshine), for assumed emission activity/radionuclides, in period 2001-2005 and 2009

4. CONCLUSION

For the modeling dispersion of radionuclides, through the boundary layer of the atmosphere routinely emitted from the ventilation of nuclear reactor "RA" in Vinca and for dose calculation, a database of meteorological data based on the ten-minute dose values is created. Meteorological data were collected with an automatic meteorological station mounted along a tower within Institute "Vinca". From 2001 to 2005 data were collected by an automatic weather station of the Institute of Physics on the tower 37 m tall, and from 2009 data were received by measurement on new automatic weather station from Slovenian company AMES on new meteorological tower 40 m tall at the location of NFS. All data were recorded as ten-minute mean values in electronic form.

Based on the analysis of average annual concentration of activity emitted into the atmosphere from sources with parameters of ventilation of nuclear reactor "RA", the maximum values are in the range of 3.9 Bqm^{-3} in 2009 to 5.6 Bqm^{-3} in 2002 and 2005. Maximum values at the same time are in the direction of WNW and NW in regard to the source and at distances from 1500m to 2000m from the source. For direction of their appearance is responsible wind from ESE and SE and taking into account the orography of the terrain and the distance from the source at which are the values, it can be concluded that for their appearance are responsible atmospheric stability categories E and F, by Pasquill-Gifford classification of atmospheric stability (moderately stable E and stable F). Fields of activity concentration in air (2m above ground) depends, besides the meteorological characteristics also from source characteristics, terrain characteristics and the physical-chemical characteristics of radionuclides.

Study have very conservative approach, considering that individual is 365 days constantly wrapped in radioactive cloud. It is assumed also that the reactor "RA" was in continuous routine work, 24 hours per day and that the emissions were constant, which differs significantly from the reactor operation during the year.

Based on all the above, with described conservative approach and assuming that the range of appropriate meteorological data for the application of the described mathematical model of five consecutive years, 2001-2005 and 2009 is enough for this type of analysis, it can be concluded that the nuclear reactor "RA" in the course of their work in 1959 up to 1984 could not affect their environment above the prescribed limit 10 µSv /year.

5. ACKNOWLEDGMENTS

The investigations presented in this paper were done at the Public Company Nuclear Facilities of Serbia, Laboratory for Atmospheric Physics and Optical Metrology at the Institute of Physics in Belgrade, and Faculty of Geography, University of Belgrade. The authors wish to thank the Ministry of Education, Science and Tehnological Development the Republic of Serbia for part financing this investigation through Projects III 45003.

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4 INDOOR/OUTDOOR AIR

4.1 THE BENZO(A)PYRENE-EQUIVALENT TOXICITY OF PARTICLES ASSOCIATED POLYCYCLIC AROMATIC HYDROCARBONS IN THE AIR OF BELGRADE METROPOLITAN

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ABSTRACT

The aim of this paper was to determine level of particle-bound polycyclic aromatic hydrocarbon (PB-PAHs) and also the benzo(a)pyrene at three sampling sites over Belgrade Metropolitan. According their Toxicity Equivalence Factor (TEF) we calculate benzo(a)pyrene-equivalent (BaPE) toxicity of particles and compare the obtained values in the air of Belgrade Metropolitan. In this this study we compared the BaPE toxicity of particles associated with polycyclic aromatic hydrocarbons using Toxicity Equivalence Factor (TEF) of 16 priority PAHs (prPAHs) collected at 3 different locations with at least two of next characteristics of sites: strong city center, frequent traffic , rural area, suburban area, strong industrial surrounding of combustion processes from thermal power plant, mining facilities and ash and coal landfills.

INTRODUCTION

Many organic chemicals including particle-bound polycyclic aromatic hydrocarbon (PB-PAHs) may cause wide range of adverse health effects including inflammatory responses. PAHs with 2–3 aromatic rings exist dominantly in the gaseous phase, while compounds with 4 or more aromatic rings, that are more toxic, are mostly associated with PM fractions. Studies performed all over the world demonstrated that major source of PAHs in urban areas were emission from vehicle, while in industrial area from combustion processes. Residential heating and biomass burning may contribute significantly to level of PAHs.

Along with rapid increase in the number of vehicles and energy consumption in urban areas, air quality is still a big problem, with atmospheric aerosols as major pollutants. Due to fast development of urban areas and negative impact that anthropogenic activity has on human health, it is very important to know concentration and chemical composition of aerosols that consist of inorganic species and organic compounds. Among them, polycyclic aromatic hydrocarbons (PAHs) are of major significance.

PAHs are formed during incomplete combustion (wood burning, combustion of fuels in engines). These compounds consist only of carbon and hydrogen in two or more fused aromatic rings. They belong to POPs (persistent organic compounds). In the atmosphere, these compounds can be present in the vapor phase, usually as low molecular weight PAHs, and associated with the particle phase, dominant as (higher molecular weight PAHs (Ravindra et al., 2008).

The PM_{10} was sampling at three sampling sites in Belgrade Metropolitan region. Belgrade Metropolitan area covers over 300.000 ha, while the city has urban area spreading at 36000 ha. The inner city zone has a population of over 1.2 million. In total, 1.65 million people live in Belgrade Metropolitan Area, making it one of the largest cities of Southeastern Europe (Statistical Office of Republic of Serbia, Belgrade, 2012). One sampling site was located in city center, while two other sampling sites were positioned within the Belgrade Metropolitan region, out of inner zone. The measurements of PAHs at each of three sites were part of local monitoring that has been running under Institute of Public Health of Belgrade (PHB).

MATERIAL AND METHODS

The study was conducted at three sampling sites over Belgrade Metropolitan that belong to local automatic station monitoring network: ***urban-traffic*** (UT) in the city center, one of the most frequent traffic at round intersection that is branches into eight streets ; ***suburban-industrial*** (SUI) far from Belgrade inner zone, but with proximity and influence of coal mine facilities and coal-fired thermal power plant “Kolubara A” and other facilities of the Kolubara mining-industrial complex; ***rural-industrial*** (RI) far from Belgrade inner zone, village in vicinity of coal-fired thermal power plants "TENT A", "TENT B" and other facilities such ash and coal landfills. 24h PAHs were collected and analyzed in PM_{10} aerosol fraction during 2010 and 2011, 8 samples per month at each sites using: EU reference sampler, quartz filters and Agilent GC/MS (6890N GC with 5973N MSD).

Collected samples were prepared according to Compendium Method TO-13A. All samples were analyzed by GC Agilent 6890 N with Mass Selective Detector Agilent 5973 MSD. Capillary column DB-5 MS (30 m x 0.25 mm x 25 µm) was used. Oven temperature program started on 70 ^{o}C (held 4 minutes), ramp 8 ^{o}C /min. till 310 ^{o}C (hold 5 minutes). Solvent delay was 5 minutes and time of run- 46 minutes.

As external standard for calibration curve we used Ultra Scientific PAH Mixture PM-831, which consists of 16 compounds, each of 500.8 ± 2.5 µg/ml concentration. As internal standard, we used Ultra Scientific Semi-Volatiles Internal Standard Mixture ISM-560 with deuterated compounds: Acenaphtene-d_{10}. Chrysene-d_{10}, 1,4-dichlorobenzene, Naphthalene-d_8, Perylen-d_{12}, Phenanthrene-d_{10}. Prior to analysis, calibration curves for the 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 (MQL) for all PAHs was 0.02 ng /m^3

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PAHs were extracted in microwave with mixture of solvents hexane: acetone (12.5 ml n-hexane: 12.5 ml acetone) according to EPA 3546.After the extraction, the solvent volume was reduced by rotary evaporation under a reduced pressure (55.6 kPa and with 0.2 ml isooctane as a keeper) to 1 ml. After that, n-hexane solution was reduced to 0.25 ml under nitrogen stream at room temperature to 0.5 ml and analyzed on GC.

RESULTS AND DISCUSION.

BaP is used as an indicator of human exposure to PAHs.. The percentage of BaP to total PAHs was from 7-10 % on all measurement sites in both seasons as it is shown in Table 1. The highest content of BaP in total PAHs was at site SUI in winter 2011 and the lowest was at site UT in summer 2011. The highest content of BaP was also at SUI in winter (9.1 %). According to Annual report of European Environment Agency for 2010 (EEA, 2012) average annual concentration of BaP exceeded the target value in six countries (Austria, Bulgaria, the Czech Republic, Hungary, Poland and Slovakia). The average concentration measured at Polish station is six times higher than target value.

In order to estimate more accurate risks assessment from exposure humans to PAH the application of benzo(a)pyrene-equivalent (BaPE) factor to PAHs was evaluated by multiplying the concentrations of each PAH with their toxic equivalent factors (TEF) (Akyüz at al., 2008, Akyüz at al., 2010). Toxic effect of some PAH is stronger, even at much lower concentrations, due to its high TEF. TEFs of individual PAHs have been reported by many researches (Knafla et al., 2006). Toxic equivalent factors (TEF) for 16 PAHs is given on Table 2.

Total BaPE concentrations for collected PM_{10} during the winter season were found to be between 6.68 and 13.92 ng/m^3, highest at the site SUI. During the summer season TEF were between 0.79 and 1,59. ng/m^3, lowest at site UT and highest at SUI . During both seasons TEF were similar at UT and RI and about two times higher at SUI sampling site. In Zonguldak, Turkey PAHs TEF was 1.241 in $PM_{2.5-10}$ in winter and 0.2684 in summer period (Akyüz at al., 2008). Mean values BaPE concentrations for whole sampling period (summer and winter season) were: in Athens, 1.6 ng/m^3 (Marino et al., 2000); in Argel, 3.4 ng/m^3 (Yassaa 2001) and in a highly traffic urban area in Florence, 2.6 ng/m^3 (Lodovici et al., 2003). In framework of this study, like in other studies, the carcinogenic risks for humans are much higher during winter time at all sites, but the highest risk is at site SUI due to strong influence from Kolubara mining-industrial complex facilities in vicinity, coal mine, thermal power plant and other.

Table 1. Average concentration of ∑ PAH, B(a)P and its ratio

			2010	**2011**
Rural industrial site	**Summer**	Numb. of samples	50	29
		∑PAH (ng/m^3)	6.99	1.09
		B(a)P (ng/m^3)	0.61	0.10
		% BaP in ∑PAH	**8.68**	**8.93**
	Winter	Numb. of samples	40	44
		∑PAH (ng/m^3)	42.18	54.06
		B(a)P (ng/m^3)	3.68	4.00
		% BaP in ∑PAH	**8.72**	**7.39**
Suburban industrial site	**Summer**	Numb. of samples	49	42
		∑PAH (ng/m^3)	7.83	11.43
		B(a)P (ng/m^3)	0.72	1.21
		% BaP in ∑PAH	**9.13**	**10.54**
	Winter	Numb. of samples	32	40
		∑PAH (ng/m^3)	82.10	102.98
		B(a)P (ng/m^3)	7.89	9.10
		% BaP in ∑PAH	**9.61**	**8.83**
Urban traffic site	**Summer**	Numb. of samples	35	38
		∑PAH (ng/m^3)	12.52	4.88
		B(a)P (ng/m^3)	1.01	0.35
		% BaP in ∑PAH	**8.10**	**7.27**
	Winter	Numb. of samples	38	37
		∑PAH(ng/m^3)	56.40	46.68
		B(a)P (ng/m^3)	4.87	4.27
		% BaP in ∑PAH	**8.64**	**9.14**

Table 2. Toxic equivalent factors (TEF) for PAHs

PAH	**TEF**	**RI**		**SUI**		**UT**	
		Summer	**Winter**	**Summer**	**Winter**	**Summer**	**Winter**
Naphtalene	0.001	0.0001	0.0008	0.0002	0.0014	0.0002	0.0012
Acenaphtylene	0.001	0.0001	0.0003	0.0001	0.0005	0.0001	0.0003
Acenaphtene	0.001	0.0001	0.0003	0.0001	0.0003	0.0001	0.0003
Fluorene	0.001	0.0000	0.0003	0.0000	0.0002	0.0001	0.0001
Fenanthrene	0.001	0.0002	0.0029	0.0002	0.0021	0.0003	0.0011
Anthracene	0.01	0.0004	0.0039	0.0005	0.0064	0.0004	0.0032
Fluoranthene	0.001	0.0002	0.0051	0.0007	0.0127	0.0004	0.0054
Pyrene	0.001	0.0002	0.0045	0.0008	0.0131	0.0005	0.0059
Benzo(a)anthracene	0.014	0.0046	0.0653	0.0139	0.1735	0.0062	0.0757
Chrysen	0.026	0.0145	0.1768	0.0367	0.3622	0.0244	0.1947
Benzo(b)fluoranthene	0.1	0.0793	0.6055	0.1130	0.8990	0.0730	0.6330
Benzo(k)fluoranthene	0.1	0.0703	0.4437	0.1010	0.6920	0.0670	0.4730
Benzo(a)pyrene	1	0.4853	3.8464	0.9400	8.5700	0.4500	4.5300
Indeno(1.2.3-cd) pyrene	0.1	0.1147	0.3459	0.0980	0.5950	0.0470	0.3360
Dibenzo(ah)anthracene	0.89	0.0972	0.5574	0.1602	0.9701	0.0623	0.4806
Benzo(ghi)perylene	0.012	0.0091	0.0404	0.0097	0.0625	0.0071	0.0467
∑ BaPE		**0.8763**	**6.0995**	**1.4751**	**12.361**	**0.7391**	**6.7872**

CONCLUSION

During measuring period, prPAHs identified as BaPE so far exceeded 1 ng/m^3 but vary for one-order-to-magnitude between heating and non-heating session. During non-heating period at frequent traffic at round intersection in the city centre BaPE was less that 1 ng/m3. In the same period, at locations in vicinity of thermal-power plans at site located in rural area BaPE was also below limit values, while at the site in suburban location the average value of BaPE was 1.5 ng/m^3. During heating season at the same site, the highest BaPE of 12.4 ng/m^3 was identified. At the other two locations, during the heating period, BaPE was 6.1 at rural-industrial and 6.8 at urban-traffic site**.**

This study confirmed that PB-PAHs in particulate matter were under strong seasonal influence, average 24h PB-PAHs as well as BaPE were between half and one order-to-magnitude much higher during heating period than in non-heating period. BaPE toxicity was similar in city centre at traffic site and in rural area in vicinity coal-fired thermal power plants “TENT A” and “TENT B”. BaPE was significantly higher at suburban site under influence of coal-fired thermal power plant “Kolubara A” and other facilities of Kolubara mining-industrial complex.

ACKNOWLEDGEMENTS

This work was supported by the following project: III41028, INGEMAS (2011-2014) funded by the Ministry of Education, Science and Technological Development of Serbia (2011-2014) ; Municipality of Belgrade, Secretary of Environmental Protection.

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4.2 PARTICULATE MATTER IN CLASSROOM INDOOR AIR OF PRIMARY SCHOOLS IN BELGRADE IN A FRAMEWORK OF THE SEARCH PROJECT

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ABSTRACT

Over the last few decades, indoor air quality (IAQ) has been rated as a problem of a great significance. But, the connection between indoor particulate matter (PM) concentrations and associated health risks is still unexplored. In particular, data about the air quality in schools are needed, since children are assumed to be more vulnerable to health hazards, while spending a large part of their time in school. Such necessity was formulated through implementation of the project SEARCH (School Environment And Respiratory Health of Children), conducted in Serbia, as well as in Albania, Bosnia and Herzegovina, Slovakia and Hungary, during a two-year period (2007-2009).

In the city of Belgrade 10 primary schools were chosen for the research. Key criteria for making a choice of a particular school were its location, according to the distance from the core central urban zone of the city: periurban settlement without busy roads, wider urban area with busy traffic, city proper zone with busy traffic. In the selected schools research was implemented on children attending classes in 44 classrooms, 4 classrooms per school.

Children were chosen to participate in the research by using random sampling method, and according to the class they are attending. In total, 746 children have participated in the research.
Assessing level of exposure to school environment in children was done by the measuring of school indoor air pollutants, school building status evaluation (assessment of its maintenance practices), and children's home environment evaluation (questionnaire). The study protocol included a standardized questionnaire for school characteristics, filled in by the school administrator, and one standardized questionnaire for classroom characteristics, filled in by the teacher. The following measurements have been undertaken in all chosen classrooms: Combination of diffuse sampling during a 4-day exposure period for formaldehyde (HCHO), nitrogen dioxide (NO_2), BTX, and continuous 24-h measuring of carbon monoxide (CO), carbon dioxide (CO_2) and PM_{10}, during school hours. Parallel to these IAQ monitoring activities, outdoor concentrations of the same specific pollutants were measured, close to school buildings.

Keywords: indoor air quality, classroom, particulate matter, primary school, exposure

1. INTRODUCTION

The indoor air quality in 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 [1]. Indoor air quality (IAQ) in schools 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 [2-5]. Children are particularly vulnerable to all types of pollutants, because their breathing and metabolic rates are high. In school they have less space, than adults working in a typical office. 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 lead to allergic reactions or ill health [6]. Therefore, it is of great importance to provide good IAQ in classrooms, to minimize these effects [7]. Sources of indoor air pollution could be: furnishings [8], IT equipment [4], bio-effluents, and external pollutants, such as nitrogen-dioxide [9] and carbon-monoxide [10]. In the indoor environment, in which people spend most of their time, both indoor and outdoor sources contribute to PM levels. Indoor PM is affected by ambient concentrations, air exchange rates, penetration factors, as well as deposition and re-suspension mechanisms. In this complex microenvironment, activities such as cleaning, walking, playing and particularly smoking cause the formation of PM in indoor air [11].

2. METHODOLOGY

The cross-sectional SEARCH study (School Environment and Respiratory Health in Children) has involved 6 European countries (Albania, Bosnia and Herzegovina, Hungary, Serbia, Slovakia and Italy). Concerning the Serbian part of the study, research was undertaken in the capital city of Belgrade. The project has been designed such that a sample of 10 schools per country is enough to get a clear picture about the level of indoor exposure of children to air pollutants in primary schools. They were chosen (sampled) to be with heterogeneous characteristics: half of them in environmentally more advantaged areas and half in less advantaged ones, especially concerning the proximity of heavy traffic (as shown in Figure 1). Study was carried out in the heating season 2007/2008, lasting for a full working week at each location.

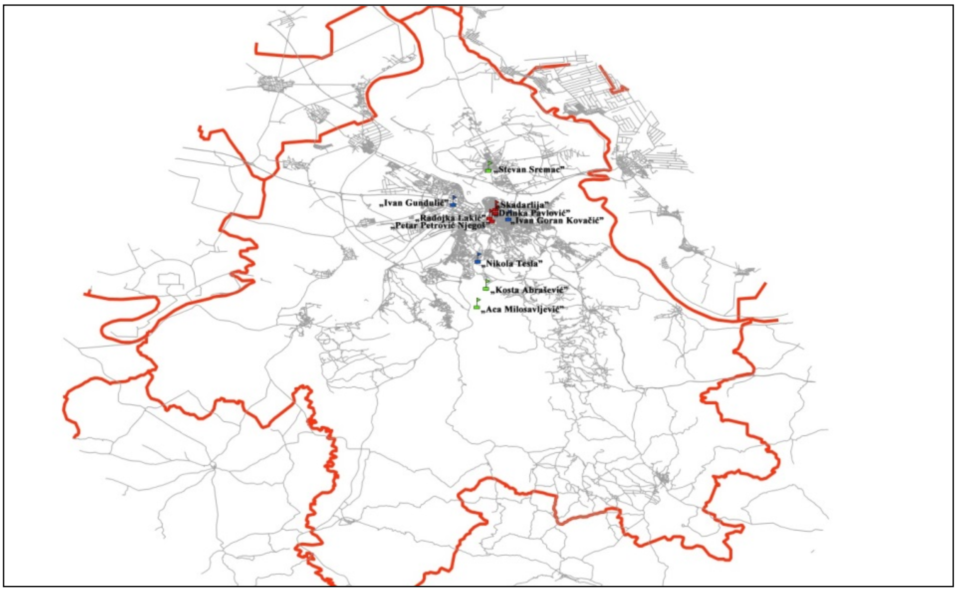

Figure 1. Map of the city of Belgrade with the position of selected schools

Main aims of the SEARCH project were: Implementation of the EU Environment and Health Strategy, Action Plan and the CEHAPE through both active involvement in European processes and the development of efficient instruments and tools for multi-stakeholder cooperation, together with the regional participation in implementation of the CEHAPE Priority Goal 3: Prevention and reducing respiratory disease due to outdoor and indoor air pollution by complex research involvement in schools [12]. The objectives were: to assess the connections between the school environment and children respiratory health, and to make recommendations to improve the air quality of the school environment.

Main objective of this paper was to show results of the PM_{10} levels sampled inside classrooms in 10 primary schools in Belgrade, and relate them to different classroom and school characteristics, using the SEARCH project methodology. For PM_{10} levels sampling, diffuse samplers were used, each of a uniform kind in every participating country (project donation). Besides the air sampling procedures, the study protocol included three standardized questionnaires: for school characteristics (filled in by the school administrator); for classroom characteristics (filled in by the teacher holding classes in it), and a questionnaire concerned with respiratory health and home environment of individual pupils (filled in by the parents). Actually, this paper will not present the data from the last mentioned questionnaire.

The paper, also, deals with the quantitative indicators of the thermal comfort zone, as given by the ASHRAE Standards [13], such as: indoor air optimal temperature (18-23 Cº), relative air humidity (40-75%), space occupancy (< $2m^2$ of indoor space per child, not suitable), correlations of thermal comfort indicators with the measure values of indoor PM_{10} levels. Finally, PM_{10} levels were correlated to the classroom cleaning practice, such as dry methods (vacuum, broom), wet methods (mop), and combined methods (with added chemicals, presumably bleach).

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} distribution type. Quantitative variables were compared using Anova F test, and categorical variables were compared using contingency tables and Chi-Square or Kruskal Wallis test. Chi-square test was used to compare IAQ PM_{10} between groups - schools or schools' position.

- Pearson correlation between variables is used for investigating the linear relationship between two variables, by schools.
- P-value less than 0.05 was considered statistically significant.

Table 1. IAQ and OAQ PM_{10} concentration (μg/m^3) related to school geographical position

Type of schools by location		No. of exposed children	Mean	SD	95% Mean Lower	95% Mean Upper	Median/Range	Min	Max
PM_{10} IAQ	Suburb schools	244	109.18	47.66	103.17	115.19	96 / 164	33	197
	Schools in broader urban area	220	66.08	37.36	61.12	71.05	53 / 126	32	158
	Downtown	271	71.09	26.90	67.88	74.31	70 / 79	32	111
	Total	735	82.24	42.43	79.17	85.31	70/165	32	197
PM_{10} OAQ	Suburb schools	244	153.90	130.39	137.46	170.34	116 / 515	34	549
	Schools in broader urban area	220	83.46	55.77	76.05	90.87	55 / 168	22	190
	Downtown	271	77.30	28.53	73.89	80.72	80 / 89	30	119
	Total	735	104.57	89.85	98.07	111.08	82/527	22	549

3. RESULTS AND DISCUSSION

To make the analysis and interpretation easier, schools were distributed in three groups:
Group 1 = Suburb schools, Rušanj / Resnik / Borca 3
Group 2= Schools in broader urban area, New Belgrade, Rakovica
Group 3 = Downtown: streets Resavska, Kosovska, Francuska, and Aleksandra Kostica
PM_{10} IAQ measured values are highest in the suburban schools, significantly higher than in other schools, (K-W test =133.454, p<0.0001), together with PM_{10} OAQ, (K-W test =69.86, p<0.0001).

Table 2. Interval distribution of IAQ PM_{10} concentration > 50 or ≤ 50 μg/m^3 by schools (%)

	Schools				
PM_{10} ranges	Aca Milosavljevic	Kosta Abrasevic	Nikola Tesla	Ivan Goran Kovacic	Skadarlija
	School 1	School 2	School 3	School 4	School 5
<=50	0,0%	0,0%	0,0%	67,2%	39,7%
>50	100,0%	100,0%	100,0%	32,8%	60,3%
PM_{10} ranges	Stevan Sremac	Drinka Pavlovic	P.P. Njegos	Radojka Lakic	Ivan Gundulic
	School 6	School 7	School 8	School 9	School 10
<=50	23,4%	32,1%	0,0%	57,8%	37,8%
>50	76,6%	67,9%	100,0%	42,2%	62,2%

Among schools, a statistically significant difference is proved for the distribution of IAQ PM_{10} concentration (p<0.0001). School 4, shown in Figure 3 has significantly higher frequency of measured values IAQ PM_{10} in the range lower than 50 μg/m^3. On the other hand, schools 1,2,3 and 8 has highest average values, and in all of them all measured indoor PM_{10} concentrations were beyond 50 μg/m^3.

Geographic position of schools

Figure 2 shows comparative values of IAQ PM_{10} and OAQ PM_{10} by groups of schools. Both indoor and outdoor PM_{10} levels are significantly higher in suburban schools than in those located in the broader urban zone: (for PM_{10} IAQ: K-W test=107.86, p<0.0001; PM_{10} OAQ: K-W test =39.43, p<0.0001). The similar level of significance appears when correlating PM_{10} levels in suburban schools, with the PM_{10} levels in schools located in the strictly urban zone: (K-W test =93.01, $p<0.0001$), and for PM_{10} OAQ, (K-W test =27.74; $p<0.0001$). Indoor PM_{10} concentrations are significantly lower in schools located within a broad urban zone, when correlated to ones in a strictly urban zone i.e., downtown (K-W test =12.943, $p<0,0001$). On the other hand, it does not count in the case of outdoor PM_{10} values, (K-W test =2.228, p=0,135).

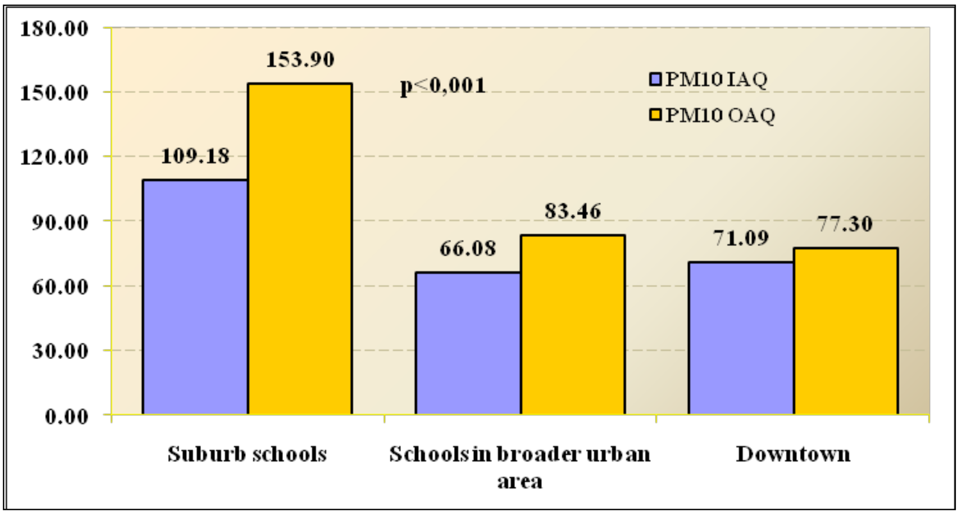

Figure 2. IAQ PM_{10} and OAQ PM_{10} according to the school geographic positions (μg/m^3)

Table 3. IAQ PM_{10} concentrations (μg/m^3) by schools

School Groups	Schools	PM_{10} IAQ (μg/m^3)		Ci 95%		Median	Range
		mean	SD	Lower	Upper		
Suburban	School 1	109,16	18,440	105,48	112,84	105,00	46,00
	School 2	162,12	41,926	151,97	172,27	183,00	106,00
	School 6	62,47	23,592	57,11	67,82	52,00	63,00
Broad urban area	School 3	99,70	45,620	89,35	110,06	72,00	107,00
	School 4	44,72	12,479	41,53	47,92	38,00	30,00
	School 10	50,40	6,224	49,03	51,77	53,00	16,00
Downtown	School 5	58,24	18,276	54,12	62,36	70,00	46,00
	School 7	65,68	26,899	58,26	73,09	51,00	63,00
	School 8	103,87	8,523	101,92	105,82	110,00	18,00
	School 9	52,31	11,222	49,51	55,12	44,00	26,00

Table 4: Outdoor PM_{10} concentrations (μg/m^3) by schools

School Groups	Schools	PM_{10} OAQ (μg/m^3)		Ci 95%		Median	Range
		mean	SD	Lower	Upper		
Suburban	School 1	105,84	26,945	100,46	111,21	106,00	78,00
	School 2	320,82	137,797	287,47	354,18	309,00	380,00
	School 6	68,27	36,277	60,04	76,51	41,00	85,00
Broad urban area	School 3	134,00	55,399	121,43	146,57	141,00	135,00
	School 4	80,33	35,626	71,20	89,45	75,00	84,00
	School 10	38,33	9,648	36,21	40,45	42,00	26,00
Downtown	School 5	83,64	30,003	76,88	90,41	96,00	87,00
	School 7	69,85	31,935	61,05	78,65	52,00	83,00
	School 8	98,00	13,862	94,83	101,17	101,00	46,00
	School 9	51,17	3,444	50,31	52,03	51,00	9,00

Table 3 presents indoor PM_{10} concentrations (μg/m^3), mean, standard deviation, median and range. The maximum PM_{10} concentrations (162.12 ± 41.93 μg/m^3) was detected in school 2, while significantly lower PM_{10} concentrations (44.72 ± 12.48 μg/m^3) was at school 4 ($p<0.001$). Table 4 presents outdoor PM_{10} concentrations (g/m^3) mean and standard deviation, median and range by groups and schools. The maximum concentration values of PM_{10} IAQ (320.82 ± 137.79 μg/m^3) was in school 2, while significantly lower concentration values of PM10 IAQ (38.33 ± 9.65 μg/m^3) was at school 10 ($p<0.01$). Highest average values of IAQ PM_{10} and OAQ PM_{10} was measured in school 2 (suburb schools).

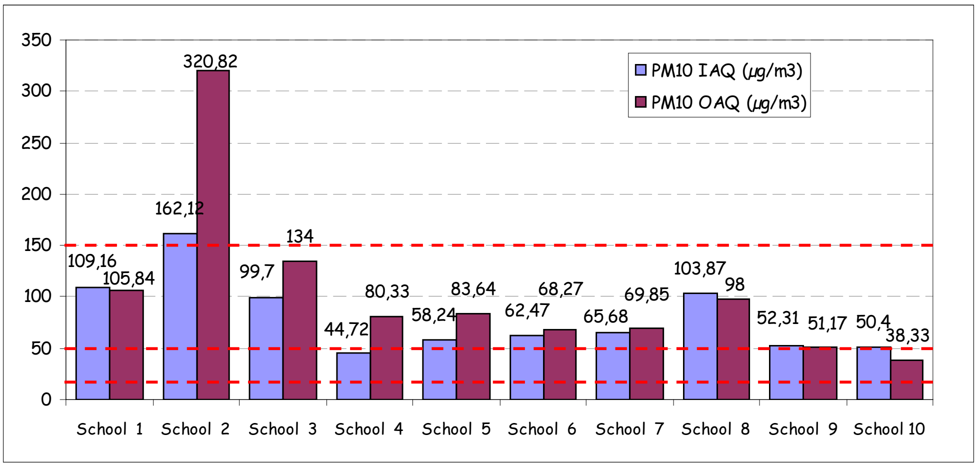

Figure 3. Average values of indoor and outdoor PM_{10} concentration by schools (μg/m^3)

Figure 3 shows the descriptive statistics for mass concentrations of PM_{10} measured outdoors and in the classrooms, by schools. None of 10 schools satisfies the World Health Organization (WHO) standard for PM_{10} annual average level, which has been set at 20 μg/m^3 [14]. However, they meet the National Ambient Air Quality Standards (NAAQS) and WHO standards for PM_{10} 24-hour average which have been set at 150 μg/m^3 and 50 μg/m^3, respectively [14]. Highest average values of IAQ PM_{10} and OAQ PM_{10} concentration were measured in school No.2 (suburb school) and all measured values IAQ PM_{10} were beyond 50 μg/m^3 (as shown in Figure 3). Interesting outcomes were that indoor PM_{10} concentration in school 4 was below 50 μg/m^3, and that outdoor mean PM_{10} level for school 10 were also below 50 μg/m^3. A statistically significant correlation exists between PM_{10} indoor and outdoor concentration, for each school ($p<0.0001$), except for the school 9 „Radojka Lakic“, ($p=0.207$), although school is located in the strictly urban zone, close to the juncture of two streets with very heavy traffic. The increase of outdoor PM_{10} concentration is significantly correlated to the increase of indoor PM_{10} values (except for the school 9).

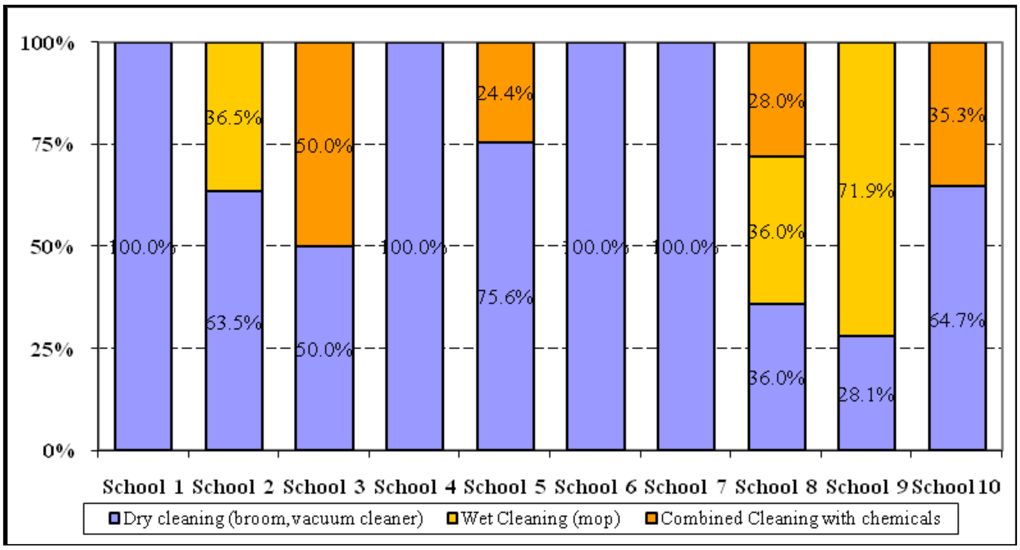

Figure 4: Distribution of exposed children by cleaning practice and school, combined with chemicals (bleach)

Cleaning practice in schools

Analyzing data on indoor PM_{10} from schools 1, 4, 6 and 7, we took into account that they were only cleaned by broom or vacuum cleaner (dry). Other schools were cleaned with different methods, simultaneously.

1. In school 3 ($p<0.01$) and school 5 PM_{10} IAQ concentration is significantly higher in the case of cleaning combined with bleach ($p<0.0001$) versus dry dust cleaning methods.
2. In school 8 PM_{10} IAQ concentration is significantly higher in the case of mop use ($p<0.02$) relating to dry cleaning methods, but not in the case of wet cleaning combined with the use of bleach.
3. In schools 9 and 10, measured PM_{10} IAQ concentration is proven to be significantly higher ($p<0.0001$) in cases of dry dust cleaning correlated to the PM_{10} IAQ values in other cleaning practice cases.

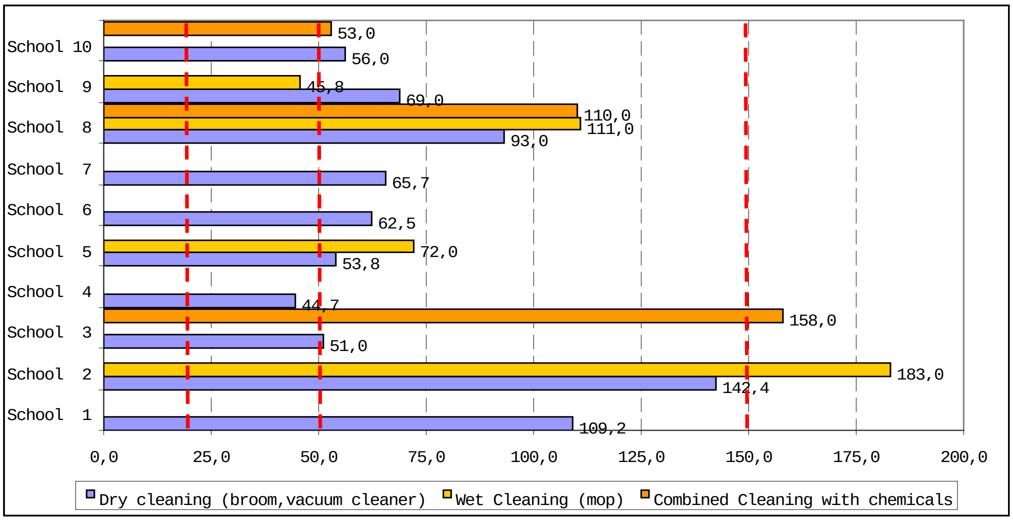

Figure 5. Distribution of indoor PM10 ($\mu g/m^3$) by schools and cleaning practice

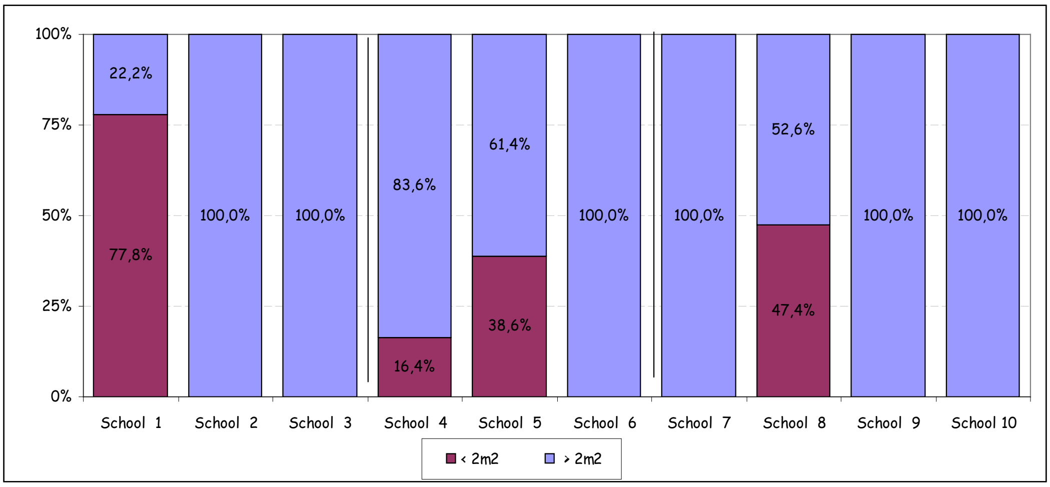

Figure 6. Child occupancy rate distributed by school (m^2/per child)

Classroom thermal comfort zone

Figure 6 presents distribution of the occupancy rate (according to ASHRAE) for each school, in m^2 per present child in the indicated classroom. Statistically significance is proved for the distribution of occupancy rate (m^2/per child), for each school, $\chi^2=340.70$, $p<0.0001$.

In school 1, which is located the suburb, and has all its measured values of IAQ PM_{10} above 50 $\mu g/m^3$, with an average PM_{10} IAQ of 109.16 ± 18.44, a significantly highest number of children, exposed to classroom indoor environment studies, is in a space with less than 2m^2 per child. Concerning the fact that there is no heavy traffic close to school, high occupancy rate, together with bad ventilation habits and cleaning practice could be the reason for such results.

In school 8 47.4% of pupils have less than 2m^2 of floor space per child, while all measured IAQ PM_{10} were above 50 µg/m^3. School 4 is worth mentioning, with only 16.4% pupils residing in the space with < 2m^2 per child, located in a broad urban zone of the city. IAQ PM_{10} values were below 50 µg/m^3, with average PM_{10} IAQ concentration being the lowest compared to other schools, 44.72 ± 12.48 µg/m^3.
On the contrary, school 3 has 100% PM_{10} IAQ measurements in space with > 2m^2 per child, located in a broader urban zone, with all measured values of IAQ PM_{10} beyond 50 µg/m^3. Average indoor PM_{10} concentration is 99.70 ± 45.62 µg/m^3. This school is cleaned mostly with the broom, and combined with chemicals use. A statistically significant difference is proven for the average PM_{10} IAQ concentration versus indicators of the classroom thermal comfort, K-W=446.697, p<0.0001.

Average indoor PM_{10} concentrations are lower in the classrooms where indicators of thermal comfort zone are satisfactory. In school 4, average indoor PM_{10} concentrations is lower in classrooms with achieved standards for indoor comfort zone indicators, with high statistical significance Z test = 6.540, p<0.0001, while in school 5 (Z=0.105, p=0.916) and school 8 (Z=1.614, p=0.107) and school 10 (Z=0.948, p=0.343) it is lower, but with not so high significance.

Table 5. Correlations between IAQ and OAQ by school

Correlation IAQ-OAQ PM_{10}	Aca Milosavljevic	Kosta Abrasevic	Nikola Tesla	Ivan Goran Kovacic	Skadarlija
	School 1	School 2	School 3	School 4	School 5
R	0.799**	0.756**	0.457**	0.956**	0.598**
significance	0.000	0.000	0.000	0.000	0.000
N	99	68	77	61	78
Correlation IAQ-OAQ PM_{10}	Stevan Sremac	Drinka Pavlovic	P.P. Njegos	Radojka Lakic	Ivan Gundulic
	School 6	School 7	School 8	School 9	School 10
R	0.744**	0.937**	0.725**	0.160	0.453**
significance	0.000	0.000	0.000	0.207/ns	0.000
N	77	53	76	65	82

Significantly highest mean values of IAQ PM_{10} concentration was measured in schools 1,2,3 and 8, were comfort zone was not achieved (p<0.001).

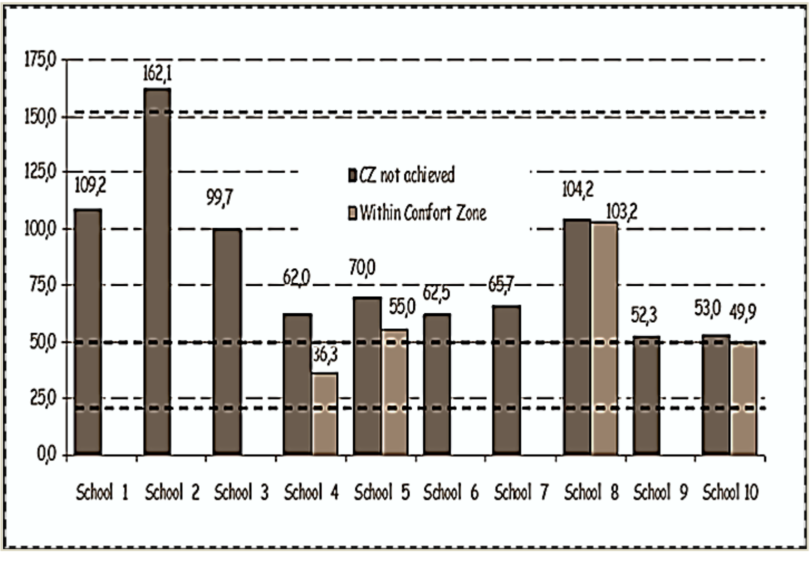

Figure 7. Indoor average PM_{10} levels related to the comfort zone indicators and by school child occupancy rate per school distribution (m^2/per child)

Table 6. Indoor PM_{10} average values related to the comfort zone indicators and by school

CLASSROOM THERMAL COMFORT ZONE by schools		IAQ PM_{10}			95% Confidence Interval	
		N	Mean	SD	Lower Bound	Upper Bound
„Aca Milosavljevic“	CZ not achieved	99	109.16	18.44	104.35	113.97
„Kosta Abrasevic“	CZ not achieved	68	162.12	41.93	156.31	167.92
„Nikola Tesla“	CZ not achieved	77	99.70	45.62	94.25	105.16
„Ivan Goran Kovacic“	CZ not achieved	41	62.00	0.00	51.29	72.71
	Comfort zone	20	36.29	3.39	28.82	43.77
„Skadarlija“	CZ not achieved	17	70.00	0.00	58.39	81.61
	Comfort zone	61	54.97	19.46	48.84	61.10
„Stevan Sremac“	CZ not achieved	77	62.47	23.59	57.01	67.92
„Drinka Pavlovic“	CZ not achieved	53	65.68	26.90	59.10	72.26
„Petar Petrovic Njegos“	CZ not achieved	50	104.24	8.53	97.47	111.01
	Comfort zone	26	103.15	8.64	93.76	112.54
„Radojka Lakic“	Comfort zone	64	52.31	11.22	46.33	58.30
„Ivan Gundulic“	CZ not achieved	13	53.00	0.00	39.72	66.28
	Comfort zone	69	49.91	6.68	44.15	55.68
Total	CZ not achieved	495	93.69	45.58	89.67	97.72
	Comfort zone	240	58.61	20.03	56.06	61.16

4. CONCLUSIONS

- Majority of surveyed children are exposed to high indoor PM_{10} concentrations (560/735; 76.2%).
- Maximum PM_{10} concentration values were measured in suburban schools, away from heavy traffic. Both indoor and outdoor PM_{10} levels are significantly higher in suburban schools, than in ones located in broader urban zone ($p< 0.0001$).
- The increase of outdoor PM_{10} concentration significantly affects increase of PM_{10} concentration in indoor air.
- A statistically significant difference exists for average IAQ PM_{10} concentrations vs. indicators of indoor thermal comfort zone ($p< 0.0001$); they are lower in the classrooms with indicators within the comfort zone.
- Depending on the school's geographic position, possible reasons for high IAQ PM_{10} values could be as fallows: vicinity of heavy traffic (strictly urban zone); solid fossil fuel combustion (rural suburbs); insufficient achievement of standards for indicators of thermal comfort zone: high occupancy rate in the classrooms (< $2m^2$ of space per child), high relative humidity (>75%) and indoor temperature beyond 23ºC; bad ventilation habits (keeping the windows closed most of the time).

5. ACKNOWLEDGMENTS

The financial support for the SEARCH project by the Italian Ministry for the Environment, Land and Sea is highly appreciated by the authors.

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4.3 COMPARISON OF PAHS LEVELS IN GAS AND PARTICLE-BOUND PHASE IN SCHOOLS AT DIFFERENT LOCATIONS

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ABSTRACT

The seasonal variation of PAHs and their partition between the gas and particulate-bounded phases in the indoor and outdoor air were determined in 4 schools in Serbia located at different representative locations. The sampling campaigns were conducted in indoor and outdoor ambient during one week at each school successively. Campaigns were conducted in schools during both, heating and non-heating, seasons in the period between December 2011 and June 2012. Significant seasonal variations of the gas and particle-bounded PAH (G-PAH, PB-PAH) concentrations were observed with higher levels during heating season. The highest total PAH values were associates with the gas phase in both sampling periods, especially in heating seasons. Most of the indoor-to-outdoor (I/O) ratios of PB-PAH for both seasons and G-PAH during heating season were less than 1.0 which indicated that the indoor PAHs were mostly from outdoor sources. The use of diagnostic ratio showed that vehicular emission and coal combustion are the major sources of PAHs in the ambient air at all sampling sites.

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a class of organic compounds produced by incomplete combustion processes of organic material such as biomass and fossil combustion, vehicular emissions, industrial processes etc. The PAHs consist of two or more fused benzene rings containing only carbon and hydrogen. They exist in the atmosphere in gas and particle-bound phase [1]. In general, 2 and 3 rings PAHs were common gas phase PAHs, whereas 5 and 6 rings PAHs formed most of the particulate phase. PAHs with 4 rings are partitioned between gas phase and particle phase. The phase distribution of the PAHs depends on the vapor pressure, the atmospheric temperature, the PAH concentration and the affinity for suspended particles [2]. Most PAHs are carcinogenic and mutagenic to human and causes serious demage to human health. The list of priority PAHs varies in different countries, but US EPA list of 16 priority PAHs is almost used [1]. Although many studies in Europe investigated concentrations, gas/particle partitioning, seasonal variation, source identification and relationship between indoor and outdoor concentrations of PAHs [2-5], measurements of PAHs and related studies in the Republic of Serbia are scarce and limited only to the PAHs in ambient air [6-9]. The aim of this paper was to investigate the seasonal variation of PAHs, their partition between the gas and particle-bound phases and identification the pollution sources using the PAHs diagnostic ratios in the indoor and outdoor air in 4 schools in Serbia which located at different representative locations in urban and rural areas in Serbia.

2. METHODOLOGY

The samples were collected in the indoor air of classrooms of primary schools and simultaneously in outdoor air in front of the windows on a balcony during December 2011 and Jun 2012. Four sampling sites were selected to match four types of representative locations : urban (school U), urban/traffic (school U/T), urban/industrial (school U/I) and rural (school R) (Fig. 1.). The urban site was school in Belgrade (44°49`N, 20°28`E) located in a densely populated residential area; the urban/traffic site was school in Zajecar (43°55`N, 22°18`E) located next to highly dense traffic street in the town centre; the urban/industrial site was school in Bor (44°05`N, 22°06`E) located 1 km west from the Copper Smelter Complex; and the rural village site was school in Zlot (44°00`N, 21°59`E) in area of low population density.

The sampling campaigns were conducted simultaneously indoor and outdoor during one week successively in each school in both heating and non-heating seasons. Samples were collected using the low volume sampler reference sampler Sven/LACKEL LVS3 (LVS) for 24h period. The air was drawn by LVS reference sampler (Sven/LACKEL LVS3) through a quartz filter (Whatman QMA, 47 mm) to collect total suspended particles (TSP) and then through polyurethane foam (PUF) to collect gas phase of pollutants. The sampling flow rate was 2.3 m^3/h (38 l/min). 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). The filters were baked at

900°C for 4 h to remove organic compounds and reduce blank values. The filters were weighed before and after sampling to determine the amount of particles captured. Air volume drawn by the sampler was used to calculate the mass concentrations of TSP and PAHs. After the sampling, filters and PUFs were extracted by aceton and hexane (1:1) for 8 h at 90°C using Soxhlet extraction for PUFs and microwave extraction for filters. Known quantities of internal standard were added to estimate the method recovery. PAHs were analyzed using Gas Chromatography coupled with Mass Selective Detector (Agilent GC 6890/5973 MSD) according to EPA Compendium Method TO-13A [10] with a DB-5 MS capillary column (30 m x 0.25 mm x 25 μm). Oven temperature program started on 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. Sixteen US EPA priority PAHs were determined: 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).

The calibration curves for the all 16 PAHs were obtained by spiking the seven know 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.

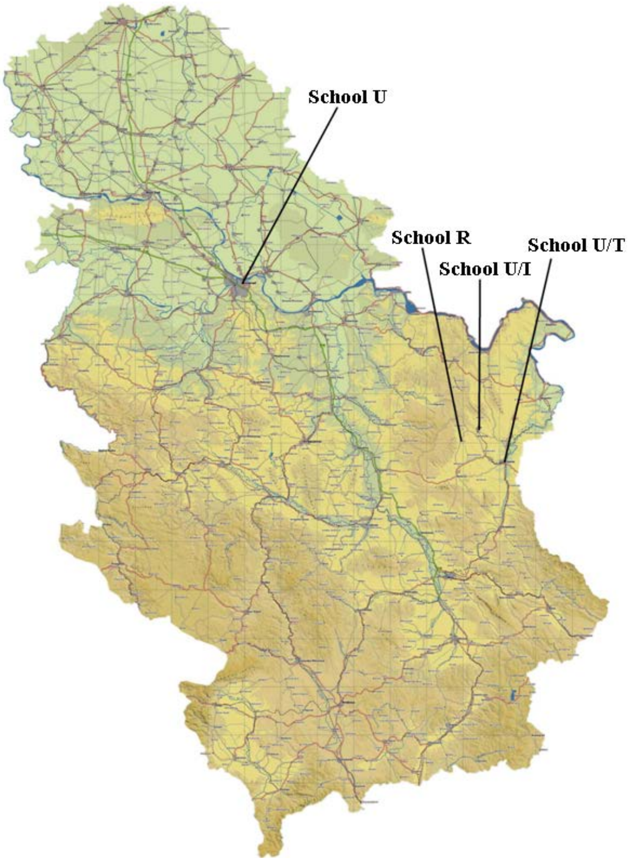


Figure 1. Map of the Republic of Serbia with the sampling sites marked

3. RESULTS AND DISCUSSION

Significant seasonal variations of gas (G) and particle-bounded (PB) phase PAH concentrations were observed with higher levels during heating season as shown in Table 1. The maximum of total PAH concentrations (median values), expressed as the sum of the individual PAH concentrations (ΣPAH), was highest in school U/T during heating season for both phases (51.37 ng/m^3 for PB and 370.57 ng/m^3 for G phase). The median value of PAHs in school U/T was higher than in the other schools mainly due to the high emissions from the traffic and coal-burning boilers for individual heating of dwellings. During non-heating period levels of PAHs ranged 1.25 - 5.39 ng/m^3 for PB phase and 35.66 – 266.18 ng/m^3 for G phase. The lower median values of PAHs in non-heating season were likely attributed to quick atmospheric dispersion of pollutants, more photo degradation and higher percentage in the air in G phase [1, 2].

The lowest median values of outdoor PAH concentrations during both seasons were in school U and school U/I. This is the oposite compared with values from avaliable literature data where the PAH values were less in rural areas than in urban areas [11-14]. This can be explained by the fact that the schools U and U/I are located in residental area without significant sources of PAHs in the surrounding. On the other hand, the school R is located in area where the dominant emission of PAHs originated from coal combustion, whileand around the school U/T the dominant emissions of PAHs originates from traffic and coal combustion for individual heating. The I/O ratios of ΣPAH for G phase were slightly above 1 for non-heating season at all sampling locations. That manifest the presence of sources of volatile PAHs in indoor environment. Most of the I/O ratios for PB phase for both seasons and G phase during heating season were less than 1.0 which indicated that the indoor PAHs were mostly from outdoor sources. The highest total PAH values were associates with the gas phase in both sampling periods, especially in heating seasons.

Table 1. The median values of ΣPAH concentrations (ng/m^3) in particle-bounde and gas phases at four sampling sites during heating and non-heating seasons (n = 5)

Sites	ΣPAH Particle-bound phase				ΣPAH Gas phase			
	heating		non-heating		heating		non-heating	
	indoor	outdoor	indoor	outdoor	indoor	outdoor	indoor	outdoor
School U	20.79	36.22	1.25	2.07	89.65	165.48	35.66	24.93
School U/T	51.37	131.04	3.67	6.69	370.57	886.11	109.18	85.34
School U/I	11.98	22.43	2.72	2.07	76.48	202.03	38.07	26.16
School R	33.94	70.04	5.39	9.17	221.33	374.68	266.18	123.15

The volatile PAHs (2 and 3 rings) were most abundant at all four schools in G phase (Fig. 2.). The highest presence of these PAHs was observed at the school U/I during both seasons. Volatile PAHs can be tracer for industrial combustion because the lower molecular weight PAHs, specifically Nap, were primarily dominated in industrial flue gases [1]. In all sampling sites 2-rings PAHs was dominant in outdoor air while 3-rings PAHs was dominant in indoor environment. This indicates an indoor sources of 3-rings PAHs (i.e. evaporation from building materials) and outdoor orgin of naphthalene [15]. The 4-rings PAHs (Fla, Pyr, BaA and Chy) were present in both phases. The highest presence of these PAHs was observed at schools U/T and R during heating season and they are probably associated with the coal combustion [16]. Indoor concentrations of 4-rings PAHs in both phases were lower than outdoor, which indicated that outdoor sources of these PAHs were prevailing. The heaviest PAHs (5 and 6 rings), which are usually asociated with vehicle emissions, was observed at all sampling sites with higher presence in indoor environment during heating season. They were dominant in the PB phase, while in the G phase they are generally not detected. The reason for such results was possibly related to air exchange rates and daily activities. Their outdoor concentrations during non-heating season were higher than indoor.

The diagnostic ratios of PAHs may be used to identify the origin of PAHs in ambient air. In this study, diagnostic ratios were calculated between outdoor G and PB phases PAHs during both season as shown in Table 2. The ratios of combustion PAHs to the total PAHs (CPAH/∑PAH) can be used to identify combustion sources. A CPAH/∑PAH ratios were higher in PB phase than those in G phase during both seasons at all sites. This values were close to unity for PB phases, which indicated that coal combastion potential source of particle-bound PAHs [17,18]. Only at school U/I value of this ratio in PB phase in non-heating season was 0.75, which suggested that diesel engine were dominant PAHs source. The ratio values of Flu/(Flu+Pyr) were determined to be <0.5 at all sampling sites in PB phase, which are similar to the values for petrol emissions, except in school U/I during non-heating season where the value was 0.57 and indicates diesel emissions [1,18]. A Flu/(Flu+Pyr) ratios for G phase were >0.5 at all sites. The ratio of Ant/(Ant+Phe) >0.1 was associated with combustion processes [1]. The values of this ratio were higher for PB phase and higher in heating than those in non-heating period. The lowest values of this ratio recorded in the schools U and U/I and can be explained by the fact that the schools are located in the vicinity of residential buildings which are heated by district heating system. The similar values were obtained for G and PB phases for Fla/(Fla+Pyr) ratios. The value for total (PB + G) Fla/(Fla+Pyr) ratios was higher at school U/I especially during non-heating season and suggests the emission from grass, wood and coal combustion [18]. The values of BaA/(BaA+Chy) ratios indicate traffic emissions particle-bounded PAHs during non-heating season at schools U and U/T [11], and mixture source of traffic emissions and coal/wood combustion during heating season at all sites [2]. The lowest recorded value of these ratio in the school U/I in heating season and may be explained that in addition to the traffic emission there is another source of PAHs.

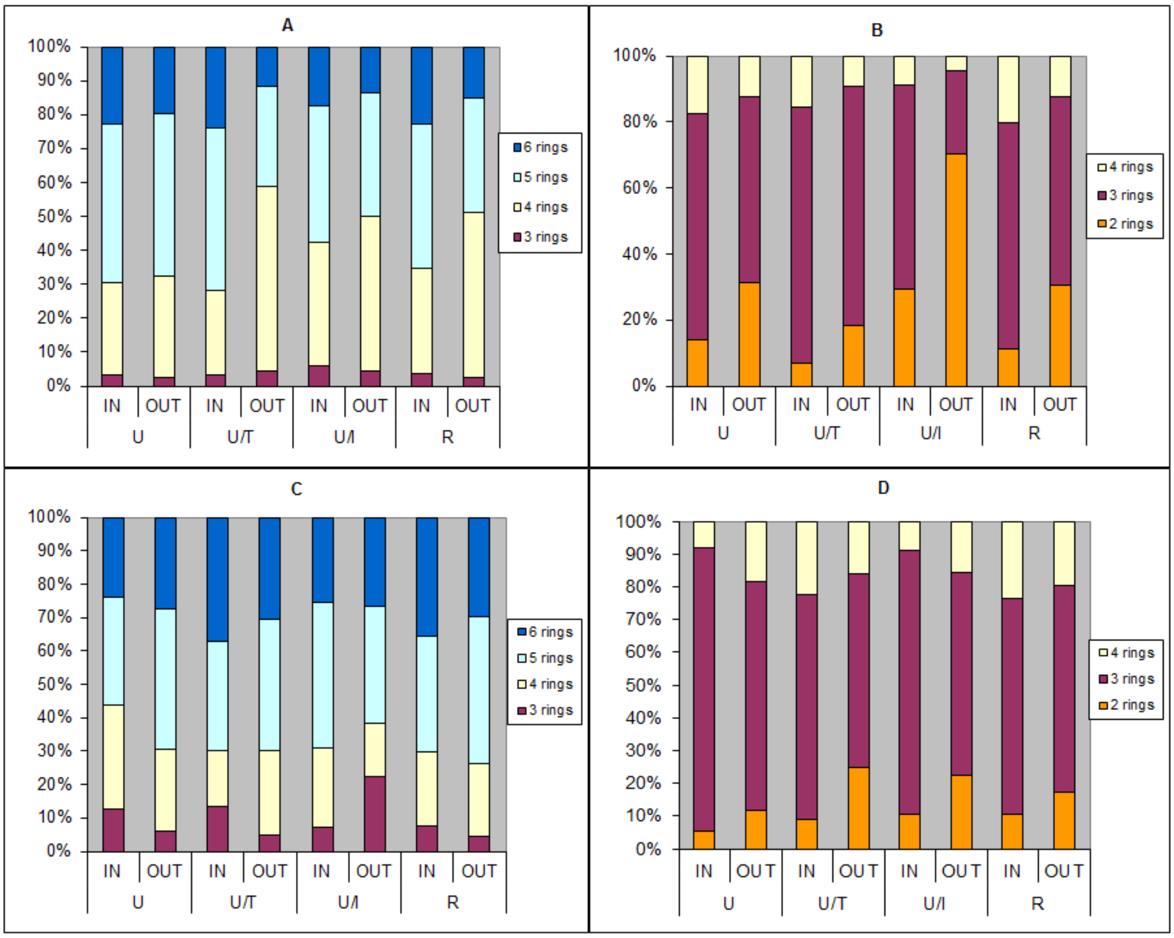


Figure 2. Ring number distribution of PAHs in schools (U-urban; U/T-urban/traffic; U/I-urban/industrial; R-rural; IN-indoor; OUT-outdoor): (A)-PAHs in particle-bound phase during heating season; (B)-PAHs in gas phase during heating season; (C)-PAHs in particle-bound phase during non-heating season; (D)-PAHs in gas phase during non-heating season.

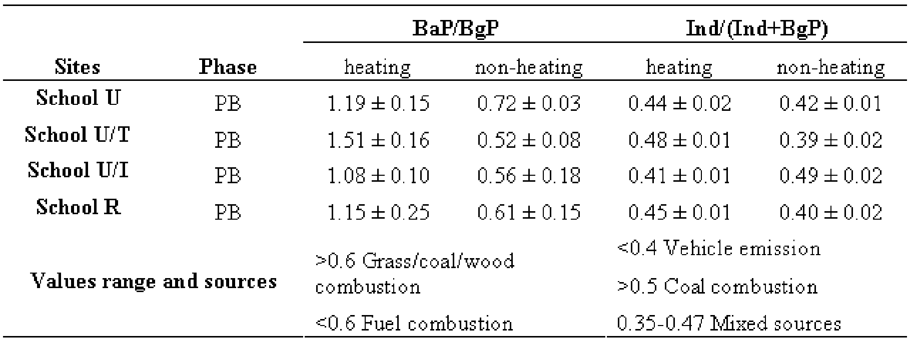
Table 2. Diagnostic ratios of PAHs (mean ± standard deviation) in outdoor PB and G phases at four sampling sites during heating and non-heating seasons.

		CPAH/ΣPAH		Flu/(Flu+Pyr)		Ant/(Ant+Phe)		Fla/(Fla+Pyr)		BaA/(BaA+Chy)	
Sites	**Phase**	heating	non-heating	heating	non-heating	heating	non-heating	heating	non-heating	heating	non-heating
School U	PB	0.95 ± 0.00	0.90 ± 0.05	0.06 ± 0.02	0.20 ± 0.09	0.22 ± 0.06	0.10 ± 0.05	0.48 ± 0.01	0.50 ± 0.07	0.39 ± 0.02	0.33 ± 0.03
	G	0.13 ± 0.04	0.18 ± 0.07	0.65 ± 0.01	0.71 ± 0.12	0.08 ± 0.01	0.09 ± 0.02	0.57 ± 0.01	0.55 ± 0.03	0.33 ± 0.04	0.44 ± 0.01
	Total	0.28 ± 0.05	0.24 ± 0.06	0.60 ± 0.02	0.70 ± 0.11	0.08 ± 0.01	0.04 ± 0.05	0.55 ± 0.01	0.54 ± 0.03	0.39 ± 0.03	0.39 ± 0.04
School U/T	PB	0.94 ± 0.02	0.90 ± 0.04	0.12 ± 0.04	0.24 ± 0.17	0.37 ± 0.17	0.14 ± 0.03	0.48 ± 0.02	0.42 ± 0.01	0.46 ± 0.01	0.36 ± 0.02
	G	0.09 ± 0.02	0.15 ± 0.04	0.72 ± 0.06	0.64 ± 0.12	0.17 ± 0.01	0.07 ± 0.02	0.56 ± 0.01	0.52 ± 0.02	/	0.40 ± 0.03
	Total	0.20 ± 0.03	0.21 ± 0.07	0.64 ± 0.06	0.63 ± 0.11	0.17 ± 0.01	0.07 ± 0.02	0.54 ± 0.01	0.52 ± 0.02	0.46 ± 0.01	0.38 ± 0.02
School U/I	PB	0.94 ± 0.01	0.75 ± 0.19	0.07 ± 0.02	0.57 ± 0.25	0.26 ± 0.08	0.08 ± 0.01	0.47 ± 0.03	0.60 ± 0.13	0.34 ± 0.05	0.43 ± 0.09
	G	0.05 ± 0.02	0.16 ± 0.05	0.72 ± 0.06	0.70 ± 0.11	0.09 ± 0.02	0.09 ± 0.01	0.60 ± 0.01	0.60 ± 0.08	/	0.41 ± 0.06
	Total	0.13 ± 0.03	0.21 ± 0.04	0.63 ± 0.05	0.70 ± 0.11	0.10 ± 0.02	0.09 ± 0.01	0.56 ± 0.03	0.60 ± 0.08	0.34 ± 0.05	0.44 ± 0.08
School R	PB	0.95 ± 0.00	0.92 ± 0.03	0.18 ± 0.06	0.12 ± 0.10	0.21 ± 0.09	0.15 ± 0.06	0.45 ± 0.01	0.39 ± 0.04	0.42 ± 0.03	0.38 ± 0.04
	G	0.15 ± 0.07	0.19 ± 0.04	0.64 ± 0.13	0.53 ± 0.15	0.15 ± 0.06	0.11 ± 0.03	0.54 ± 0.01	0.52 ± 0.02	0.39 ± 0.02	0.48 ± 0.12
	Total	0.27 ± 0.06	0.25 ± 0.07	0.58 ± 0.10	0.52 ± 0.15	0.15 ± 0.01	0.11 ± 0.03	0.52 ± 0.02	0.51 ± 0.02	0.41 ± 0.03	0.44 ± 0.10
Values range and sources		0.73 Gasoline engine 0.78 Diesel engine 0.87 Coal combustion ~1Combustion		<0.5 Petrol emissions >0.5 Diesel emissions		<0.1 Pertogenic >0.1 Pyrogenic		<0.4 Petrogenic 0.4-0.5 Fossil fuel combustion >0.5 Grass, wood, coal combustion		>0.35 Coal combustion 0.2-0.35 Vehicular emission 0.43 Wood combustion	

CPAH- total concentration of Fla, Pyr, BaA, Chy, BbF, BkF, BaP, Ind, BgP.

Because in the G phase 5 and 6 rings PAHs is not detected the ratios BaP/BgP and Ind/(Ind+BgP) are taken only for PB phase (Table 3.). The ratios of BaP/BgP indicated emissions mainly from coal combustion during heating season and fuel combustion during non-heating season at all sites [19]. Without site difference, the values of Ind/(Ind+BgP) ratios indicate mixed sources of PAHs at all sites and traffic emissions at school U/T in non-heating season [19].

Table 3. Diagnostic ratios of PAHs in outdoor PB phase at four sampling sites during heating and non-heating seasons



Sites	Phase	BaP/BgP		Ind/(Ind+BgP)	
		heating	non-heating	heating	non-heating
School U	PB	1.19 ± 0.15	0.72 ± 0.03	0.44 ± 0.02	0.42 ± 0.01
School U/T	PB	1.51 ± 0.16	0.52 ± 0.08	0.48 ± 0.01	0.39 ± 0.02
School U/I	PB	1.08 ± 0.10	0.56 ± 0.18	0.41 ± 0.01	0.49 ± 0.02
School R	PB	1.15 ± 0.25	0.61 ± 0.15	0.45 ± 0.01	0.40 ± 0.02
Values range and sources		>0.6 Grass/coal/wood combustion <0.6 Fuel combustion		<0.4 Vehicle emission >0.5 Coal combustion 0.35-0.47 Mixed sources	

Taking into account the diagnostic ratios, clear differences in the origin of PAHs at school U/I were recognized in comparison with the other schools. This points out that the dominant contribution source was diesel engine. This is related to the use of oil as fuel in the manufacturing and processing of copper [20]. The same ratio trends is result of the atmospheric reactions and should be used with the caution because it is often difficult to determine a difference between some potential sources. As show above, the values of diagnostic ratio are different for G and PB phase and should be used together into account. Many studies focus on the calculation of diagnostic ratios only for PB phase, but it is wrongly because PAHs are partitioning and repartitioning between G and PB phases [1,18].

4. CONCLUSIONS

The PAHs levels in 4 schools, 3 in urban and 1 rural area, were monitored during heating and non-heating seasons. PAH seasonal variations and distributions between G and PB phase were investigated. Significant seasonal variations of G and PB phase were observed with higher levels during heating season. The median values of ΣPAH concentrations in G phase were much higher then in PB phase.

Based on the ring number distribution and diagnostic ratios, it was found two main sources of PAHs at all sites that were traffic emission and coal combustion. Vehicular emissions were the major source during non-heating season, while coal combustion was the major source during heating season. Significant differences between diagnostic ratios for G and PB phase were shown. Only the diagnostic ratios at school U/I were showed significant deviation compared to other schools and suggest diesel engine as the main source of PAHs that have been related to the use of oil during the manufacturing and processing of copper.

5. ACKNOWLEDGEMENTS

This paper is supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia projects: III42008 and III41028 (2011-2014).

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4.4 CHARACTERIZING PARTICULATE POLLUTANT IN AN ENCLOSED MUSEUM IN SHANGHAI, CHINA

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ABSTRACT

The first simultaneous measurements of particle number concentration, particle mass concentration, water soluble organic carbon, organic carbon, element carbon, morphology and main elemental properties conducted in a museum located in Shanghai central downtown area were reported and analyzed here. The impact of level, particle size and flooring on particle characteristics were investigated. Size fractionated particle number concentration in display halls belong to the same level exhibited similar daily variation. The results showed particles in the range of 0.3-0.5 μm was one of the important contributors due to that flooring, carpet easily caused the resuspension of particles with large size. In addition, a series of suggestions were proposed according to the corresponding findings.

1. INTRODUCTION

A number of studies have concluded that particulate matter capable of causing soiling due to large particles are abrasive and may cause surface scratching [1-4]. Such particles are in the large size span and heavy enough to settle in still air. In comparison to small size particles remain suspended in air until being trapped or held down on certain surfaces caused by electrostatic attraction. Particles in the small size span can enter display cases, deposit on objects, and thus soil the surface. In turn more serious damage could occur when chemical reactions happens involving gases and the acid components of the deposited particles, which will affect all acid-sensitive materials [5]. Normally such particles are hygroscopic to attract water and cause corrosion of metals. They may also contain traces of metals such as iron to speed up the deterioration of organic materials. High level of salt crystals in the air affects coastal areas as well. This is because that salt absorbs water from the air, creating droplets with high salt concentrations [7], so that corrode most unprotected metals. In addition, new concrete emits alkaline particles as well [6]. They darken oil paint films and decolour some dyes and pigments. In addition, the C-rich component, are regarded as one of the most harmful and dangerous type for the valuable historical objects, owing to they can easily stick to the surfaces on account of the strong adhesive properties [8]. Therefore it is essential to document the spatial and temporal variability of particles as well as the component and investigate its related factors on its characteristics exhibited inside the museum.

A limited number of particulate pollutant have been identified inside museums in several countries: A daytime and nighttime total suspended particulate matters were collected in Emperor Qin's Terra-Cotta Museum, China [9], they concluded that both size distributions and particle types were impacted by visitor significantly; The monitoring conducted in Plantin-Moretus Museum, Belgium concluded S-rich particles were frequently observed indoors in summer compared to that Ca-rich and Ca-Si rich particles found in winter [10]; It was observed in the museum in Goudi, urban area of Athens that resuspension lead to fine and coarse particles' increased by a factor of 30 and 80 times, respectively [11]; The measurement conducted in archaeological museum of Thessaloniki, N. Greece found out thatincreased PM2.5 acidity was observed indoors due to the presence of partially neutralized ammonium sulfate [12]; The study on single particle analysis showed that the relative abundance of carbon-rich particles inside the Royal Museum of Fine Arts, Belgium was greater than outside [13]; In the Correr Museum, Italy, the majority of samples from both campaigns appeared to be composed of six to eight different particle types from which the Ca-rich particles and the aluminosilicates as well as organic material was the most important contributors [14]; The sampling in Royal Museum of Wawel Castle, Poland [15] also concluded that the number of museum visitors was related to the increase of the TSP concentration as well as the particle component.

In this study, monitoring the indoor particulate matter of a museum located in Shanghai CBD was conducted. This study aimed to investigate the particle characteristics exhibited inside the museum as well as to determine the emission sources.

2. METHODOLOGY

2.1 Study location and particulate matter collection

A museum in Shanghai was chosen as the sampling location between September, 2009 and October, 2010. The museum was selected because it may provide a wide representation of pollutant sources, as located in Shanghai CBD, closing to the intersection of two elevated roads. There are tens of origin stations and transfer stations of buses surrounding the museum. The open time of the museum was from 9:00 to 16:50. The museum covered 39,200 m^2 in total, in which, the display area accounted for 12,000 m^2. It should be stressed that the whole museum was maintained at the constant temperature and humidity throughout the year. A total of 9 display halls and 1 lobby were investigated in this study as follows: Ancient Chinese Bronze hall (BR), Ancient Chinese Sculpture hall (SC) and the lobby on ground level, Ancient Chinese Ceramics hall (CE) situated on level 2, Chinese Calligraphy Archive (CA), Ancient Chinese Painting Gallery (PA) and Ancient Chinese Imperial Seal hall (SE) located on level 3. Ancient Chinese Jade hall (JA), Ancient Chinese Coin hall (CO), and Chinese Ming and Qing Furniture hall (FU) belonging to level 4. Regarding each display halls, the particle number concentration was continuously sampled from the open time to midnight. Particle mass concentration was monitored in the main hall on ground level for 7 days.

2.2 Instruments and pollutants.

2.2.2 Measurement of particle number concentration. The sampling of particle number concentration was performed using laser particle counters (LASAIR II 310B) [16] with a flowrate of 28.3 L and cut sizes of 0.3, 0.5, 1.0, 3.0, 5.0, 10.0 μm. The data was logged at a time interval of 60 sec.

3. RESULTS AND DISCUSSION

3.1Particle number concentration

The impact of level

Fig.1 illustrates the average half-hourly particle number concentration varied in 6 size intervals obtained inside the9 display halls, respectively: 0.1-0.3, 0.3-0.5, 0.5-1.0, 1.0-3.0, 3.0-5.0 and 5.0-10.0 μm. We observed that particles ranging between 0.1 and 0.5 μm dominated the particle number concentration and nearly maintaining constant values throughout the entire monitoring period. The particle within this range was account for the contribution of ambient air entering from ventilation system. Comparatively, particles in the other 3 size intervals, in addition to the specific feature appeared in all display halls on the same level, all the curves increased again during the time period of 19:00-21:00, which was due to the cleaning time in the museum. It can be observed that for the same floor, particle number concentration presented the similar pattern for all size intervals, respectively. The museum is closed at 16: 50, therefore, the staff would remind tourists to leave at the time about 30 minutes early. It was found large size particle initiated dropping at about 16:20, which concluded large size particles were affected by tourists significantly, especially particles within the size range of 1.0~10.0 μm.

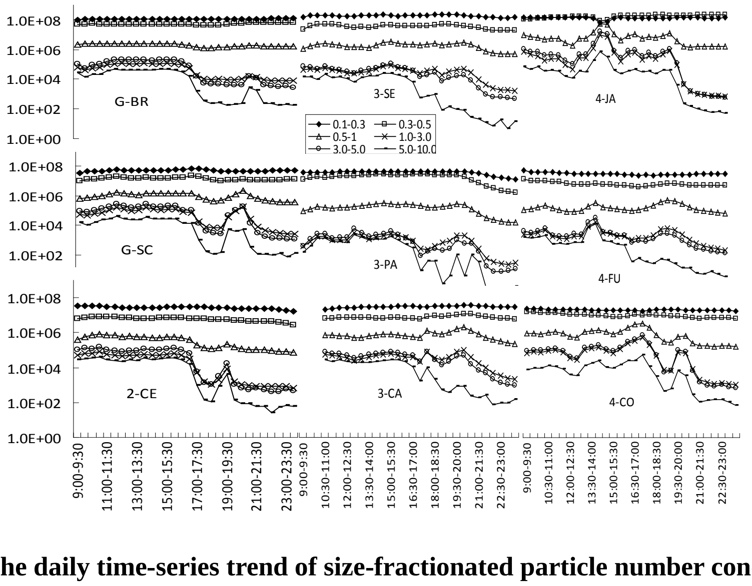

Figure 1. The daily time-series trend of size-fractionated particle number concentration

The impact of particle size

The total particle number concentration in each display hall was given in Fig.2, exhibiting the identical trends. The contribution of the size-fractioned particles was further investigated to find out particles ranging from 0.1 to 0.5 µm dominated over 95 % of the total particle number concentration. The percentage of particles in this range was represented using column bars in Fig.2. We found that greater particle number concentration occurred in the display hall of BR, PA, JA and CO with the percentage value of $PNC_{0.3\text{-}0.5}$ 31.6 %, 35.5 % , 52.3 % and 30.9 %, respectively. Accordingly, it can be observed that the larger percentage of the particles in the range of 0.3-0.5 µm, the higher particle number concentration appeared in the corresponding display hall. The results of further analysis of the trace metal contained in $PN_{0.3\text{-}0.5}$ showed that the mass concentration of S accounted for 16.26 % of the total mass, suggesting that their precursors were possibly released from vehicle emissions. The ratio of Al and Fe existing in $PN_{0.3\text{-}0.5}$ was calculated to further evaluate the likely source, which was about 0.13. This was an enhanced proof for $PN_{0.3\text{-}0.5}$ originating from vehicle emissions due to that the AL/Fe value in $PN_{0.3\text{-}0.5}$ produced from anthropogenic activity was less than 1 but about 1.9 for the $PN_{0.3\text{-}0.5}$ in soil. Based on above, we would suggest high efficiency particulate air (HEPA) filter installing for the air-conditioning system in museums.

The impact of flooring

Aiming to further investigating the impact of flooring and tourists' movements on the particle characteristics, the particle number concentration of each size interval monitored in each display hall was summarized, shown as Fig.3. Ferro et al. concluded that submicron particles only contribute to less than 1 % of the suspended particle [24], and considering the $PN_{0.1\text{-}0.3}$ and $PN_{0.3\text{-}0.5}$ nearly kept stable throughout the daily sampling period, which meant nearly no influence from flooring as well as tourists' movement, so that only the particles in the size range from 0.5 to 10 µm were plotted for investigation of the floor impact. A substantial greater number concentration could be observed in JA and CO. In addition, BR, SC and CE exhibited relatively higher particle number concentration for most cases (Except $CE_{0.5\text{-}1}$ and $SC_{5\text{-}10}$). To give an explicit interpretation, we summarized the flooring in each display hall, listed in Table 1.

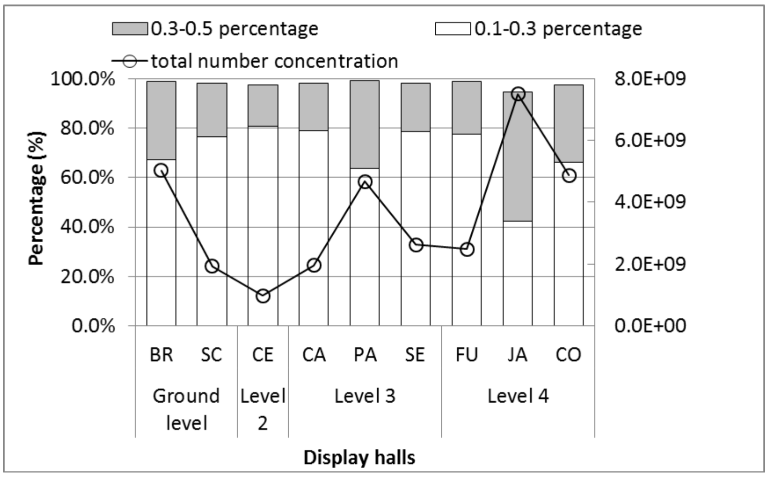

Figure 2. The total particle number concentration of each display hall and the percentage of particles in the size range of 0.1-0.3 and 0.3-0.5µm

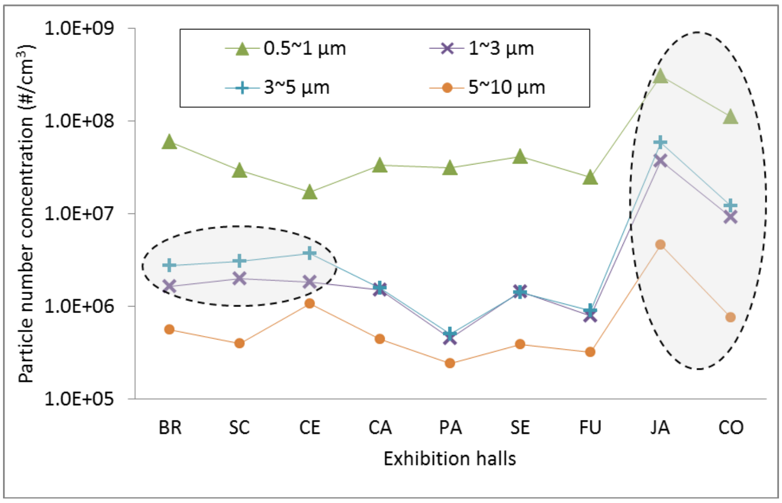

Figure 3. Size-fractionated particle number concentration in each display hall

Table 1 illustrated that both JA and CO were covered with block carpet on the floor, o BR, SC and CE were decorated with thick carpet.

Table 1 Flooring of each display hall

Display halls	**BR**	**SC**	**CE**	**CA**	**PA**	**SE**	**FU**	**JA**	**CO**
Flooring	Thick carpet	Thick carpet	Thick carpet	Solid wood	Solid wood	Solid wood	Solid wood	Block carpet	Block carpet

Resuspension rate is the net result of adhesion forces and removal forces acting concurrently on particles deposited on a surface. Regarding the adhesion force, the Van der Waals force between a particle and a nearby surface (flooring in this study) is decided by the Hamaker constant [25] and the separation distance between the particle and the surface. The greater the Hamaker constant, the stronger the Van der Waals force, and it is oppositely that the greater the separation distance, the smaller the Van der Waals force. The Hamaker constant between particles and wood is larger compared to that between particles and carpet, but opposite result for the separation distance. Consequently, weak van der Waals force existing between carpet and particles was found in this study. Regarding the removal force, it was concluded that occupant thermal plume may play a significant role in transporting pollutants from floor level to the breathing zone [26, 27]. The friction force between the tourists' shoes and the carpet would get the floor charged in comparison with solid wood, for this reason, likely to cause an enhanced thermal plume microenvironment, leading to particle resuspension. Generally, museums use carpet for the flooring considering its feature of good appearance and sound insulation, however, such flooring easily results in the resuspension of particles in space. Therefore, intense physical activities of visitors inside museum cause either resuspension of previously deposited particles. Therefore human activity seems the most important factor accounting for the particles in the size range of 0.5 and 10 μm. We would advise using less carpet inside museums or wearing shoe covers has to be requested to tourists prior to entering.

4. CONCLUSION

Investigating the characteristics of airborne particles inside museum has become increasing crucial. This study for the first time conducted a multiple-parameter monitoring in a museum located in Shanghai CBD. The impact of level, particle size and flooring on particle characteristics were analyzed. It was found that particles in each display hall on the same level exhibited similar patterns of daily time-series trend. Particles in the size range of 0.3-0.5 μm dominated the largest amount of number concentrations. The flooring of carpet easily caused the resuspension of particles of large size, harming to the heritage conservation as well as human health.

ACKNOWLEDGEMENTS

This work is supported by the Fundamental Research Funds for the Central Universities (WB1113005), scientific research innovation fund of Shanghai education Commission (12ZZ054) and also supported by China Science and technology support program (2010BAK67B15). The author would like to thank our

colleague and staff from the museum for their contribution to this work.

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4.5 CHARACTERIZATION OF WATER-SOLUBLE ORGANIC CARBON IN $PM_{2.5}$ AND IMPLICATIONS FOR SOURCE IDENTIFICATION

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ABSTRACT

Particulate matter (PM) with an aerodynamic diameter ≤2.5μm (PM2.5) was collected from Sept. 2008 to July, 2009 in Shanghai, China. Organic carbon (OC), elemental carbon (EC), water-soluble organic carbon (WSOC) and ionic compositions in PM2.5 were measured. The WSOC concentration ranged from 1.11±0.033 to 12.42±0.37μg/m3 and was the highest in winter and lowest in spring WSOC/OC ratios ranged from 0.21 to 0.85, but the average value approximated to 0.45 and changed less with seasons. Strong correlations of WSOC to TC , OC, EC, OC1, and OC2 were found. The volatile-OC was 36 % of the total OC with no significant seasonal differences. According to comparison with SOC, char-EC/soot-EC and ionic compositions, it was implied that the WSOC at sampling site originated from both primary sources and gas-particle chemical transformation. VOCs control in Shanghai should be considered to reduce ground ozone level as well as to decrease aerosol concentrations simultaneously.

1. INTRODUCTION

$PM_{2.5}$ has been investigated worldwide because it has been recognized as an important factor in relation with human health as well as the deteriorative air quality and visibility. The scattering and absorption of solar radiation, together with cloud properties are highly sensitive to the tiny changes in the chemical composition of $PM_{2.5.}$ Carbonaceous aerosols, originating mainly from anthropogenic activities, forest fires and biomass burning, are a major components of atmospheric particulate matter, accounting for up to 70% of the $PM_{2.5}$ mass (Jacobson et al., 2000). Aerosol carbon is commonly classified as organic carbon (OC) or elemental carbon (EC).

It has been found that the constituent OC features significantly chemically complex. Their sources and formation mechanisms are not completely understood. As an important fraction of secondary organic aerosols (SOA), water-soluble organic compounds (WSOC) are receiving increasing attention. This is because WSOC could alter the hygroscopic properties of ambient aerosols to cause them to transform into more effective cloud condensation nuclei (Huang et al., 2006). WSOC typically accounts for 40%～60 % of the mass of organic matter and the highest WSOC/OC ratio could exceed 90 %. The amount of WSOC in particles is comparable to the amount in inorganic ions occurred in some rural areas (Krivácsy et al., 2001). Both primary and secondary sources contribute to aerosol WSOC (Kumagai et al., 2009). Identified primary source includes biomass burning (Mayol-Bracero et al., 2002) and vehicle emissions (Ruellan et al., 1993), and in comparison to secondary formation of WSOC it has been regarded as the dominant source. Despite that WSOC distribution pattern varies with locations, seasons and meteorology parameter, WSOC concentration has been observed to be relatively similar in three sites (Amsterdam, Barcelona, and Ghent) among different seasons (Viana et al., 2007), which has also showed a dependence on meteorological parameters including air temperature, wind speed and wind direction (Kumagai et al.,2009). Both the origin and composition of WSOC has not been thoroughly understood (Snyder et al., 2009).

In this study, the seasonal characteristic of carbonaceous aerosols and WSOC in $PM_{2.5}$ has been investigated, and the source identification has been discussed by analyzing the composition of OC and its correlation to WSOC.

2. METHODS

2.1 Sampling

$PM_{2.5}$ samples were collected on the top of a lab building of the East China University of Science and Technology in Shanghai (31.08°N, 121.25°E) from September 2008 to July 2009, which collected on 47 mm quartz-fibers (Whatman QMA) at a flow rate of 5 L/min with a portable low-volume $PM_{2.5}$ sampler. The quartz filters were pre-fired at 600℃ lasting for 4 hours prior to sampling. The mass concentration of $PM_{2.5}$ was determined by weighting the filters (±0.01 mg) in a micro analytical balance in the condition of controlled RH (50% ±5%) before and after exposure. The samples were then stored frozen (-18℃) until further analysis. Meteorological data was obtained from http://www.wunderground.com/history .

2.2 Chemical analysis

2.2.1 OC and EC measurements

A portion of each sampled filter was analyzed for OC/EC using a Thermal/Optical Carbon Analyzer (DRI Model 2001, USA) operated in compliance with the IMPROVE protocol (Cao et al., 2004). The protocol involves heating a 0.526 cm^2 punch aliquot of a sample quartz filter stepwise at temperatures of 120 ℃ (OC_1), 250 ℃ (OC_2), 450 ℃ (OC_3), and 550 ℃ (OC_4) in a non-oxidizing helium atmosphere, respectively, and 550 ℃ (EC_1), 700 ℃ (EC_2), and 800 ℃ (EC_3) in oxidizing atmosphere of 2% oxygen in a balance of helium, respectively. The amount of carbon measured after oxygen is added until the reflectance achieves its original value is reported as optically detected pyrolized carbon (OP). The IMPROVE protocol defines TC is defined as OC+EC, OC as $OC_1+OC_2+OC_3+OC_4+OP$ and EC as $EC_1+EC_2+EC_3-OP$. Han et al. (2007) defined EC1-OP as char-EC and EC2 + EC3 as soot-EC. To evaluate the contribution of VOCs to carbonaceous aerosols, we defined OC1+OC2 as Volatile-OC and OC3+OC4+OP as Non-volatile-OC. The TOR methodology is incapable of measuring elements, other than carbon, such as oxygen, nitrogen, sulfur, hydrogen, chlorine, and other species associated with the organic mass (OM). The aerosol organic mass-to-organic carbon ratio (OM/OC) has been widely used in the past decades, but its application still remains controversial. A factor of 1.4 is usually adopted (Countess et al., 1980), while Turpin and Lim (2001) recommended values of 1.6 ±0.2 and 2.1 ± 0.2 for urban and rural areas, respectively. Considering the sampling site of this study was in urban area and there was no significant heating necessity even in the winter of Shanghai, a factor of 1.6 was adopted in this study.

The analyzer was calibrated with the known quantities of CH_4 every day. Average field blanks were 1.85, 0.53, 0.40 and 0.13 μg/m^3 for OC, EC, char-EC, and soot-EC, respectively. The duplicate differences were <5 % for TC, and <10 % for OC, EC, volatile-OC, char-EC, soot-EC, Volatile-OC and Non-Volatile-OC, respectively.

2.2.2 WSOC measurement

One-quarter of the sample filter was placed into 15 mL ultrapure water for extraction of WSOC. Samples were ultrasonically extracted for 30 min, and then extracts were filtered (pore size, 0.45μm) to remove any suspended particles. WSOC concentration was determined by a Total Organic Carbon analyzer (Liquid TOC Elementar, Germany).

2.2.3 Inorganic composition analysis

One-quarter of the sample filter was placed into 15mL ultrapure water to be pretreated as the same steps of WSOC measurement. The extraction solution was drawn to Ionic Chromatograph (IC) analyzer for ion analysis. Anions (SO_4^{2-}, NO_3^-, Oxalate) were measured with IC analyzer (Dionex ICS3000, Dionex Corp., USA) and cations (K^+, NH_4^+) were measured with an chromatograph (DX-120, Dionex Corp., USA). The duplicate differences were smaller than 3%.

3. RESULT AND DISCUSSION

3.1 Seasonal variation of OC, EC and WSOC

Fig. 1 shows the concentration of OC, EC and WSOC in different seasons during the experimental period. WSOC concentration ranged from 1.11 to 12.42μg/m^3, with the average value of 5.82±3.55, 8.34±2.95, 3.41±1.63 and 5.28±2.79 in fall, winter, spring, and summer, respectively. The concentration was higher than the results reported in the past decade, such as 1.2-3.5 μg/m^3 in Maebashi of Japan (Kumagai et al, 2009), 1.0-1.9 μg/m^3 in Holland (Viana et al., 2007) and 1.58-2.75 μg/m^3 in Gosan of South Korea (Yang, et al; 2004). During sampling period, the average WSOC was lowest in spring and largest in winter. Although the comprehensive seasonal variation pattern needs more data to support, it implies that WSOC might not predominantly depended on temperature and might result from complex conversion reactions combined with meteorological conditions. When the ambient air temperature was higher in summer and fall, WSOC accordingly increased compared with that in the spring. It can be theoretically explained if WSOC is determined by photochemical conversion. However, it was not observed that lower level happened with lower temperature in winter. This could be associated with different formation mechanisms. Higher temperature can accelerate secondary formation of WSOC but low temperature helps to the direct condensation of gaseous WSOC on particles. The composition of WSOC might be different but the data therein the paper is too limited to reveal the formation mechanism. Kumagai et al. found the similar results in Maebashi and Akagi of inland Japan (Kumagai et al., 2009), but the seasonal variation characteristics might be influenced by the wind direction or rainfall. As shown in Fig.1, the daily WSOC fluctuated greatly due to weather conditions. WSOC in the period of Sept 10 -16, 2008 was not as high as expected due to heavy rain occurred within the time.

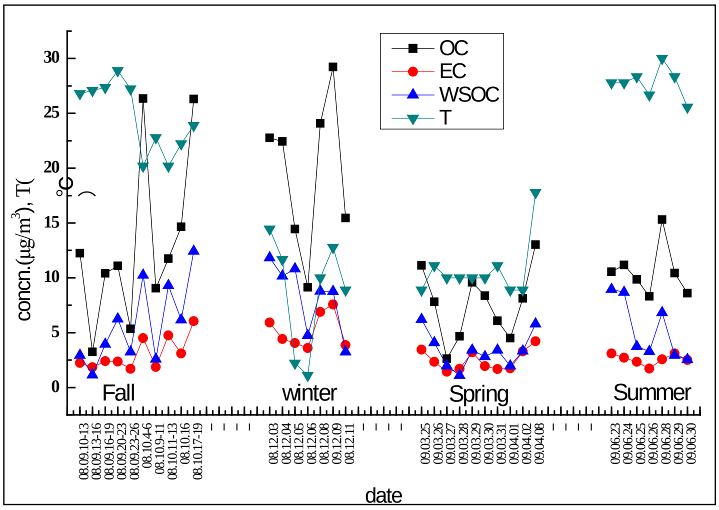

Fig. 1 The variation of OC, EC, and WSOC concentration sampled in 2008 and 2009. T is the ambient air temperature.

3.2 Relationship between WSOC and carbonaceous composition

3.2.1 OC, EC and TC

Fig.2 illustrated the correlations between WSOC and TC, OC plus EC, respectively.

The correlation coefficient to TC, OC, and EC were found to be 0.813, 0.807 and 0.766, respectively, which were all greater than the critical correlation coefficient (n=35, $\gamma_{(0.01,\ 30)}$ =0.4487). The strong linear link of WSOC with both OC and EC can be reasonably caused by the common sources.

3.2.2 Volatile-OC and non-Volatile-OC

The volatile OC and non-volatile OC were summarized and presented in Fig.3. Volatile-OC took up to averagely 36 % of OC compared to that non-volatile OC occupied about 64 % of the amount. Gaseous VOC and its synergistic interaction with the aerosol surface should be characterized as well to identify the different combustion sources such as biogenic emission, fossil fuel burning (Hennigan, 2008). Fig. 4 (a) and (b) showed that the WSOC concentration increased with the increase of non-volatile-OC/OC and decreased with the increase of volatile-OC/OC, but WSOC/OC tended to vary less with the change of volatile-OC/OC or non-volatile-OC/OC, demonstrating that WSOC was a complex organic mixture.

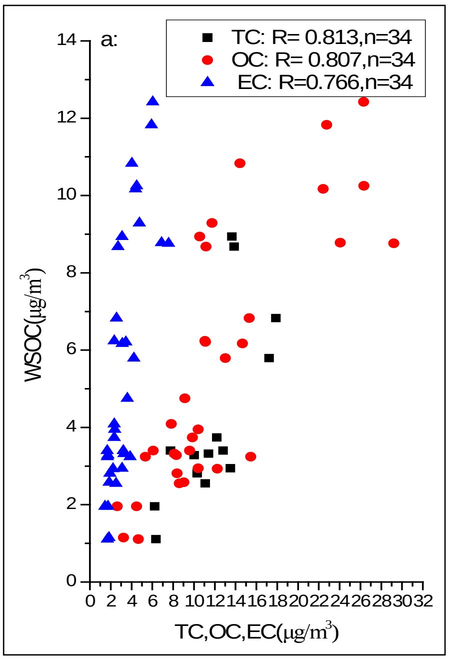

Figure 2. Correlation of WSOC to TC, OC, EC and OC/EC

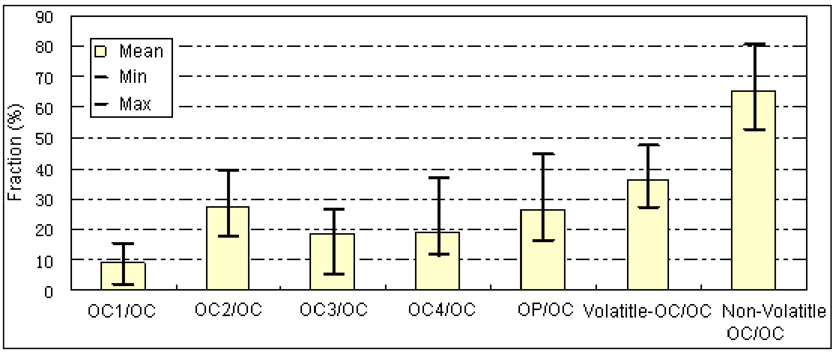

Figure 3. Fractions of different organic carbon

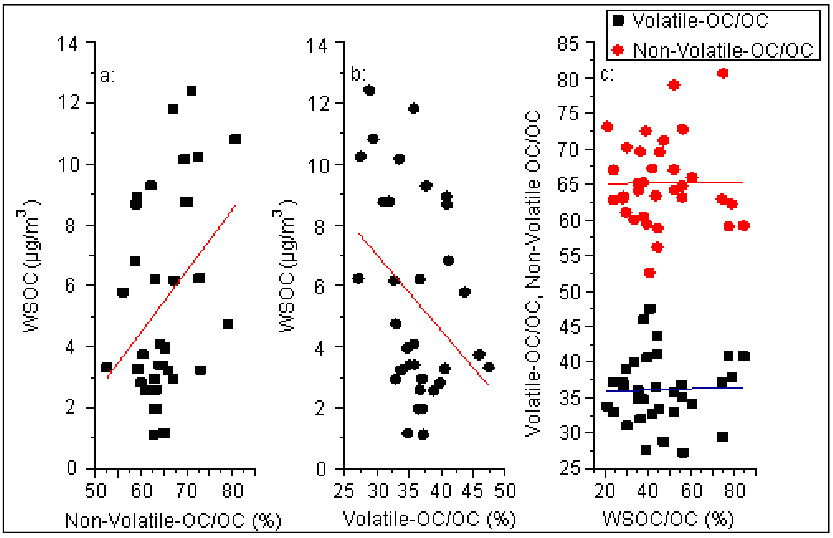

Figure 4. Relationship of WSOC , WSOC/OC and Non-Volatile-OC/OC, Volatile-OC/OC

3.2.3 Correlation in Char-EC and soot-EC

Char-EC/Soot-EC has been recently used to identify the origin of carbonaceous aerosol instead of OC/EC because Char-EC/soot-EC ratios from biomass burning and coal combustion were generally higher than that from motor vehicle exhaust (Han et al. 2008; Chow et al. 2004). Soot-EC generally is formed from volatiles condensed from the high-temperature gas phase, while char-EC form is from the solid residues of combustion and tends to keep its parent characteristics.

The concentration of char-EC and soot-EC were ranged from 0.30-6.89μg/m^3 (mean value of 2.50μg/m^3) and 0.19-1.47μg/m^3 (mean value of 0.74μg/m^3), respectively. As illustrated in Fig. 5, WSOC had a stronger correlation to char-EC rather than soot-EC and increased significantly with the increase of char-EC/soot-EC, which suggested that coal burning and biomass combustion processes might produce higher primary WSOC compared with vehicle exhaust emission and soil re-suspension.

Additionally, WSOC/OC displayed no distinct correlation to char-EC/soot-EC, as shown in Fig.5(d), but more higher WSOC/OC values was observed when char-EC/soot-EC was lower. Since the lower char-EC/soot-EC was usually result from vehicle emission (Chow et al, 2004), stationary sources and living sources such as coal burning, cooking exhaust and industrial process emission might be more important for higher WSOC.

3.3 Implication for source identification

3.3.1 Estimation of secondary organic aerosols

Based on the theoretical calculation equation OCsec=OCtot-EC×(OC/EC)min , Where OCsec was the secondary organic carbon, OCtot was the total OC and (OC/EC)min the minimum ratio observed (Castro et al. 1999), SOC was ranged from 1.4 μg/m^3 to 18.4 μg/m^3 (mean value of 7.0 μg/m^3) . 36 % of WSOC was greater than SOC calculated.

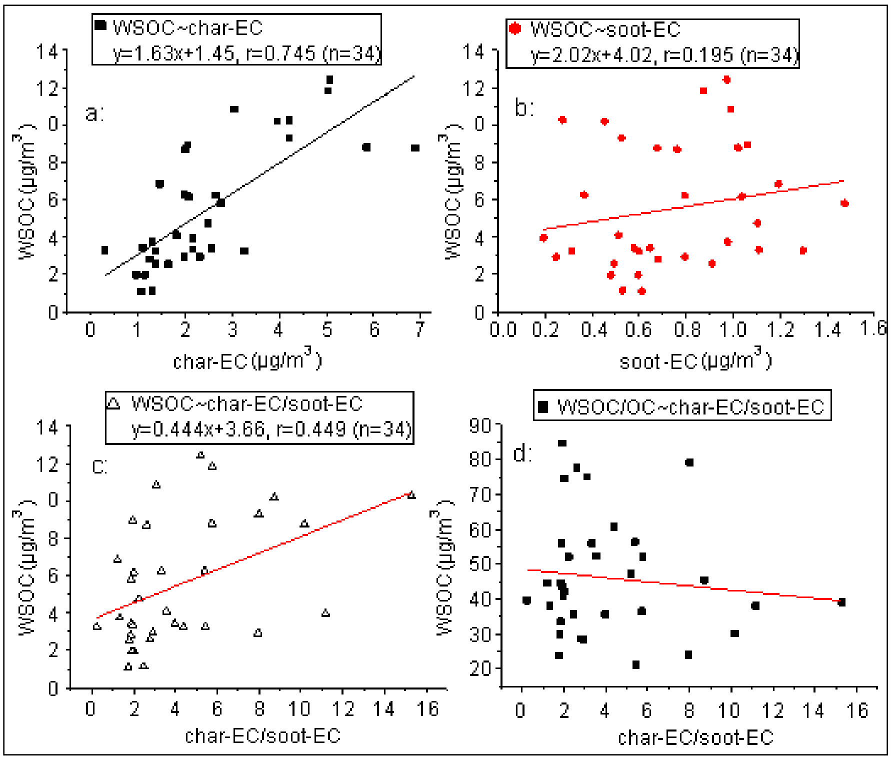

Figure.5 The dependence of WSOC on Char-EC and Soot-EC

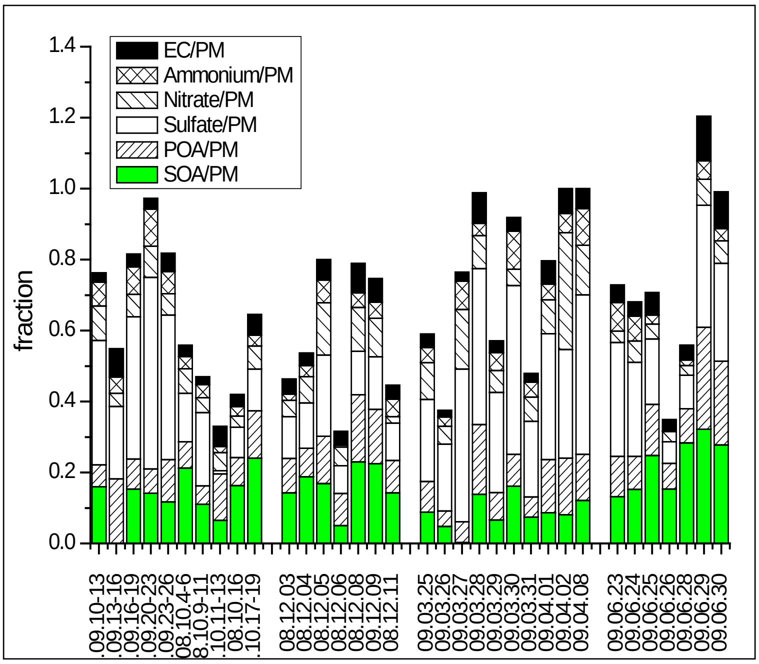

Figure 6. Mass percentage of the estimated SOA and other major components at sampling site

WSOC correlated predominately to both SOC and EC with R=0.70 (n=33, p<0.01) and R=0.831(n=34, p<0.01), respectively. Therefore, WSOC at sampling site was compounded by primary emission and secondary formation. The ratio of OM/OC was assumed to be 1.6 here for SOA estimation and 1.3 for POA (Turpin, 2001). The percentage of SOA, POA and other major ionic components obtained in this study was shown in Fig.6 The percentage of SOA ranged from 0.01 % to 34% and the seasonal average was larger in summer (22%) while lower in spring (9%). In general, SOA had a larger percentage than POA , about 1.5 times as much as POA except 0.8 times in spring. In spring, SOA was only 0.26 times as much as sulfate as well. It might be influenced by long distance transported aerosol from northwester China.

4. CONCLUSIONS

(1) WSOC in Shanghai $PM_{2.5}$ stayed in a higher level and took up to around 45 % of OC (ranged from 21 % to 85 %), 10.5 %~72.5 % (mean value of 35.4 %) of TC , 3.1~15 % of $PM_{2.5}$. WSOC/OC ratio was higher compared to other reported data.

(2) The data here demonstrated that biomass combustion was an important source of precursor pollutants, besides fossil fuel combustion. Meanwhile, the variation pattern of WSOC was distinctly different from that of WSOC/OC ratio which implied that the aged aerosol during long range transportation also impacted the WSOC characteristics in Shanghai.

(3) Because 36 % OC was in volatile form, gaseous VOC and its synergistic interaction on aerosol surface should be characterized as well. Despite the formation mechanism of WSOC is still unclear, VOCs control should be made in Shanghai aiming to not only reducing ozone concentration but also alleviating aerosol pollution.

ACKNOWLEDGEMENTS

We are greatly appreciated for the assistance from our group members.

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4.6 DIURNAL VARIATION OF PARTICULATE MATTER AND CARBON DIOXIDE IN OCCUPIED AND UNOCCUPIED SCHOOL ENVIRONMENT

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ABSTRACT

Air quality is of the great importance for children's health as children are particularly vulnerable sensitive population on the air pollution. This study was performed in two naturally ventilated schools located in the same municipality. First school was located in urban area, at residential – industrial site, while second was situated in rural area. Schools were chosen based on urban environment features. Environmental air quality was the main reference for choosing the school buildings. The measurements were obtained during heating and non-heating period for five consecutive working days. The objective of the study was to analyze the indoor air quality in the classrooms with special emphasis on levels and diurnal variations of particulate matter (PM) and carbon dioxide (CO_2) in occupied and unoccupied indoor environment. The results show that concentrations of PM and CO_2in occupied classrooms were high. High correlation between the PM and CO_2 concentrations was also determined.

Key-Words: indoor air quality, environmental air quality, carbon dioxide, PM

1. INTRODUCTION

Indoor air quality (IAQ) became a widely recognized issue that attracts researchers and occupants attention towards improving the air quality inside buildings[1–4].IAQ is defined as human need to perceive fresh and pleasant air with no negative impacts on their health and productivity. IAQ is especially important in the schools in order to enhance children's learning ability. Total working capacity of children decreases with illnesses and absence from school [5, 6].

The primary purpose of school buildings and facilities is to provide children with healthy and satisfactory places for their learning and development. School buildings are complex spaces to design as they need to perform well in all aspects of environmental conditions, while accommodating periods with very high occupant densities. The typical classroom has on average four times as many occupants per square meter as the typical office building.

Air quality is of the great importance for children's health as children are particularly vulnerable and sensitive population to the presence of air pollutants. The main factors that contribute to air quality in school are: outdoor air pollution, the way of interior ventilation, number of children in classrooms and their activities, lesson durations, breaks between lessons, etc. Outside of the home, children spend most of their time indoors at schools[7]. At this developmental stage in their lives, children are vulnerable to a range of environmental exposures that can have long-term adverse consequences [8].There is an abundance of studies showing high contamination levels of carbon dioxide in classrooms[9–14]. In recent years, several studies were published on particulate matter contamination in classrooms [15–20].

The objective of the study was to analyze the indoor air quality in the classrooms with special emphasis on the particulate matter (PM) and carbon dioxide (CO_2), their levels, diurnal variations, and correlations in occupied and unoccupied classrooms.

2. METHODOLOGY

The measurement was performed in two naturally ventilated schools located in the same municipality. First school (school A) is located in urban area, at the residential-industrial site, and the second (school B) is situated in rural area. The distance between the schools was about 15 km. Two measuring campaigns, each in duration of 5 working days (from Monday morning to Friday evening), were performed. The first one campaign was during the heating, winter(W),and the second during non-heating, summer (S), period. The schools are different with respect to age, construction and size. The school A, located in the urban area, was built in seventies of last century. However, the school B, located in the village, is more than 100 years older than school A, and it was not renewed for a long time. Classrooms with similar features were selected. Average number of occupants ~ 17 and ~ 28, in classrooms in school A and B respectively.

Sampling equipment

The PM concentrations presented here were monitored with the portable direct reading airborne particle monitor Turnkey OSIRIS. The simultaneous 24h PM_{10} and $PM_{2.5}$samples collected with the reference gravimetric samplers, Sven/Leckel LVS3, were also carried out. The PM_{10} and $PM_{2.5}$levels measured by the OSIRIS monitor were corrected on a daily basis using the results obtained by the gravimetry method.
CO_2 was measured using the Testo 435 devices (precision of ± 50 ppm, range 0 - 5000 ppm). The equipment was calibrated at the beginning of each measuring campaign. CO_2sampling device was located about one meter above the floor, away from doors and windows, thus avoiding possible disturbances resulting from air stream.
During the measurement every 2 days OSIRIS monitor has changed the location. The monitor was moved to another classroom to keep track of PM concentrations in the school. In both schools, the CO_2 measurements were conducted at four measuring points, in three classrooms and outside the school.

3. RESULTS

Table 1. shows average CO_2 concentrations in the schools during both heating and non-heating period. In the heating season, daily average CO_2 concentrations were higher in school located in rural area then in school located in urban area. There were no such differences in non-heating period. In the heating season, due to low temperature (–14°C), the lessons were shortened from 45 to 30 min. These shortenings could contribute to overall lowering of CO_2 levels in the heating period.
Significant seasonal variations in PM concentrations were observed with the higher levels during the heating season at both locations. The indoor PM concentrations were higher in the school located in rural area compared to school in urban area, especially in the heating season. That was probably caused by the resuspension of particles from floors.

Table 1.Average concentrations of CO_2, PM_{10} and $PM_{2.5}$ in schools in urban and rural area.

ambient	CO_2 (ppm)					PM_{10}/ $PM_{2.5}$ (µg/m^3)			
	urban		rural			urban		rural	
	W	S	W	S		W	S	W	S
indoor	812	767	1305	973	Average	44.21/25.16	42.31/12.73	49.35/28.59	21.14/17.76
					Median	40.46/23.32	40.33/13.55	44.91/23.03	19.44/21.80
outdoor	424	516	524	583	Average	54.74/45.87	16.15/13.37	38.28/32.97	35.32/15.58
					Median	52.96/42.74	16.92/13.56	39.28/39.87	34.37/15.95

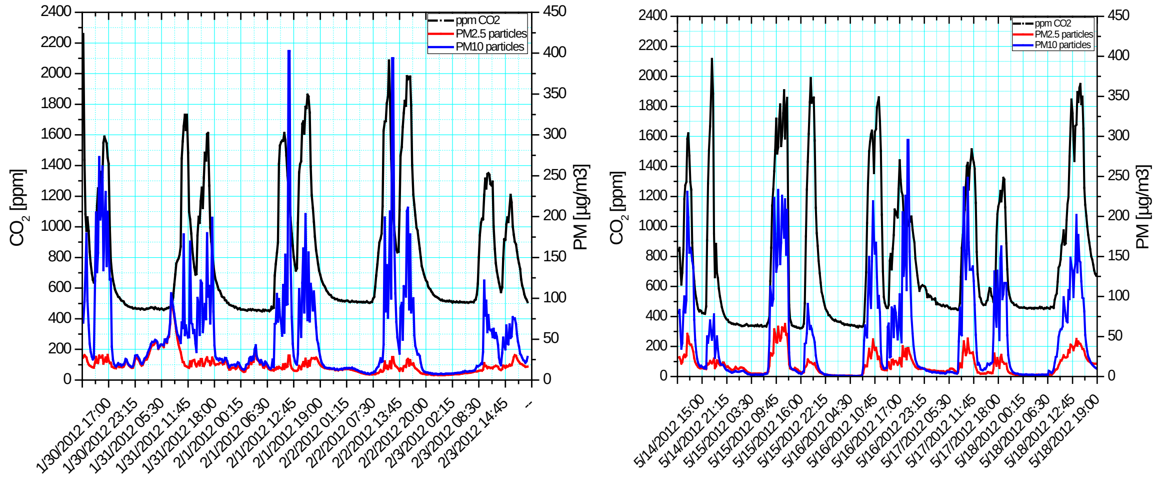

Figure 1.CO_2, PM_{10} and $PM_{2.5}$ levels in the school in urban area during one week campaign; heating (W) and nonheating (S) season.

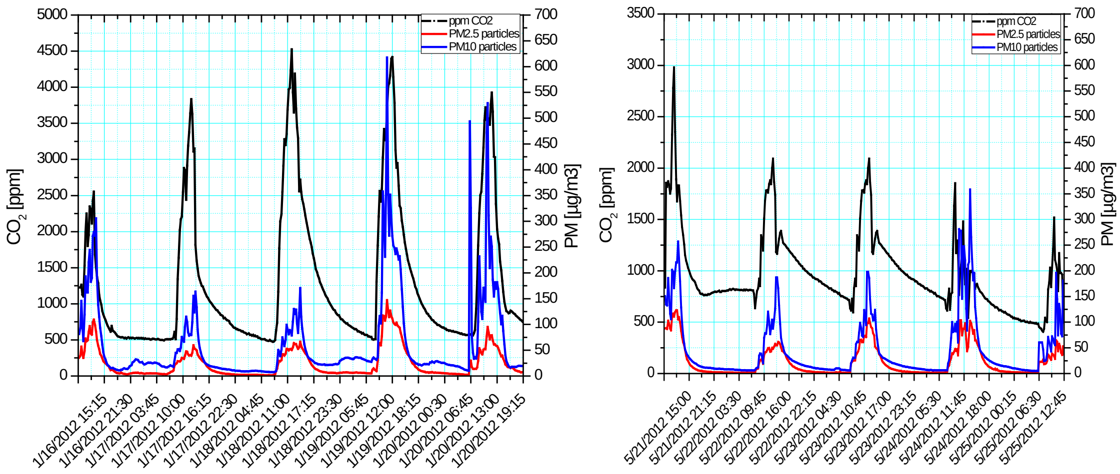

Figure 2.CO$_2$, PM$_{10}$ and PM$_{2.5}$ levels in the school in rural area during one week campaign; heating (W) and nonheating (S) season.

During school days, PM and CO$_2$ concentration increased from the time when the pupils enter the classroom, and reaches its maximum at the end of the morning shift (as shown in Fig.1. and Fig. 2.). Then, during a break between shifts, the concentration of CO$_2$ decreases, while in some classrooms PM concentration increases. With the start of afternoon classes, in school A, PM and CO$_2$ concentration begins to rise again. At the end of the school day, the value of the indoor PM and CO$_2$ concentration starts to decrease. The results also indicates that concentrations of PM and CO$_2$were high in the time intervals when the pupils are in school. The increased PM concentrations for such periods and their correlation with high CO$_2$ concentrations also points out that role of ventilation in indoor air quality in schools.

Correlation

The correlation between CO$_2$and PM concentrations was calculated for all period of measurement and for the period when classrooms were occupied with pupils. During the measurements in the heating period in the school located in urban area (A), the mean outdoor temperature was about-14°C and about 14°C in non-heating period. During the measurements in the heating period in the school located in rural area (B), the mean outdoor temperature was about 1°C and about 20°C in non-heating period. At school A, in the heating period, the lessons were shortened and the temperatures in the classrooms and outside were low, so it is necessary to repeat the campaign and analyze the results again. Table 2 shows correlation coefficients between the PM and CO$_2$ concentrations.

Table 2. Correlation coefficients between the PM and CO$_2$ levels.

Correlation coefficient		urban		rural	
		W	S	W	S
PM$_{10}$andCO$_2$	Occupied period	0.64	0.73	0.79	0.69
	all period	0.39	0.77	0.72	0.63
PM$_{2.5}$andCO$_2$	Occupied period	n/a	0.76	0.88	0.77
	all period	n/a	0.80	0.79	0.72

4. CONCLUSION

Our results, as well as findings from earlier studies, clearly indicate that exposure to particulate matter and carbon dioxide in the observed schools is high. The analysis of measuring results showed high correlation between the PM fractions and CO$_2$ concentration, not only in the period when pupils are in classrooms, but also in the whole period of measurements. Presented data was sufficient to indicate the need to improve the ventilation and cleaning practice in the selected schools. This study demonstrate a solid basic for implementation of the fresh air supply strategy in naturally ventilated schools and for design further investigations in the aim of ensuring improved indoor air quality.

5. ACNOWLEDGEMENTS

This work was funded by the Grant of the Ministry of Education, Science and Technological Development of Republic of Serbia, as a part of Projects III42008: “Evaluation of Energy Performances and Indoor Environment Quality of Educational Buildings in Serbia with Impact to Health”

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4.7 ASSESSMENT OF PM LEVELS AND INDOOR-OUTDOOR RELATIONSHIPS OF PM_{10} AND $PM_{2.5}$ IN A SELECTED PRIMARY SCHOOL IN NIŠ, SERBIA

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ABSTRACT

City of Niš is the center of Southeastern Region of the Republic of Serbia with about 350,000 inhabitants. It is well known that dominant sources of air pollution in Niš are traffic, local heating and industry. The main goal of this paper is to present PM_{10} and $PM_{2.5}$ levels in ambient air and inside the selected primary school in Niš. The school is located in the city center of Niš, on a busy street. The relationships between the indoor and outdoor PM levels are also presented in the paper with a comparison of PM levels measured by the standard gravimetric method with PM levels obtained by the automatic monitoring device. Simultaneous indoor and outdoor measurements of PM_{10} and $PM_{2.5}$ concentrations were conducted in heating season in the time interval from March 20th to April 5th in 2013. Daily mean PM_{10} levels were 54.6 $\mu g/m^3$ indoors and 47.9 $\mu g/m^3$ outdoors. Daily mean $PM_{2.5}$ levels were 38.5 $\mu g/m^3$ indoors and 41.4 $\mu g/m^3$ outdoors. $PM_{2.5}/PM_{10}$ ratio in the school was 0.70 and 0.87 in ambient air. High $PM_{2.5}/PM_{10}$ ratios points to considerable influence of pollution sources of anthropogenic origin, such as traffic and fossil fuels combustion.

1. INTRODUCTION

The relationships between outdoor air pollution and health are beyond doubt. But the influence of indoor air pollution on health is complex and still unexplored in detail so receives more attention of researchers at the moment. In the indoor environment, in which people spend most of their time, both indoor and outdoor sources contribute to PM levels. The indoor environment is legislatively a difficult one due to the many public and private actors involved [1]. In addition, information about indoor air quality generally lacking, and there are almost no systematic monitoring programs. A European Observatory on Indoor Air SINPHONIE [2] is developing a monitoring framework and collects data for assessment of health related aspects of European schools. Several project concerning to air pollution in schools are also in place in Serbia [1]. The main goal of this paper is to present PM_{10} and $PM_{2.5}$ levels in the ambient air and inside the primary school ‘‘Vožd Karađorđe’’, located in the city center, on a busy street. Another goal is to determine the relationships between the indoor and outdoor PM_{10} and $PM_{2.5}$ levels. A comparison of PM_{10} and $PM_{2.5}$ levels measured by the standard gravimetric method with PM_{10} and $PM_{2.5}$ levels obtained by the automatic monitoring device is also presented in the paper. Simultaneous indoor and outdoor measurements of PM_{10} and $PM_{2.5}$ levels were conducted in heating season in the time interval from March 20th to April 5th in 2013.

2. METHODOLOGY

The European reference low volume samplers, LVS3 (Sven/Leckel LVS3) [3] with size-selective inlets for PM_{10} and $PM_{2.5}$ fractions, were used to collect particulate matter in indoor and ambient air. Mass concentrations for the LVS3 samplers were obtained from gravimetric analysis of filters and sample volume, which is logged by the sampler throughout the sampling period. The LVS3 sampler flow rate (2.3 m^3/hour) was calibrated using the certified flow meter just before the measurement campaign. Quartz fiber filters (Whatman QMA 47 mm diameter filters) were used throughout this study for the collection of particulate matter. Pre-conditioning and post-conditioning of filters was undertaken in accordance with the general requirements of EN12341. Approximately 15% of all gravimetric samples were collected as field blanks. After preconditioning in a clean room, filters were weighing using the Mettler Toledo semi-micro balance (with minimum 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 (2.5 µg) was subtracted from net mass of the sample filters. The detection limit was 2.7 $\mu g/m^3$ calculated as three times the standard deviation in net mass of the field blanks divided by the nominal sample volume. Indoor air is sampled in the lobby at ground floor while ambient air is sampled on the balcony at height of 10 m above ground. The ambient PM_{10} and $PM_{2.5}$ levels obtained by gravimetric method were compared with the results obtained by automatic PM monitor. The Serbian Environmental Protection Agency (SEPA) Automatic Monitoring Station - AMS Nis Traffic, is situated near the Public Health Institute of Niš, 0.5 km east from the selected school as shown in Figure 1. The AMS contains meteorological station and GRIMM EDM180 dust monitor [4], which providing PM_{10} and $PM_{2.5}$ mass concentration levels simultaneously in the real-time. GRIMM EDM180 uses a light scattering (90°) technique to determine the concentration of airborne dust in the particle size range from about 0.25 µm to about 32 µm. The data used in this paper were originally available as daily averages (LVS3) and 1-hour averages (EDM180). For calculation the daily averages, minimum 90% of 1-hour averages were required, otherwise the value is considered as the missing one.

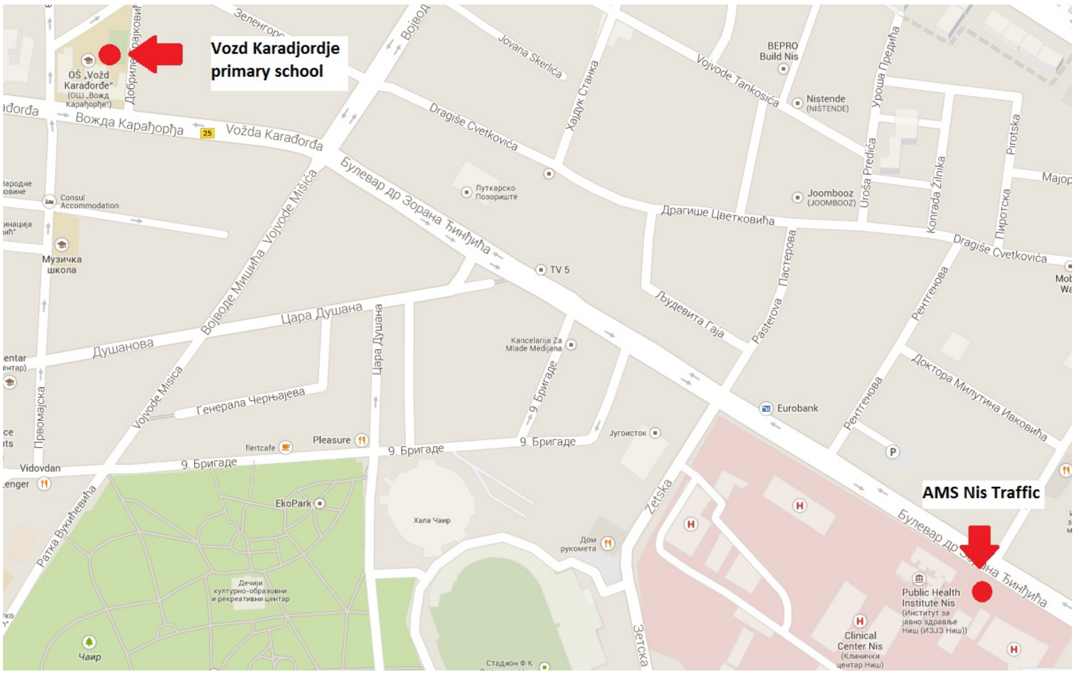

Figure 1. Niš city map with measuring sites marked: 1. Primary school ''Vožd Karađorđe,'' 2. Public Health Institute of Niš (AMS Nis Traffic)

3. RESULTS AND DISCUSSION

Statistics of some meteorological parameters during the measurements campaign is shown in Table 1. The concentrations of PM_{10} and $PM_{2.5}$ in ambient air and their ratios are summarized in Table 2. Exceeding the limit value for PM_{10} concentrations in ambient air (daily mean of 50 µg/m^3) occurred in 35% of days in which measurements were performed. Similarly, exceeding the WHO daily mean guideline value (25 µg/m^3) for $PM_{2.5}$ concentrations occurred in 71% of days.

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

Period	T (^{0}C)	RH (%)	WS (m/s)	P (mbar)
20.03. - 05.04.2013.	6.9±3.9	74.9±9.5	1.1± 0.3	993.8±4.5

Table 2. Summary statistics for PM_{10} and $PM_{2.5}$ concentrations in ambient air (SD - standard deviation)

Sampling site	PM_{10} OUTDOOR			$PM_{2.5}$ OUTDOOR			Ratio $PM_{2.5}/PM_{10}$	n
	Average	Range	SD	Average	Range	SD		
School	47.9	20.0-88.0	22.8	40.8	18.2-85.5	18.9	0.87	17
AMS Nis Traffic	32.8	20.3-62.8	12.5	27.1	14.8-54.0	10.9	0.90	17

The indoor PM_{10} and $PM_{2.5}$ levels and their ratios are summarized in Table 3. Exceeding the daily limit for PM_{10} levels indoors occurred in 53% of days in which measurements were performed. Similarly, exceeding the daily limit for $PM_{2.5}$ levels occurred in 88% of days.

Table 3. Summary statistics for indoor PM_{10} and $PM_{2.5}$ concentrations (SD - standard deviation)

Sampling site	PM_{10} INDOOR			$PM_{2.5}$ INDOOR			Ratio $PM_{2.5}/PM_{10}$	n
	Average	Range	SD	Average	Range	SD		
School	54.6	26.1-91.9	17.6	38.5	15.3-68.6	13.8	0.70	17

According to Tables 2 and 3, average $PM_{2.5}/PM_{10}$ ratios were 0.87 in ambient air and 0.70 inside the school. The ambient $PM_{2.5}/PM_{10}$ ratios found in Niš are comparable to $PM_{2.5}/PM_{10}$ ratios calculated for various sites throughout Europe [5]. High $PM_{2.5}/PM_{10}$ ratio points to considerable influence of pollution sources of anthropogenic origin, such as traffic and fossil fuels combustion. The indoor/outdoor (I/O) PM concentration ratio is often used to justify presence of indoor sources (I/O >1) or infiltration of ambient air (I/O≤ 1). According to Table 4, during the whole measurement period, the I/O ratios for PM_{10} levels varied between 0.65 – 2.12 (mean 1.25 or 1.38 without weekends). Similarly, I/O ratios for $PM_{2.5}$ levels varied between 0.64 - 1.27 (mean 1.00 or 1.07 without weekends). This indicates to particles resuspension caused by intense movement and activity of pupils. These findings are consistent with the results obtained for seven primary schools in Athens that has a similar PM_{10} I/O concentration ratios, range 0.60 - 2.76 (mean 1.65) while I/O concentration ratios for $PM_{2.5}$, range 0.62 - 2.61 (mean 1.67) [6]. The current study's $PM_{2.5}$ I/O concentration mean ratio (1.00) during heating period is similar to that from a study in Southern California (1.03), Birmingham (1.00), Stockholm (0.97) and Bor (1.11) [7, 8].

Table 4. Daily mean I/O ratios for PM_{10} and $PM_{2.5}$

Sampling site	Ratio PM_{10} INDOOR/PM_{10} OUTDOOR	Ratio $PM_{2.5}$ INDOOR/$PM_{2.5}$ OUTDOOR	n
School	1.25 (0.65 – 2.12)	1.00 (0.64 – 1.27)	17

Table 5. Pearson correlation coefficients of daily mean PM levels at corresponding sites

	School PM_{10} OUTDOOR	School $PM_{2.5}$ OUTDOOR	School PM_{10} INDOOR	School $PM_{2.5}$ INDOOR	AMS Nis PM_{10} OUTDOOR	AMS Nis $PM_{2.5}$ OUTDOOR
School PM_{10} OUTDOOR	1					
School $PM_{2.5}$ OUTDOOR	0.90	1				
School PM_{10} INDOOR	0.82	0.84	1			
School $PM_{2.5}$ INDOOR	0.87	0.93	0.95	1		
AMS Nis PM_{10} OUTDOOR	0.84	0.86	0.87	0.87	1	
AMS Nis $PM_{2.5}$ OUTDOOR	0.86	0.93	0.95	0.80	0.86	1

The results of comparison of PM_{10} and $PM_{2.5}$ levels measured by standard gravimetric method with the PM_{10} and $PM_{2.5}$ levels obtained by the GRIMM EDM180 dust monitor shows that automatic monitor underestimated PM_{10} levels by approximately 30% and $PM_{2.5}$ levels by approximately 27%, relative to the reference gravimetric sampler. Pearson correlation coefficients of daily mean concentrations of PM_{10} and $PM_{2.5}$ are presented in Table 5. Strong correlations between indoor and outdoor $PM_{2.5}$ and PM_{10} concentrations ($r>0.8$) were observed.

4. CONCLUSIONS

The results presented in the paper showed that indoor and outdoor PM_{10} and $PM_{2.5}$ levels were similar in the selected primary school in Niš. High PM levels together with a large number of days with PM levels over limits were observed in both indoor and outdoor environments. Outdoor $PM_{2.5}$ seems to penetrate less, but indoor sources compensate. Limited ventilation in school and high outdoor PM levels are probably the most possible reasons for the elevated indoor PM levels found in the present work. Daily mean $PM_{10\ INDOOR}/PM_{10\ OUTDOOR}$ ratio was 1.25, while $PM_{2.5\ INDOOR}/PM_{2.5\ OUTDOOR}$ ratio was 1.00. This shows a strong contribution of particle resuspension caused by activity of occupants. High outdoor $PM_{2.5}/PM_{10}$ ratios points to considerable influence of pollution sources of anthropogenic origin, such as traffic and fossil fuels combustion. Strong correlations between indoor and outdoor $PM_{2.5}$ and PM_{10} concentrations ($r>0.8$) indicate that both concentrations are driven by a common phenomenon: pollution dispersion. Overall our findings indicates that indoor school environment offer little protection against combustion-related particles in outdoor air.

5. ACKNOWLEDGEMENTS

This work was partly funded by the Grant of the Ministry of Education, Science and Technological Development of Republic of Serbia, as a part of Project III42008: “Evaluation of Energy Performances and Indoor Environment Quality of Educational Buildings in Serbia with Impact to Health.” We wish to thank the Serbian Environmental Protection Agency for assistance in technical issues and providing the useful pollutant and meteorological data.

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Tasić V., Kovačević R., Milošević N., 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

4.8 PRELIMINARY MEASUREMENTS OF PM$_{10}$ IN APARTMENTS IN BOR, SERBIA

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ABSTRACT

The aim of this paper is to present PM$_{10}$ levels in apartments in the vicinity of the Copper Mining and Smelting Complex Bor, eastern Serbia. The results of measurements of PM$_{10}$ levels in four apartments located at the different distances from the copper smelter are presented. Daily mean PM$_{10}$ levels at all apartments were beyond the limit (50 μg/m^3) in less than 5% of measured days. However, outdoor PM$_{10}$ levels exceeded the daily limit in 22% of measured days. Daily mean PM$_{10}$ indoor-to-outdoor mass concentration ratios (I/O) were within range 0.47 - 0.63 during warm (April – September) and 0.51 - 0.64 in cold (October – March) periods. Such ratios indicate that there were no significant indoor sources of PM$_{10}$ particles in the apartments. Correlation coefficients between daily mean PM$_{10}$ I/O concentrations vary from 0.54 to 0.84 during warm and from 0.61 to 0.73 in cold period. This also points to conclusion that the most of indoor PM$_{10}$ particles originates from outdoor air.

1. INTRODUCTION

The Bor town is assumed as representative of hot spot urban-industrial environment in the Republic of Serbia. The main source of air pollution with sulfur dioxide, toxic metals and metalloids in particulate matter is the Copper Mining and Smelting Complex Bor Company which has been in operation for more than a century [1]. Monitoring of sulfur dioxide, total suspended particles (TSP) and toxic metals content of TSP has been carried out for many years in the Municipality Bor within local monitoring network. Serbian Environmental Protection Agency (SEPA) started measuring particulate air pollution with automatic monitors in the Municipality Bor since 2007. According to SEPA annual report for 2010 [2] annual mean PM$_{10}$ level in Bor at sampling site Town Park was 31 μg/m^3. That PM$_{10}$ concentration appear to be the similar as in the European urban and industrial sites [3], or even lower, as shown in Table 1. In fact, annual mean PM$_{10}$ levels recorded in Bor were among the lowest compared with PM$_{10}$ levels in other Serbian cities [2]. In the most of Serbian cities PM$_{10}$ levels have been much higher in cold than in warm period of year. However in Bor, in the time interval 2007-2010, PM$_{10}$ levels were just 10% higher in the cold period than in warm period [1].

Numerous exposure studies have associated the level of outdoor particulate matter with mortality and morbidity [4-7]. Thus the relationships between outdoor air pollution and health are beyond doubt. But the influence of indoor air pollution on health is complex and still unexplored in detail, so receives more attention of researchers at the moment. In the indoor environment, in which people spend most of their time, 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, 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.

In this paper indoor and outdoor PM$_{10}$ levels and their ratio (I/O) in four apartments in the Bor town urban area were presented. Measurements were carried out in the time interval 2010-2012. Apartments were selected to be on same direction but at the different distances from the copper smelter. The nearest apartment is about 500 m and the furthest 2.5 km far from the copper smelter, as shown in Figure 1. Each apartment was occupied with 3-4 non-smoking persons.

Table 1. Average outdoor PM$_{10}$ levels (μg/m^3) in some European urban areas [3]

City	Belgrade	Stockholm	Vienna	Llodio	Frankfurt	Palermo	Madrid	Athens
Period	2003-2006	2003-2004	1999-2000	1999-2006	2001-2002	2005	1999-2000	2001-2002
PM$_{10}$	70.1	36	30.38	32	32.6	36	47.68	73.8

2. METHODOLOGY

PM_{10} levels were monitored by using the standard European gravimetric samplers Sven/Leckel LVS3 [8]. In each apartment one sampler was placed in the center of a living room, at breathing height. Outdoor measurements were conducted on the terrace, just outside the living room. No ventilation system exists, and windows remained closed during the measurements campaign. Measurements were conducted in both cold and warm periods of year in duration of at least 30 days per apartment per season. Mass concentration of PM_{10} particles was obtained from gravimetric analysis of filters. Quartz fiber filters (Whatman QMA 47 mm) were used throughout this study. Pre-conditioning and post-conditioning of filters was undertaken in accordance with the requirements of SRPS EN 12341:2008 standard. Approximately 15% of all gravimetric samples were collected as field blanks. After preconditioning in a clean room, filters were weighing using the Mettler Toledo semi-micro balance (with minimum 10 μg mass resolution). PM_{10} mass concentrations were calculated using average (each filter is measured three times) weight of filters. Average change in the field blank weight was subtracted from net mass of the sample filters. The detection limit was calculated as three times the standard deviation in net mass of the field blanks divided by the nominal sample volume. The LVS3 samplers flow rate (2.3 m^3/hour) was calibrated using the certified flow meter before each campaign of measurements.

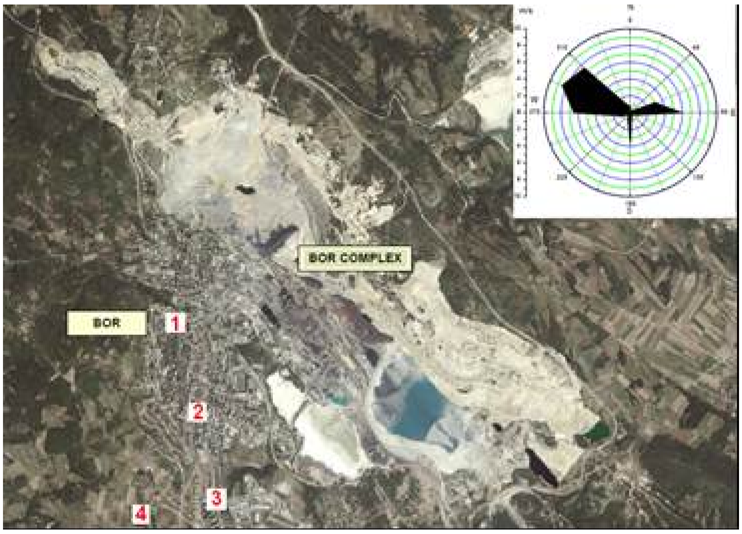

Figure 1. Bor town map with the apartment locations marked together with rose of winds (2007-2012)

3. RESULTS AND DISCUSSION

Summary statistics of PM_{10} mass concentration levels measured in the apartments in Bor during warm and cold periods are presented in Tables 2 and 3. In average, at all apartments indoor PM_{10} levels were beyond the daily limit (50 μg /m^3) in less than 5% of measured days. However, outdoor PM_{10} levels exceeded the daily limit in 22% of measured days. In reference [9] Pekey et al. investigated indoor and outdoor PM_{10} levels during summer and winter in 15 homes in Kocaeli, which is one of the most industrialized areas in Turkey. PM_{10} levels from our study together with results from other studies [9] are presented in Table 4.

Mean daily PM_{10} indoor-to-outdoor concentration ratios (I/O) were determined within range 0.47 - 0.63 during warm and 0.51 - 0.64 in cold periods. Thus, there is no significant difference between PM_{10} I/O ratios in the warm and cold season. These indicate absence of significant indoor sources of PM_{10} particles in the apartments that we observed. These findings are consistent with the results obtained in [9] for Kocaeli in cold period, where PM_{10} I/O concentration ratio was 0.56 and for a typical residence in the center of Athens [10] where PM_{10} I/O concentration ratio was in range 0.61.

The PM_{10} I/O relationship was also investigated by the linear regression analysis, as shown in Tables 2 and 3. Moderate to strong correlations between indoor and outdoor PM_{10} concentrations were observed. Pearson's correlation coefficients between the daily mean PM_{10} I/O concentrations were determined within range from 0.54 to 0.84 (average 0.69) in warm period and within range 0.61 to 0.73 in cold period (average 0.70). This also points to conclusion that the dominant sources of PM_{10} particles in all the apartments included in our study, originates from outdoor air.

Table 2. Summary statistics for PM_{10} levels ($\mu g/m^3$) in warm period

Measuring location	Indoor	Outdoor	Indoor/Outdoor	Correlation
Apartment 1	23.2	41.2	0.57	0.65
Apartment 2	19.7	42.8	0.47	0.54
Apartment 3	24.0	42.1	0.58	0.72
Apartment 4	26.1	40.4	0.63	0.84
Average	23.2	41.6	0.56	0.69

Table 3. Summary statistics for PM_{10} levels ($\mu g/m^3$) in cold period

Measuring location	Indoor	Outdoor	Indoor/Outdoor	Correlation
Apartment 1	35.1	74.4	0.51	0.61
Apartment 2	24.0	46.9	0.54	0.72
Apartment 3	21.5	38.7	0.64	0.73
Apartment 4	23.7	50.3	0.52	0.74
Average	26.1	52.6	0.55	0.70

Table 4. Comparison of PM_{10} levels ($\mu g/m^3$) from various studies with PM_{10} levels from our study

Site	Summer (warm period)			Winter (cold period)			Number of apartments	References
	Indoor	Outdoor	I/O	Indoor	Outdoor	I/O		
Kocaeli, Turkey	45.5	59.9	0.76	56.9	102.3	0.56	15	Pekey et al. 2010 [9]
Zurich, Switzerland	26.5	12.8	2.07	32.8	23.4	0.7 – >1.8	10	Monn et al. 1997 [11]
Hong Kong, China				63.3	69.5	0.88 – 1.04	34	Chao and Wong 2002 [12]
Washington, USA				11.93	13.47	0.88	16	Jansen et al. 2005 [13]
Santiago, Chile				103.8	115.3	0.90	18	Rojas-Bracho et al. 2002 [14]
Lisbon, Portugal				72.7	68.0	1.07	1	Borrego et al. 2006 [15]
California, USA				21.1	23.6	0.89	13	Geller et al. 2002 [16]
Athens, Greece					68.2	0.61	1 weekends	Diapouli et al. 2008 [10]
Athens, Greece					96.3		1 weekdays	
Bor, Serbia	23.2	41.6	0.56	26.1	52.6	0.55	4	This study

4. CONCLUSIONS

This study presents indoor and outdoor PM_{10} levels measured in 4 apartments in Bor, Serbia, during cold and warm periods. No clear seasonal changes in PM_{10} levels observed in both indoor and outdoor environments. Daily mean PM_{10} levels observed in all apartments were beyond the limit in less than 5% of measured days while at the same time outdoor PM_{10} levels exceeded the limit in 22% of measured days. No significant difference found between PM_{10} I/O ratios in the warm and cold period. Correlations between PM_{10} I/O concentrations were in average 0.7 in the both periods of year. All these findings point to absence of significant indoor sources of PM_{10} particles in the apartments. So, the most of indoor PM_{10} particles originates from outdoor air. To confirm these findings further studies in this area should include a greater number of apartments and chemical analysis of collected samples. Thus, origin of particular pollutants content in PM and it's relation with the Copper Mining and Smelting Complex Bor as well as other sources of PM should be resolved in the near future.

5. ACKNOWLEDGEMENTS

This work was partly funded by the Grant of the Ministry of Education, Science and Technological Development of Republic of Serbia, as a part of Project III42008: “Evaluation of Energy Performances and Indoor Environment Quality of Educational Buildings in Serbia with Impact to Health.” We wish to thank the Serbian Environmental Protection Agency for assistance in technical issues and providing the useful pollutant and meteorological data.

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4.9 TSP LEVELS AND ELEMENTAL CONTENT (PB, CD, NI, AS) OF TSP IN URBAN-INDUSTRIAL AREA OF BOR, SERBIA

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Bor is a town located in eastern Serbia, near the border with Bulgaria and Romania. It is an industrial town with intensive urbanization, developed infrastructure and copper smelter facilities less then 1 km far from the nearest residential areas. A century of copper mining and metallurgy in Bor Municipality have a large influence on the degradation of the environment, both in urban as well as in rural areas. Pyrometallurgical processing of copper concentrate in Bor causes emissions of sulfur dioxide and particulate matter emitted from diffuse and point sources: (1) Diffuse (surface) sources including the largest open pits (active and inactive) and municipal solid waste landfill (dump), (2) Point sources of metallurgical complex (especially within the copper smelter plant).
Thus, air pollution in the Bor Municipality is strongly related to the Copper Mining and Smelting Complex Bor operation. Air pollutants with levels that are often above the air quality limits are sulfur dioxide and toxic elements in suspended particulate matter (arsenic, cadmium, lead).

Air quality control in Bor Municipality is done through local and national monitoring networks: (1) Two monitoring sites for sulfur dioxide and soot, and four monitoring sites for Total Suspended Particles – TSP, in a local monitoring network operated at municipal level, (2) Three automatic stations as part of national network of automatic monitoring stations, operated by Serbian Environmental Protection Agency – SEPA.

This paper compares TSP levels and elemental content (Pb, As, Cd and Ni) in TSP during 2012 with levels of pollutants in the period 2006 -2011 at 4 locations in Bor urban area: Jugopetrol, Town Park, Technical Faculty and Mining and Metallurgy Institute (MMI) monitoring sites. The samples were collected with Sven/Leckel LVS3 sampler equipped with KAR8 filter changer successively for one week per month at each location. Chemical analyses were performed by AAS (Pb, Cd, As) and ICP-AES (Ni). Mining and smelting processes contribute somewhat to levels of Cd and Ni, and strongly to As and Pb levels in particulate matter. During 2012, similar to the 2006-2011 period, the average levels of TSP were above the annual limit (70 µg/m^3) at 3 locations (Jugopetrol, Technical Faculty and MMI). At all sites, Ni levels were under the detection limit (< 0.001 mg/l). However, average annual levels of Cd in 2012 at all monitoring sites (2 – 8 ng/m^3) were similar as in the time period 2006 – 2011 (3 – 8 ng/m^3).

The average annual levels of Pb in 2012 at all measuring sites (0.2 – 0.7 µg/m^3) were at least two times higher than in the time period 2006 – 2011 (0.06 – 0.2 µg/m^3). The average annual levels of As in 2012 at three monitoring locations (Town Park, Jugopetrol and Technical Faculty) were at least four times higher than in the time period 2006 – 2011 (19.5 – 22.5 ng/m^3). In 2012, the average levels of As detected at Jugopetrol and Town Park were about 125 ng/m^3 and at Technical Faculty 92.3 ng/m^3. The average annual level of As at MMI (45.2 ng/m^3) was two times higher than in 2006 – 2011 (22.5 ng/m^3). Spatial variability of pollutants is mainly due to the position of the monitoring sites relative to the Copper Mining and Smelting Complex Bor, meteo conditions (wind speed and direction, atmospheric pressure, humidity and temperature). Temporal variability and occasionally higher levels of Pb and As, is due to copper smelter operation mode, type of ore and production intensity. According to the presented data, air quality in Bor was very poor during 2012, regarding levels of As in TSP. This situation warrants the need for serious steps to be taken to improve air quality, such as finalization of a new copper smelter and sulfur acid factory.

5 ALTERNATIVE METHODS

5.1 CITI-SENSE: HOW VIABLE IS THE CITIZEN'S CONTRIBUTION TO PARTICULATE MATTER SCIENCE?

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ABSTRACT

Citizens are one of the key actors in the efforts to achieve acceptable air quality, yet they often do not have the means to decide whether to be active. The means may include knowledge, information, understanding, awareness and suitable tools. This lack of means is making the efforts to reduce health hazards from air pollution rather difficult and dependent on authorities and their legally determined actions. For a number of air pollutants, it may be difficult to reduce exposures without direct citizen participation; this is also true of particulate matter in the urban settings. Particulate matter exhibits temporal and spatial variability and variability in physical and chemical properties, all in relation to meteorological conditions, types of environments, distance to and strength of contributing sources. Exposure to particulate matter also strongly depends on human behaviour.

The CITI-SENSE project is seeking to provide means to citizens to be able to understand and influence the environments they are living in, and to establish if citizen contributed information can be used in global observing systems and for environmental research.The project takes advantage of the current technological offer in sensing and information and communication technologies, to build citizen's observatories that would enable citizens to gather and share objective information about their environments using own measurements combined with other information sources. This paper describes the main elements CITI-SENSE plans to develop.

1. INTRODUCTION

Involving citizens as active partners in environmental monitoring, and enabling them to contribute to decision-making, is seen as one way towardsbetter protection and enhancement of our environment. The EU FP7 collaborative project CITI-SENSE (www.citi-sense.eu) aims to support citizens to contribute to environmental governance, providing a range of tools and services related to the environment, and developing participatory sensing tools and methods. This is possible due to continuous advance on smaller and less expensive monitoring technologies and ubiquitous use of information and communication technologies. It is also in line with recent activities within "citizen science" and "participatory sensing". While seen as desirable and even game-changing by some, such approaches also generate new issues to address.

There is a difference in information content and properties between (1) what information may be useful to citizens or their group, (2) what is appropriate for legislation and air quality management, and (3) what information is sought by scientists (and for what purpose). Taking example of particulate matter, what are the issues that may be of interest to these three groups? Elevated levels of particulate matter area risk for human healthbut complying with the limits in the legislation constitutes a challenge for air quality managers. How are the different groups contributing to addressing this challenge? And how best can we strengthen citizens capabilities to participate in actively reducing the health hazards? In this paper, we discuss the different perspectives, and provide examples of how we intend to complement the different information gathering methodologies.

1. INFORMATION SUPPLY AND DEMAND

Information on particle concentrations exists on urban and regional scale in Europe (EEA, 2013a; EMEP 2013). Large municipalities run compliance networks and inform their citizens about the results and warn them in situation of increased hazard, and an international network of regional background sites is in place. These continuous long-term high precision data are complemented by research findings. But types of questions the authorities ask and the researchers ask are not necessarily identical to the types of questions the public is asking as information needs for each of these actors differ.

Different information users have also different requirements on properties of the information. This is well illustrated by an example of data from compliance monitoring. With the basis in legislation, European cities are obliged to perform monitoring of air quality to determine compliance with national/EU legislation. The requirements for such networks specify station placement, parameters to be measured, methods to be used, quality control and assurance procedures, and obligatory reporting of the results. Such monitoring is highly demanding operation. The requirements are set to ensure wide comparability of the results across Europe, and globally. The data allow monitoring of progress in pollution mitigation, and are used as input to modelling. The data support specialized scientific research e.g. in environmental epidemiology or atmospheric sciencesbut they are not providing the spatial and temporal information needed, nor the types of pollutant constituents required at any time. Thus, despite being of high quality and comprehensive,these data do not provide the municipalities with all the necessary input for hazard-based mitigation of pollution effects on human health, even when coupled with further modelling exercises (as was summarized e.g. by EEA 2013, ETC/ACC 2013). That is because exposureis determined not only by atmospheric physical and chemical phenomena but also by human movement patterns and activity level, as has been illustrated many times, including de Nazelle et al (2013).

The direct benefit to citizens from the regulatory activities is a general level of protection of their health. But can a more active approach be enabled? Can citizens contribute to gathering data of value to science and to management, and are there other plausible reasons for their involvement? Both top-down, and grassroot or bottom-up activities have been known to succeed in involving citizens, indicating that the citizens saw value in their involvement. Burke et al (2009) describe the concept of participatory sensing, and discuss some of its aspects. Boulos et al (2011) give a comprehensive overview of the technological challenges involved in making the participatory sensing happen.

In CITI-SENSE, we will use several methods to involve citizens and to provide them with means to both gather and retrieve information. By comparing a number of different situations (localities), we will have a better possibility to derive vital parameters of the information received from citizens. We mayalso be able to complement the current knowledge of air pollution and exposure.

2. TECHNOLOGICAL CAPABILITIES AND CHALLENGES

Technologies enabling ubiquitous monitoring of air pollution are available for a number of metrics related to chemical composition or physical properties: size-distributed mass in several fractions, total mass, visibility-related particles concentrations. Mead et al (2013), Jovasevic-Stojanovic et al (2013)give good examples of the technological capabilities.Current uses are described comprehensively in Snyder et al (2013). From the point of view of exposure related to ambient air and spatial and temporal representativeness, the metrics that are used range from central site or interpolated monitoring data, regional pollution levels predicted using air pollution dispersion models or measurements combined with air quality models, models that include satellite data, to statistical approaches combining modelling and measurement data.

Another set of technological challenges is in the field of information and communication technologies, covering providing data from sensors and data sharing between CITI-SENSE and other activities including the Global Observing Network of Networks GEOSS, and providing information to users/citizens using mobile phones or web applications. Some of the challenges are touched upon by Boulos et al (2013) and Burke et al. (2013). Many authors have documented the need for standardization, and several organisations including the OpenGeospatialConsortium (http://www.opengeospatial.org/) are providing the necessary organisational infrastructure within which such standards can be developed. CITI-SENSE builds upon such activities.

In CITI-SENSE, perhaps central in the effort to enable data sharing and use is the development of the core ontology network for citizen'sobservatories and applications (CITI-SENSE, 2013). Its goal is: "(...) to reconcile various initiatives in ontology development for the creation of city observatories apps". A starting point is the Semantic Sensor Network ontology developed in the context of the W3C incubator group on Semantic Sensor Networks and investigate possible extensions towards capturing aspects such as time, geography, city-related resources, etc. Besides, ontologies focused on the topics of CITI-SENSEcase studies will be developed in such a manner that they can be also applied in other similar contexts, that is, modularization will be considered as a key element in thisprocess.

Several questions need to be addressed: How do we deal with the data CITI-SENSE collect? And can it be gathered and provided in a standard way such that citizens and stakeholders can benefit or do we need to develop new concepts? We will develop a new CITI-SENSE ontology that will be used to annotate the data gathered by sensors, calculated data (over sensor data) and responses to questionnaires, with the aim to disseminate these data and to provide interoperability among these heterogeneous data sources. The dissemination will be achieved by the publication of the CITI-SENSE observatories dataset under the Linked

Data paradigm as open data, linking it to other linked datasets in the Linked Open Data Cloud, compatible with the INSPIRE Directive (http://inspire.jrc.ec.europa.eu/)which specifies how to share environmental data using common data specifications and internationally recognised open standards.

3. UNDERSTANDING USER NEEDS

Requirements of scientists and authorities are well understood, and there are continued efforts to meet them.Citizensrequirements and needs are much less understood. One way to study this issue is through involving citizens and their groups, employing "citizen's observatories". CITI-SENSE aims to develop a suitable concept, and build the citizens observatories, with the aim to empower citizens and citizens' groups to participate in environmental governance in order to support policy priorities and decision making and contribute to monitoring activities. This implies that we must apply state-of-the-art knowledge on what is effective in citizen participation and decision-making.

To enable effective citizen participation and involvement in CITI-SENSE we not only need to provide citizens with means to participate, but also todevelop methods for observing and studying citizen participation and methods to involve citizens in iterative development processes of the project tools. Citizen involvement should be regarded as a continuum from low involvement (citizens get relevant information) to high-involvement (they contribute environmental data and co-decide what will be done). A practical way of how stakeholders can be engaged and involved includes the use of online tools, crowdsourcing mechanisms, verification and integration of citizen-created data with public information, science and citizen participation and citizen-created visualizations and applications based on open data.

From the point of view of the citizen, it may seem important to know how the data the citizen contributes to the Citizen's observatory are used further, and if they are of value for assessments and research, e.g. in a way described by Lahoz (2013).

4. CITI-SENSE CASE STUDIES

The field work of CITI-SENSE is being done in a series of three so-called Empowerment Initiatives (EI) in the areas of (1) Urban Quality (2) Public Spaces from the point of view of their objective (thermal, ultraviolet radiation, noise) and perceived quality, and (3) Indoor Environment at schools. In all, nine cities are objects of investigation, spanning north-south and east-west of the European region.

An overview of the Urban Quality EI is presented in Table 1. Eight cities are involved, and an overview of the pollutants we will target is in Table 2. The aims of the individual urban case studies vary, but in general, we would like to investigate a set of questions, such as: Why are citizens (not) concerned about air quality?Why are citizens (not) concerned about their contribution to air pollution?Do citizens appreciate the value of good environmental quality?What will happen if citizens can measure and sense air quality and air pollution, and «see» their contribution to the environmental load?

Table 1. Overview of the CITI-SENSE Urban Quality Empowerment initiative.

Aims	Users	Physical Sensors	Social Sensors	Measurements
Improving quality of life in cities Identifying indicators Evaluating sensors Facilitating stakeholder interaction	Citizens • Activists • Sports • Health compromised Authorities	Low-cost sensors Static platforms Mobile platforms	Volunteer Information	Pollution Meteorology Noise Health parameters Biomarkers UV exposure

The Public Spaces EI is being developed in Vittoria-Gasteiz, ES, the Green Capital of Europe 2012. It aims at involvement of citizen's in the planning process, and undersanding the citizen's movements in the city. Parameters to be investigated are visual, acoustic and thermal comfort, urban well being. Physical measurements will involve own sensors/mobile collection of levels of selected gases (NO_2), temperature, noise, locality photos and exposure to ultraviolet radiation.

Table2. Environmental parameters suggested for monitoringin the EI Urban Quality
(PM_{opc}…will measure PM in one size fraction if a suitable sensor can
be integrated in the monitoring kit; ROS: Reactive oxygen species).

City	Environmental parameters			
Barcelona, ES	T+RH, Pressure, CO, NO_2, $PM_{opc,}$ SO_2	NO, O_3, CO_2, Noise	---	---
Belgrade, RS	T+RH, Pressure, CO, NO_2, $PM_{opc,}$ SO_2	NO, O_3, CO_2, Noise	---	$PM_{2.5,}$ ROS
Edinburgh, UK	T+RH, Pressure, CO, NO_2, $PM_{opc,}$ SO_2	NO, O_3, CO_2, Noise	---	---
Haifa, IL	T+RH, Pressure, CO, NO_2, $PM_{opc,}$ SO_2	NO, O_3, CO_2, Noise	VOC	TSP
Ljubljana, SI	T+RH, Pressure, CO, NO_2, $PM_{opc,}$ SO_2	NO, O_3, CO_2, Noise	VOC	
Oslo, NO	T+RH, Pressure, CO, NO_2, $PM_{opc,}$ SO_2	NO, O_3, CO_2, Noise		---
Vienna AT	T+RH, Pressure, CO, NO_2, $PM_{opc,}$ SO_2	NO, O_3, CO_2, Noise	---	---
Ostrava, CZ	T+RH, Pressure, CO, NO_2, $PM_{opc,}$ SO_2	---	VOC	PM

The Schools Indoor Quality EI is developed in four cities (Oslo, NO; Belgrade, SR; Ljubljana, SL; Edinburgh, UK). Good environmental quality is essential to good learning outcome. Understanding of factors that influence environmental quality indoors is thus essential. This EI works with school stakeholders including teachers and students, administration, maintenance personnel to develop a comprehensive solution combining monitoring of physical parameters in classrooms or other indoor spaces (selected air pollutants, radon radiation, selected physical variables), making these data available to stakeholders including students to increase their understanding of processess in the indoor environment and how the users/occupants influence those, and finally, enabling the schools to modify their occupancy behaviour and cleaning routines to improve the indoor environment.

5. CONCLUSIONS

The CITI-SENSE project is a four-year journey where we wish to develop solutions and provide suitable means that would enable citizens to participate in environmental decisions taken by authorities but also taken by the citizens, for the improvement of quality of life in cities. We also will investigate to what extent can citizens contribute useful data into global observing systems, and for use in atmospheric sciences. CITI-SENSE combines technological expertise in air quality monitoring, developing miniature sensor solutions, information and communication technologies, with expertise in disciplines relevant to citizen's empowerment and risk communication, including different disciplines of social sciences. Thus, it poses great challenges inside the consortium on interdisciplinary interactions. The project is organized as a matrix where field/case studies are done in nine cities (one matrix dimension) supported by methodological work (a second matrix dimension). This organization also poses challenges on communication as sharing of information is essential to success of the project.

After one year, the project is on tracks.Several types of air quality monitoring devices have been built and first data are already being collected. Methods were developed across all disciplines in the projects. While the first and second years are devoted to methods development and pilot studies, the third year of the project (2015) will see a Europe-wide Citizen's Observatories exercise. The progress of the project can be monitored on www.citi-sense.eu.

6. ACKNOWLEDGEMENTS

The project "Development of sensor-based Citizens' Observatory Community for improving quality of life in cities" (CITI-SENSE) is a Collaborative Project partly funded by the EU FP7-ENV-2012 under grant agreement no 308524.

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5.2 PARTICIPATORY AND UBIQUITOUS SENSING IN EXPOSURE SCINECE: RECENT ADVANCES

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Exposure science addresses human contact with chemical, physical, or biologic stressors[1] (EPA 2003; EPA 2011b) over space and time and the fate of these stressors within humans. Methods of exposure assessment depend on the situation. There are, however, two primary goals of exposure science: to understand how stressors affect human health, and to prevent or reduce human contact with harmful stressors (e.g., air pollution exposure) or to promote contact with beneficial stressors to improve public health (e.g., contact with park areas and green spaces).

Here weuse a framework for exposure science adapted from the U.S. National Academy of Science report “Exposure Science in the 21st Century” (Figure 1) (National Research Council, 2012). This framework reflects a view of the role of exposure science in human-health protection that is broader than the definition of exposure science. The major elements of exposure science are identified: sources of stressors, environmental intensity (such as pollutant concentrations), time–activity and behavior, contact of stressors and receptors, and outcomes of contact. This framework also highlights the role of upstream human and natural factors and the roles of both external and internal environments within exposure science. At the same time it alsomaintains that exposure is measured at some boundary between the source and receptor, and that dose is the amount of material that passes or otherwise has influence across that boundary to come into contact with the target system, organ, or cell to produce an outcome. This framework also recognizes the feedbacks inherent in exposure science such as how a diseased person may change his or her behavior in a way that may influence his or her subsequent exposure.

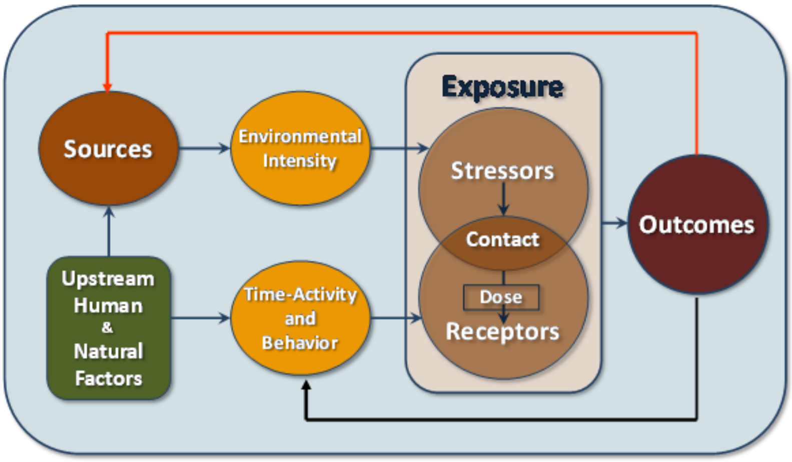

FIGURE 1 Core elements of exposure science. (National Research Council, 2012).

Exposure assessment is a major component of environmental epidemiology yet it has been and continues to be a major weakness in epidemiology. The main focus of many environmental epidemiology studies traditionally has been on a single chemical, biologic, or physical stressor. In reality, humans are exposed to multiple stressors at the same time, often with highly correlated patterns of spatiotemporal variation, making it is difficult to identify which stressor or stressors are associated with a particular outcome.

Due to the financial and logistical costs of personal monitoring, most epidemiologic studies have relied on surrogate estimates of exposure, usually focused on ambient conditions and assigned to the home location of study subjects. Although those exposure assignments have revealed important health risks, reliance on proxy methods may impart large exposure-measurement error. Depending on the exposure-error type, health-effect estimates may be attenuated and biased toward a null result, obscuring the true benefits of control measures.

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[1] The Environmental Protection Agency defines a stressor as “any physical, chemical, or biological entity that can induce an adverse response” (EPA 2011a).

Innovations from telemedicine are now spurring fields known as “ubiquitous”, “embedded”, and “participatory” sensing that may transform exposure science in epidemiological studies.

Reducing exposure error is critical for epidemiologic investigations. Previous air-pollution health-effects studies have underlined the importance of capturing spatial variability, particularly in urban areas (Logue et al. 2010; Bell et al. 2011). Accurate assessment of human exposures to atmospheric pollution requires knowledge of the spatial distribution of pollutants over cities on scales of 1-100 m (Chow et al. 2002). Improved resolution is expected not only to reduce exposure-assessment error, but generally to result in larger health-effects estimates. For example, Jerrett et al. (2005) applied kriging techniques to study the association between within-city $PM_{2.5}$ exposure gradients and mortality and found a substantially larger effect than previously reported with the city-average exposures.Yet many complexities exist in assessing exposure measurement error and the specific influence on health effects may depend on the relationship between the true and measured distributions (Szpiro et al. 2011).

Innovations in science and technology provide opportunities to overcome limitations that have led to exposure measurement errors and may guide exposure science in the 21st century to deliver knowledge that is timely and relevant to current and emerging environmental-health challenges. Telemedicine will increase the pace of innovation in scientific and technologic methods that will benefit the field of exposure science. In telemedicine, cellular-telephone technologies increasingly contribute to improving diagnostics and patient care and hence to improving our ability to anticipate the effects of exposures. The major societal investments occurring in telemedicine and related logistics fields have resulted in technological advances that have and will create beneficial spin-offs for exposure assessment in epidemiological studies. These innovations are now spurring fields known as “ubiquitous”, “embedded” and “participatory” sensing.

We define ubiquitous sensing as a network of embedded sensors, such as a dense array of air pollution or water contamination monitors that would have wide spatial coverage in urban areas. Similarly, a ubiquitous system may rely on remote-sensing instruments that continuously supply information on particular phenomena, such as surface temperature or aerosol optical depth, which has virtual global coverage. Participatory sensing is defined as a means of obtaining detailed information on personal and population exposures via volunteers who supply this data often in exchange for useful information that might allow them to better understand and prevent the harmful exposures they face. These two categories, however, should not be considered mutually exclusive as a participatory study with the use of cell phones combined with global positioning systems (GPS) and sensors could provide information that could be considered ubiquitous.

Embedded sensors are now being piloted in the city of Rome, Italy to help with tracking mobility patterns of pedestrians, bicyclists, and vehicles and for managing traffic flows. Given the role of traffic in air pollution, noise, and accident risk, better information on traffic and other modes of transportation are needed. Rome’s embedded sensor system relies on a Telecom Italia’s Localizing and Handling Network Event Systems (LocHNESs) software platform, which uses anonymous information on location from cell phone users in combination with embedded location tracking from public transit vehicles. The system is being tested to supply near real-time traffic monitoring and management information (Calabrese et al. 2011). Such information on traffic could be combined with models to estimate noise or air pollution levels throughout the city. The system can output data into a variety of formats, including a 40*40 m grid cell resolution showing levels of traffic congestion. LocHNESs illustrates how ubiquitous mobile phones can supply anonymous information on location that can be combined with embedded tracking networks on public infrastructure to deliver real-time data on environmental exposures.

Increasing availability of ubiquitous mobile devices—particularly smart telephones with motion sensing, GPS, and wireless capabilities—has created opportunities to develop new tools and methods to study and intervene to address sedentary lifestyles, obesity, and ambient risk factors, such as air pollution, noise, or ultraviolet radiation. One example of the potential is CalFit software. CalFit is an application that runs on mobile telephones that use the Android operating system. The software uses the accelerometry and GPS sensors that are typically built into all smart telephones to record activity counts and energy expenditure and the time and location in which an activity occurs. The device consists of a single telephone that can be carried and used as a normal telephone by participants in a study or by the general public. The software program has a single on–off switch for data-logging and, once turned on, will continuously collect data as a background service and not stop until turned off (Seto et al. 2010). Pilot studies testing CalFit with 35 free-living human volunteers in Barcelona, Spain, indicate that the software collects data on location and physical activity that compares well with commercially available stand-alone triaxial accelerometers (de Nazelle et al. 2011; Seto et al. 2011) When combined with dispersion or other models of ambient exposure, CalFit offers the potential for adjusting, for example, the dose of air pollution received by a person to account for exposure to air pollutants, rather than relying on exposure concentration in the home or workplace. The system is also capable of serving as a base station for other sensors that operate via Bluetooth radio to collect such data as air pollution, light, and noise.

CalFit and other cellular-telephone–based systems can also be used to implement context-specific ecologic momentary assessment (CS-EMA). CS-EMA measures real-time exposures and outcomes with sensors that are inside and outside the telephone. The system can communicate information, telling a person to respond to a survey when particular events are observed, such as a period of physical activity, exposure to air pollution, use of steroid inhalants, or consumption of particular food. Responding to these surveys provides opportunities to obtain important information about an exposure or outcome, such as mood, stress, behaviors, and other information (Intille 2007; Duntun et al. 2010).

Participatory sensing refers to systems of distributed data collection and analysis in which participants decide on what, where, and when to monitor in their environments (Mun et al. 2009). Such systems operate on various scales—for example, individual, group, urban, and global—depending on what is being measured (Burke et al. 2006). Participatory sensing systems often combine embedded and ubiquitous systems with Web-based applications that allow participants to share information on their exposures and to understand exposures of others in the participatory system.

One example of participatory sensing is the Personal Environmental Impact Report (PEIR) system that operates in Los Angeles, California (Mun et al. 2009). The system measures four main outcomes: exposure to fine particulate matter ($PM_{2.5}$), exposure to fast food outlets, output of transportation-related greenhouse-gas emissions, and output of transportation-related $PM_{2.5}$ emissions near sensitive receptors. PEIR relies on cellular-telephone locational and speed information and on a sophisticated activity-classification system that uses information from GPS, cellular-telephone towers, and data on land use and traffic. Activities are classified as walking or driving with a Markov chain algorithm.

Once activities are classified, exposures can be assessed through a near real-time dispersion model for $PM_{2.5}$ that combines the likely exposure levels and a person’s location to assign a likely concentration. People also can examine their exposure to fast food, generation of transportation-related $PM_{2.5}$ emissions near sensitive receptors, or their impact on transportation-related greenhouse gas emissions.

The PEIR system has been piloted by 30 volunteers. Respondents, using a Facebook application, can join a social network to review their exposures and emissions in comparison with those of others in the social network. The movement of the processed information into a continuing report that can generate information on exposures and impacts constitutes an innovative fusion of new media, such as Facebook, with mobile sensing platforms. For example, users have access to a weekly impact report and a locational trace of where they have been.

This paper provides a discussion of the various technological advances that will shape exposure assessment in the 21st Century. How these new technologies relate to the NAS framework for exposure science is shown in Figure 2. New developments in geographic information technologies are leading to rapid adoption of new information obtained from satellites via remote sensing (RS), and improved information on people’s location and physical activity obtained with global positioning systems (GPS) and related geolocation technologies. Many of these advances are integrated through geographic information systems (GIS)[2] that operate either through stand-alone computing platforms or through the World Wide Web. The increasing development of personal environmental monitors can be used in both ubiquitous and participatory sensing. As novel sensing technologies such as these become more widely available and more accurate, the need for models will remain, but the focus will shift from interpolation to exploitation of massive datasets. A key function of models is not just to provide point estimates of individual exposures but to quantify the uncertainty in exposure estimates and to understand measurement error in health analyses. The convergence of these scientific methods and technologies raises the possibility that in the near future embedded, ubiquitous, and participatory sensing systems will facilitate individual-level exposure assessments on large populations of humans or other species.

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[2] GIS is defined as a system for performing numerous operations involving the acquisition, editing, analysis, storage, and visualization of geographic data (Longley et al. 2005).

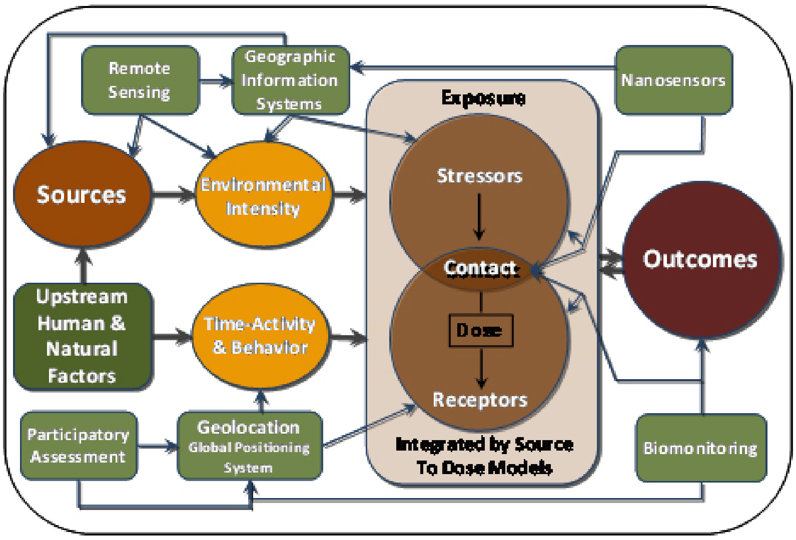

FIGURE 2 **Selected scientific and technologic advances considered in relation to the NAS conceptual framework. (National Research Council, 2012)**

We conclude with discussion of future challenges and trends. Participatory and ubiquitous sensing offer tremendous promise for improved exposure assessment, yet many challenges remain before these advances fundamentally change the way exposures are assessed in epidemiology. Protection of personal privacy, analysis of the voluminous “big” data generated by the sensors, and integration with other emerging methods from molecular epidemiology represent critical areas for research and development. These are active areas of research that will require extensive work to resolve over the next five to ten years.

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5.3 AVAILABILITY OF SMALL AND CHEAP SENSORS FOR INDICATIVE CITIZEN-BASED CONTINUOUS MONITORING OF RESPIRABLE PARTICULATE MATTER

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ABSTRACT

Respirable aerosol particles(RPM) present in outdoor and indoor environments are a health hazard. Their concentrations can vary with steep gradients on short temporal and spatial scales, and their chemical composition and physical properties vary considerably. For characterization of the hazard as well as for identification of mitigation measures with most relevance to health, it is important to better capture these differences. Existing networks of aerosol particle measurements have as their objective compliance monitoring related to current air quality legislation, and thus consist of limited number of monitoring stations not designed to capture the strong heterogeneity in particles that exists in numerous outdoor and indoor locations. In addition, current 24-hour and annul air quality standards of particulate matter are based on the total mass of particles with diameters less than 10 and 2.5 μm, and do not take into account other characteristics, such as particle size or total number. As a consequence, the existing monitoring networks are limited for personal exposure assessment needed for hazard evaluation. Technological advances have led to development of new technologies for assessment of several of the key particle properties based on small portable devices with low-cost chemical or physical sensor technologies. In this paper, we review availability, characteristics and selected application trials of such small and cheap sensors and monitors. These devices may be used for building additional assessment networks and for better determination of indicative levels of exposure to RPM for individuals as well as for larger populations. We present an analysis of sensors characteristics with respect to limit of detection relevant to the current EU legislation and WHO guidelines.

1.INTRODUCTION

A number of epidemiological studies have demonstrated that respirable particulate matter (RPM) may act as a health hazard causing respiratory mortality and morbidity [e.g., Pope and Dockery, 2006]. In order to protect the living environment and health of citizens, it is of major interest to obtain the levels of RPM in the ambient air with high temporal and spatial resolution. Current air quality monitoring networks aim at compliance monitoring and consist of a limited number of stations using standardized QA/QC protocols. These reference and other ambient PM and gaseous monitoring units, that are in use by communities and research studies, are neither able to cover large areas nor to be used as personal monitors for widespread measuring of location-specific levels of pollutants. Small and cheap sensors represent an opportunity for building sensor networks for monitoring indicative levels of the ambient RPM. Together with appropriate infrastructure, the sensors have a potential to offer unique opportunities for citizen-participatory sensing.

Prior to using low cost RPM sensors in practice, their characteristics need to be assessed. It may be necessary to perform complex procedures of calibration checks prior to deployment to determine a list of various parameters such as: (a) detection limit, (b) concentration range, (c) temperature range, (d) humidity influence, (e) stability of response –comparability and variability between individualsensor devices (f) concentration differences and calibration factor between sensor device and reference PM monitor. For citizen-based continuous monitoring when a device is intended for extensive use in measuring location-specific (static or mobile use) or personal-specific indicative levels of PM, one of the most important issues is comparability, or variability of response between devices used by each person.

This paper gives an overview of available cheap miniature RPM sensors that offer indicative information about RPM. They are currently either fully commercially available or in a late development phase. Furthermore, an analysis of sensors characteristics is presented, in particular with respect to the limit of detection relevant to the current EU legislative [EC, 2008] and WHO [2005] guidelines regarding the levels of particulate matter.

2. CURRENT STATE OF RPM ROUTINE AND SUPPLEMENTARY AMBIENT AIR MONITORING NETWORKS

For characterization of PM in ambient air there are important properties that must be taken into account: (i) total mass concentration of selected fractions of particulate matter, (ii) particles number concentration, (iii) particles size distribution, (iv) daily variations of concentrations, peak values (v) chemical composition.

Based on evidence e.g. from epidemiological studies, the WHO proposes recommended values for short (24h) and long-term exposure (1 year) to PM_{10} and $PM_{2.5}$ [WHO, 2006]. EU standards and objective for PM monitoring,summarized in Table 1, concern limit and target values of PM_{10} on 24h and annual basis and $PM_{2.5}$on annual basisas well as annual average chemical contents of selected species(lead, arsenic, nickel, cadmium, and PAHs) in PM_{10}[EC, 2008].US EPA [2012] paid more attention to $PM_{2.5}$and set limit values for both 24h and annual concentration of fine particulates, and their content of lead. Methods that fulfill requirements for monitoring PM air pollutionare based either on collecting data with reference samplers and weighing of the mass of collected PM, or on using reference-equivalent continuous instruments.

Table 1. EU standards and objective for PM monitoring, [EC, 2008]

PM fraction	Concentration	Averaging period	Legal nature	Permitted exceedances each year
PM_{10}	50 µg/m^3	24 hours	Limit value entered into force 1.1.2005**	35
	40 µg/m^3	1 year	Limit value entered into force 1.1.2005**	n/a
$PM_{2.5}$	25 µg/m^3	1 year	Target value entered into force 1.1.2010	n/a

It is well known that concentration of RPM also vary on daily and seasonal basis. To improve understanding of the health effects associated with various time periods of PM exposures, including not only short-term (daily or multiday) and chronic (months to years) exposures, but also peak PM exposures (<24 h), it is necessary to rely on continuous monitoring instruments.

Identification of variability of particulate matter level in outdoor and indoor environment is a key factor in personal exposure assessment. Beside temporal variability, it is necessary to provide data with high spatial variability. For example, it has been shownthat immediately downwind of or adjacent to streets and roads with densetraffic, PM concentrations (measured as different metrics including Black Carbon and Ultra FineParticles) can vary significantly within only tens to hundreds of meters from sources of pollution. Similar situation occurs during heating session in the area with dense sources of local heating using fossil fuels, wood or other biomass. Moreover, there are large differences in PM levels in indoor environment, where people spend 90% of time: this depends on location characteristics, type of dwellings and behavior related to e.g., tobacco smoking.

The monitoring paradigm is changing. Using expensive, complex, stationary equipment, providing comparable data but limiting who collects data, why and what data are collected, and how data are accessed, is increasingly supplemented with the low cost, small and easy-to-use air pollution monitors and sensors which may be widely used, giving opportunity to provide high-time resolution data in near real-time [Paprotnya et al, 2013].

3. CURRENT STATE OF RESPIRABLE PARTICULATE MATTER LOW-COST SENSORS

Low cost air pollution sensors can be separated according to principle they employ to determine the concentrations of particulate matter. The cheapest devices for PM detection fall in range of from 10 to 1000 EUR in price and are about one tenth in size of the large laboratory based instruments. Commercially available low cost monitors and sensors utilized within RPM detection, presented in Table 2, are particle counters that work on light scattering principle. Up to now, commercial optical sensors manufacturers claim to detect and count PM of size above 0.5 μm and even 0.3 μm, and then covert the count to mass.

Sensors that are the cheapest as Sharp GP2Y1010 [Sharp, 2006] and, Syhitech DSM501 [Appolo,2013], need interfacing with an external microcontroller and display. The price of Shinyei [2010] and Dylos monitors [Dylos, 2013] with built in microcontroller and on screen display is in the range of 200-1000 EUR. M-Dust Monitor has analogue output of data and an external PM_{10} or $PM_{2.5}$ filter for control when replacement is necessary or when the vacuum pump requires a re-calibration [myHermessSrl, 2013].

Table 2. List of commercially available low-cost PM sensors and monitors [Apollo, 2013; Dylos Corporation, 2013; myHermessSrl. 2013; NIDS Sensor Technologies, 2005; NIDS Sensor Technologies, 2006; Shinyei, 2010; Sharp Corporation, 2006]

	Sensor	Country of origin	Dimensions	Weight	Concentration Range	Particle size Range	Temp range	Power	Price
1	Sharp GP2Y1010	SHARP, **Philippines**	46x30x18 (mm)	16g	0-0.6 mg/^{3}	unknown	-10 ~ +65	20mA	11-13.5 EUR
2	SYhitech DSM501	AppoloOptronicsCo.Ltd, **China**	45x59x20 (mm)	25 g	0-1.4 mg/m^3	>0.7µm	-10 ~ +65	90mA	7$
3	Shinyei PPD42NS	Shinyei Technology , **Japan**	59x49x22 (mm)	24 g	0 - 800 000 Pcs/ft^3	1µm or 2.5µm	0 ~ 45℃	90mA	200$
4	Shinyei PPD 20PV	Shinyei Technology, **Japan**				n/a	n/a		n/a
5	Shinyei PPD 60PV	Shinyei Technology, **Japan**	88x60x22 (mm)		0 - 2 000 000 Pcs/ft^3	>0.5µm	n/a		420$
6	Shinyei AES-1	Shinyei Technology, **Japan**	90x90x23 (mm)	120g	300 – 300 000 Pcs/ft^3	> 0.3µm -10µm	0 ~ +40℃	300 mA	1100$
7	Shinyei AES-4	Shinyei Technology, **Japan**	90x90x23 (mm)	120g		> 0.3, > 0.5, >1, >2.5 (5.0) µm	0 ~ +40℃	300 mA	n/a
8	NIDS-PSX-01D	NIDS Co. Ltd, **Korea**	50 x 2 x29 (mm)	21g	0.1 ~ 2.0mg/m^3	1µm	0 ~ +40℃	90mA	n/a
9	NIDS-PS02C-PWM	NIDS Co. Ltd, **Korea**	59 x 45 x20 (mm)	21g	0.1 ~ 2.0mg/m^3	1µm	- 10~+45℃	90mA	n/a
10	NIDS-PS02F	NIDS Co. Ltd, **Korea**	n/a	n/a	n/a	n/a	n/a	n/a	n/a
11	Dylos DC1100	Dylos Corporation (Riverside California)**USA**	7x 4.5x3 (in)	1,2 lb	n/a	>0.5and >2.5µm			199$
12	Dylos DC1100 PRO	Dylos Corporation (Riverside California) **USA**	7x 4.5x3 (in)	1,2 lb		>0.5and >2.5µm			260$
13	Dylos DC1700	Dylos Corporation (Riverside California)**USA**	7x 4.5x3 (in)	1,2 lb		>0.5and >2.5µm			425$
15	M-DUST II	**Italy**	116.5x144x55 (mm) Vacuum pump 32x51x74 (mm) Sampling head Ø 51 x 26 (mm)	750 g	0-80 µg/m^3	0.4<PM<2.5µm	-20~ +40℃		-300 EUR -100 EUR (kit with 120 filter), 40 EUR pump re-calibration every 50h
16	M-DUST II	**Italy**	116.5x144x55 (mm) Vacuum pump 32x51x74 (mm) Sampling head Ø 51 x 26 (mm)	750 g	0-2.5 mg/m^3	0.4<PM<10µm	-20~ +40℃		-600 EUR -100 EUR (kit with 100 filters), 40 EUR pump re-calibration every 50h

Budde et al compared concentrations of PM measured with the Sharp GP2Y1010 with a TSI DustTrak DRX 8533 and found that at least coarse determinations regarding the particulate load are possible with very simple PM sensors [Budde, 2013]. Recently, the same team tried to incorporate particulate matter sensor Sharp GP2Y1010 in a mobile telephone to be used as a PM dosimeter [BuddeBusse, Beigl, 2013]. First results correspond very well to the TSI DustTrak, down to concentration levels of ~10 mg/m^3, which is enough to detect smoke or coarse PM, but not sufficient for the detection of typical fine particulate matter concentrations.

In Philadelphia, a preliminary screening system was developed with the ambition to be a cost effective alternative to the current method of evaluating the amount of particulate matter in ambient air [Arling et al, 2010]. As part of the system, software was incorporated in the platform that converts the output of the used Dylos DC1100 Pro monitor, from particles/.01 ft^{3}to µg/m^3. The conversion is an approximation, based on the following assumptions: (1) all particles are spherical, with a density of 1.65E12 µg/m^3 (2) Mass median diameter is different for particles in range less than $PM_{2.5}$ and for particles in range $PM_{2.5}$ -PM_{10}. (3) Application of a correction factor for different ranges of humidity.

Study of Northcross et al [2013] shows that modified DYLOS monitor, i.e., particle counter, with calibration, may be used for accurately estimating particle mass in a wide range of settings:

- Modified DYLOS pro into a system called the Berkeley Aerosol Information Recording System (BAIRS), performances were compared against standard commercial instruments (a) in chambers using polystyrene latex spheres, ammonium sulphate, and woodsmoke, and (b) in an urban ambient setting.

- Overall it was found that the limit of detection of the BAIRS is less than 1 µg/m^3 and the resolution is better than 1 µg/m^3 for $PM_{2.5}$.

- The BAIRS sizes small (<0.5 mm) particles, and is able to accurately estimate the mass concentration of particles of varying composition including organic, inorganic, and ambient particles. It is able to measure concentrations up to 10.0 mg/m^3.

Low-cost devices that directly measure particle mass concentrations are in developing phase. They are based on principles such as the FBAR (film bulk acoustic resonator) and QCM (impaction on piezoelectric sensors) [paradigm]. Recently published results by Paprotnya et al [2013] about novel, portable MEMS PM monitor (with Film-Bulk Acoustic Resonator – FIBR) are paving the way to create a low cost low power air quality monitoring system that may effectively detect a wide range of PM including even fractions smaller than what currently available commercial sensor devices can detect. Disadvantage of such devices is sensitivity to changes in temperature and relative humidity.

4.CONCLUSIONS

Suitable sensor technologies available today can be used by the public and provide highly time-and-space specific results of known quality. This information has the potential to contribute significantly to information vital for exposure assessment and thus hazard mitigation. To enable wider use of such sensors and data they collect we need however to develop appropriate infrastructure and quality assurance and control systems.

4.ACKNOWLEDGEMENTS

The project “Development of sensor-based Citizens’ Observatory Community for improving quality of life in cities” (CITI-SENSE) is a Collaborative Project partly funded by the EU FP7-ENV-2012 under grant agreement no 308524.

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5.4 A PROPOSED WEB-BASED TOOL FOR ACTIVE COMMUTERS TO MITIGATE THEIR EXPOSURE TO PARTICULATE MATTER IN URBAN ENVIRONMENTS; A COMPONENT OF THE CITI-SENSE BARCELONA CASE STUDY

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ABSTRACT

Bicycle commuting is becoming more popular in urban environments like Barcelona, Spain, due to initiatives increasing the commute modal share of bicycles and increased new bicycle sales. However, in Barcelona, levels of traffic-emitted pollution, including particulate matter (PM), are among the highest in Europe, posing a public health risk. The aim of this initiative is to provide a smartphone and web-based information service for bicycle commuters to make an informed route choice in regards to air quality withexpected consequential reduced exposure and health impacts.Forty static sensor nodes will be strategically deployed around the city of Barcelona. Temporally-dynamic land-use regression (LUR) modeling will be performed to create a near-real-time map layer of urban environmental health indicators, including PM. Bicycle commuters utilising the web-based tool may reduce their exposure to air pollution such as PM by identifying a bicycle commute route that may be of higher air quality than their typical/fastest route, consequentially making an informed-decision to mitigate their exposure to PM.

1. INTRODUCTION

Bicycle sales are surpassing those of motor vehicles in Spain (Association of the European Two-Wheeler Parts' & Accessories' Industry 2012). Adding to the recent increase in the popularity of bicycle commuting, the local government of Barcelona is introducing initiatives to increase the commute modal share of bicycles, such as extending the bicycle lane network and supporting a public bicycle sharing scheme(Ajuntament de Barcelona 2012). Meanwhile, in Barcelona, levels of traffic-emitted pollution, including particulate matter (PM), are among the most highly-concentrated in Europe(Wang et al. 2013).Importantly, population-wide exposure to traffic-related air pollution has been linked to cardiovascular mortality (Beelen et al. 2009) and lung cancer risk (Beelen et al. 2008). Therefore, poor air quality conditions for the increased number of bicycle commuters may pose a public health risk.

Bicyclists may have the lowest trip-weighted ultrafine particle (UFP; the most concerning and relative particle size emission range) exposure concentrations compared to the other most common modes of transport (Knibbs et al. 2011). Further, cost-benefit analysis of bicycling, including the positive of increased physical activity and the negative of heightened pulmonary ventilation, has highlighted that the benefits of such activity can outweigh the risks (de Hartog et al. 2010; Rojas-Rueda et al. 2011). However, the commute route that a bicyclist chooses may vary the exposure level to traffic-related emissions (Cole-Hunter et al. 2012; Cole-Hunter et al. 2013) and therefore a route of lower exposure may facilitate the greatest gains in physical activity.

LUR-based models have previously been successfully produced, such as in the European-wide ESCAPE study (Eeftens et al. 2012; Wang et al. 2013). From the ESCAPE study, an LUR-based model is currently available for Barcelona (among other cities in the same study) that can be temporally-adjusted with input from existing air monitoring stations in the area. Therefore, with information on the time and location of an individual (for example a bicycle commuter), the level of exposure can be estimated. Further, more accurate estimate considering pulmonary ventilation rates may be obtained when including accelerometry data which is becoming readily-available from smartphone (and in-built accelerometer) use.

Previously, a web-based route planning tool aiming to reduce bicyclists' exposure to traffic-related NO_2 using spatial monitoring data has been developed in Montreal, Canada; theoretically, this tool facilitated a significant reduction in cumulative nitrogen dioxide (NO_2) exposure by advising users to take the 'cleanest' rather than the shortest route (Hatzopoulou et al. 2013). Accordingly, an initiative is proposed with the objective of providing a smartphone and web-based information service (or 'tool') for bicycle commuters to make a dynamic, informed route choice in regards to air quality with consequential reduced exposure and health impacts.

The main aims of this initiative are to:

1) Strategically-deploy and validate ‘cheap’ and portable static node PM sensors;
2) Feed validated PM readings into near-/real-time land-use regression (LUR) model; and,
3) Create and validate (with mobile node sensors) a smartphone-/web-based tool for user group access.

2. METHODOLOGY

Initially, in collaboration with the local and state government of Barcelona, Catalunya, a limited number of GeotechAQMeshstatic sensornodes <http://www.geotechuk.com/products/outdoor-air-quality/aqmesh.aspx> have been deployed with air monitoring station instruments to validate the AQMesh output data to the Envirologger server<http://envirologger.com/aq_mesh>. The data being collected by the battery-powered AQmesh nodes, transmitted to the Envirologger server via GPRS, will be processed with correction algorithms and converted to absolute values. Once data output has been validated in temporally-dynamic environmental conditions such as at the highly-influenced motorised traffic site of Palau Reial proximal to Diagonal Avenue, Barcelona (see Figure 1), dynamic land-use regression (DLUR) modeling will be performed and adjusted in near-real-time to create a continuously-updated map layer of urban environmental health indicators, including PM and other motorised traffic-related emissions such as CO_2, NO_2, and noise.

Figure 1. Temporally-dynamic environmental data validation will occur at the highly-influence motorised traffic site of Palau Reial proximal to Diagonal Avenue, Barcelona.

Feeding into this model will be data from the 40 static sensor nodes (measuring CO_X, NO_X, O_3, $PM_{2.5}$ and noise, as well as temperature, relative humidity and atmospheric pressure) deployed around the city of Barcelona following a deployment strategy previously established with the European Union’s Seventh Framework Programme Theme study ‘European cohort on air pollution’ (ESCAPE) (Brunekreef 2008). The ESCAPE project measured concentrations of $PM_{2.5}$, PM_{10}, NO_2, NO_X, noise in 20 sites of Barcelona (and other cities) in 2009 to establish LUR models for assessing small-scale spatial variation in air pollution concentrations and estimating individual exposure for participants of cohort studies. To improve the accuracy of this LUR modeling, a range of GIS-derived predictor variables (including traffic intensity, population, and land-use) are evaluated to model spatial variation of annual average concentrations to assist model development.

Previously, Hatzopoulou and colleagues have used a back-end ArcGIS server to compute the shortest-distance and lowest-NO_2 alternative route for potential bicycle trips in the city of Montreal (Hatzopoulou et al. 2013). A server plots the shortest-distance and alternative lowest-NO_2 routes according to input origin and destination addresses on a NO_2 LUR model layer (see Figure 1 for example of Hatzopolou et al. 2013). The outcome of this calculation is the provision of hypothetical advice on a map interface of the route of shortest distance and also the route of lowest NO_2 levels (see Figure 2 for example of Hatzopolou et al. 2013).

Citizens that frequently bicycle commute will be engaged to identify and evaluate the contemporary environmental health issue of in-commute exposure to traffic-emitted PM. Engagement will include enquiry to perceived risk of air pollution and benefit of a tool that reduces exposure to air pollution and associated risk (see Figure 3 for illustration of end-to-end information chain and proposed web-based tool, courtesy of the European Service Network).

Click on the map to define the starting and ending points of your trip.

The shortest route and the cleanest route will be shown. The cleanest route is the one over which the least amount of NO2 would be inhaled.

Additional clicks will extend the route.

	🟦	🟩
Distance (km)	15.67 (-4.9%)	16.43 (+4.9%)
Accumulated NO2 (km.ppb)	224.70 (+19.4%)	188.18 (-19.4%)
Avg NO2 along route (ppb)	14.34 (+25.2%)	11.45 (-25.2%)

Figure 2. Previous theoretical example of web-based tool: (a) Commute routes by origin to destination on land-use regression (LUR) model to calculate commute exposure for suggested 'quickest' or 'cleanest' route (Hatzopoulou et al. 2013); (b) The user interface with input for addresses of commute origin and destination to estimate both the shortest and the 'cleanest' route.

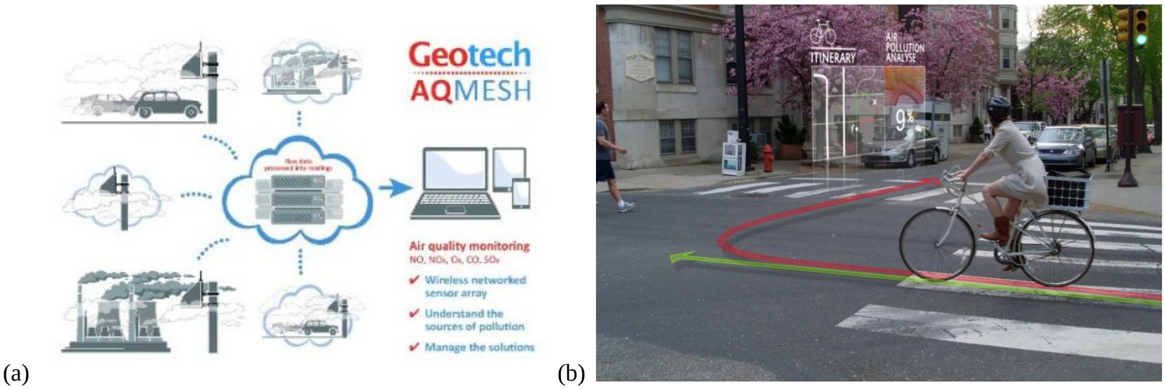

Figure 3– End-to-end web-based tool for active commuters to mitigate their exposure to particulate matter in urban environments: (a) the GeotechAQmesh static sensor node data input and server processing; (b) thematic of the CITI-SENSE Barcelona case study web-based tool.

3. EXPECTED RESULTS AND DISCUSSION

The static sensors will facilitate LUR modeling, temporally-adjusted (hourly) and complementing existing air monitoring network information, to produce advice for citizens via software applications. The web-based tool will be created using the Google Map engine and a temporally-adjusted LUR model map layer to inform bicycle commuters of the cleanest route (e.g. as an alternative to the quickest route). Citizen enquiries with the online tool may be anonymously-logged to evaluate the amount of exposure reduced, and the time added, between commute route choices of the quickest and cleanest route for evaluation of the tool's efficacy. The bicycle commuter user groups, Barcelona city council and bicycle advocates will assist the development, and long-term sustainment, of the final product via sought feedback.

In summary, the expected outcomes of this CITI-SENSE Barcelona Case Study initiative are to:

1) Facilitate LUR PM modeling, temporally-adjusted (hourly) and complementing existing air monitoring network information
2) Produce advice for citizens via software applications; to inform active commuters of the cleanest route (as alternative to quickest route)
3) Estimate exposure reduced, and the time added, between commute route choices of the quickest and cleanest route dissemination
4) Involve local city council and bicycle/environmental advocates, to improve quality of life for bicycle commuters and all residents

4. CONCLUSIONS

Bicycle commuters utilising the web-based tool may reduce their exposure to air pollution such as PM by identifying a bicycle commute route that may be of better air quality than their typical/fastest route, consequentially making an informed-decision to mitigate their exposure to PM in while performing the daily bicycle commute to their place of study or work.

5. ACKNOWLEDGEMENTS

The authors would like to acknowledge the CITI-SENSE Consortium for their contribution towards the development of the proposed web-based tool, and the ESCAPE Consortium for their provision of intellectual property without which the proposed web-based tool would not be possible. Further, the authors would like to acknowledge the Seventh Framework Programme of the European Commission, as CITI-SENSE is a Collaborative Project partly funded by the EU FP7-ENV-2012 under grant agreement n.308524.

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5.5 TO SONICATE OR NOT TO SONICATE: THE INFLUENCE OF SONICATION ON CHEMICAL COMPOSITION OF PARTICULATE MATTER

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ABSTRACT

A common means for particle collection is sampling onto filters. If further chemical or toxicological analysis is desired in most of cases the particulate matter (PM) needs to be extracted from the filters. Ultrasonic agitation (sonication) is a very commonly used method for extraction of PM from the filters. Sonication can be performed either by immersing a sonication probe into the sample solvent mixture or placing the sample solvent mixture into a sonication bath. Extraction times are generally between 10 min and 1 hr. The energy of ultrasonic waves causes formation and collapse of tiny cavitation bubbles or cavities in the solution. Inside the collapsing cavities the temperature can reach close to 5000 K and pressure can reach several hundred atmospheres. Such conditions lead to pyrolysis of the molecules present inside the cavitation bubbles (gases dissolved in the liquid and solvent vapours), which results in production of free radicals and new compounds formed by reactions with these free radicals. For example, sonication of water will result in generation of hydroxyl radicals in water, which is the main oxidant in the atmosphere. Therefore, extraction of PM off the filters using sonication technique could result in chemical changes as well as thermal degradation of PM collected onto filters.

Keywords: sonication, radicals, organic PM

1. INTRODUCTION

Ultrasound is a sound wave with a frequency greater than 20 kHz and it is responsible for a great number of physical and chemical effects. The effect of ultrasound in liquid medium was first recognized almost 100 years ago but bigger interest in sonochemistrystarted in 1960s, when ultrasonic cleaning baths became popular for cleaning laboratory glassware, forming dispersions and cell disruption. Since then, sonochemistry has been mainly used in synthesis (organic and inorganic), polymer chemistry (initiation of polymerization and degradation) and in the last 30 years there has been an increased interest in the use of ultrasound to destroy organic pollutants present in water and/or wastewater, as this approach is safe, clean and does not cause secondary pollution.

In this article, a short review of sonication technique and its radical-generating capacity will be given, as well as an overview of implications it could have on organic PM. It will also provide recent evidence demonstrating radical generation upon sonication.

1.1. Fundamentals of Ultrasonic Irradiation

When ultrasound propagates through a liquid it produces an alternating compression and rarefaction of the liquid being irradiated, resulting in positive and negative pressures being exerted on the liquid. During rarefaction, when a large negative pressure is applied to the liquid, the average distance between the molecules increasesand the liquid breaks down, resulting in creation of voids or cavities. The cavitation bubble contains gases, solvent vapour and any volatile substance present in the liquid.

Acoustic cavitation can be divided into two types, stable and transient.Stable cavities oscillate radially about some equilibrium size for many acoustic cycles, whereas transient cavities grow with each acoustic cycle until they reachan unstable size and violently collapse during the compression part of the wave. It was found that this size at which cavities collapse depends on the liquid and the frequency of sound; for example, at 20 kHz this critical size is ~ 170 μm[1] During the collapse the temperature and pressure within the cavity become extremely high, around 5000 K and 500 atm, respectively[2].Several factors affect acoustic cavitation, such asreaction temperature, hydrostatic pressure, ultrasonicfrequency, acoustic power, the nature of dissolved gases and the physicochemical properties of the solvent. Cavities are more readilyformed when using a solvent with a low viscosity, and low surface tension and high vapor pressure, but theintensity of cavitation is greater when using solventswith opposing characteristics (i.e., low vapor pressure,high viscosity, and high surface tension).At very high frequencies (i.e. several hundred kHz), the cavitational effect is reduced, so in thepast, most sonochemical reactions were carried out atfrequencies between 20 and 50 kHz. Lower frequency ultrasound producesmore violent cavitation (i.e. higher localizedtemperatures and pressures at the cavitation site),but higher frequency ultrasound can actually increase thenumber of free radicals in the system because, despite the less violent cavitation (due to shorter cavity lifetime and, thus, smaller maximum cavity size), there are more cavitationalevents and, therefore, more opportunities for free radicals tobe generated[3].

1.2. The Chemistry of Ultrasonic Degradation

High local temperatures and pressures within collapsing cavities (both stable and transient) are considered to be responsible the chemical effects of ultrasonic irradiation.Sonochemical reactions can happen at three different regions: interior of gas bubbles, thin liquid layer between the collapsing gas bubble and the bulk solvent and the bulk of the solution. As a result of extremely high temperature and pressure, interior of the gas bubble is like a micro combustion chamber wherepyrolysis of the molecules present inside the cavitation bubbles occurs (gases, solvent vapour and any volatile species present in the solution). When water is used as a solvent, such conditions will lead to the formation of highly reactive species such as hydrogen atoms and hydroxyl radicals. If molecular oxygen is present, oxygen atoms will be formed as well. The formation of H atoms and OH radicals in sonolysis of water has been confirmed by an Electron Spin Resonance (ESR) and spin-trapping studies [4]. They are generated via the following reactions:

$$H_2O \rightarrow H\cdot + OH\cdot$$
$$2H\cdot \rightarrow H_2$$
$$H\cdot + O_2 \rightarrow HO_2\cdot$$
$$HO_2\cdot + HO_2\cdot \rightarrow H_2O_2 + O_2$$
$$2OH\cdot \rightarrow H_2O_2$$
$$2OH\cdot \rightarrow H_2O + O\cdot$$
$$H\cdot + H_2O_2 \rightarrow OH\cdot + H_2O$$

These radicals can attack solute molecules or combine o form H2, H2O2 or water. If there are no hydroxyl radical scavangers, the most common reaction upon sonolysis of water is dimerisation of the hydroxyl radical or hydrogen-peroxyl radicals producing hydrogen peroxide[5].

The second region is the thin liquid layer immediately surrounding the collapsing cavity, which has been estimated to extend around 200 nm from the cavity surface and to have the temperature of around 2000 K[6]. This layer contains less volatile species and any possible surfactants. Thermolysis and radical abstraction reactions occur in this region and oxidative degradation by hydroxyl radicals may take place if solutes are present in sufficiently high concentrations. If the solute is not volatile enough to enter this region, the reaction may not be enhanced by the use of ultrasound.

The third region is the bulk liquid, where no primary sonochemical reactions occur, although a small portion of free radicals produced in the cavities or at the interfacial region may move into the bulk liquid and react with the compounds present there.

The sonolytic production of free radicals in aqueous mixtures of solutes with vapor pressure higher than water (e.g. acetone, acetonitrile, methanol, ethanol) has also been demonstrated previously using the ESR in combination with spin trapping [7, 8], where in addition to hydrogen atoms and hydroxyl radicals, carbon-centered radicals were also found. Cavitation can occur in organic solvents as well. The sonolysis of organic liquids (e.g.dimethylformamide, methylformamide, dimethylacetamide, toluene,*n*-alcohols, *n*-alkanes, cyclohexane, dioxane, and tetrahydrofuran) has also been investigated previously using ESR and spin trapping [9]. Various C-centered and N-centered radicals (depending on the liquid) were identified during exposure of argon saturated organic liquids to 50 kHz ultrasound.

1.3. Degradation of Organic Compounds by Ultrasonic Irradiation

Over the last three decades ultrasonic irradiation has been studied extensively in the context of removing organic compounds from wastewaters. The compounds studied include aromatic compounds, such as phenol, chlorophenols, benzene, toluene, xylene, polycyclic aromatic hydrocarbons (PAHs), then chlorinated aliphatic hydrocarbons, alcohols, explosives, herbicides, pesticides, organic dyes and other organic compounds (reviewed in [10]). The controlling mechanism for the destruction is usually dependent on the compound in question as well as the cavitational intensity, which depends on the operating conditions of the ultrasonic reactor. Pyrolysis within collapsing cavities plays the dominant role in the degradation of hydrophobic and volatile compounds, while the polar and less volatile compounds (e.g. phenol, chlorophenol, etc.) degrade mainly by reaction with OH radicals in the bulk phase or in the interfacial region between the collapsing cavity and the bulk solution, depending on their hydrophobicity. Degradation rate of non-volatile compounds is generally lower than for volatile compounds as volatile compounds are more easily transferred into interior of a cavity [11]. The time scales of treatment reported in the literature are generally in the range of minutes to several hours for complete degradation [10].Even though ultrasonic irradiation is effective in degrading organic pollutants, total mineralization (degradation to CO_2 and H_2O) is difficult to achieve with ultrasound alone, not even after several hours of ultrasonic irradiation.

Similarly to degradation of organic compounds in wastewaters, extreme temperatures and pressures created in the interior of the collapsing bubbles could induce changes in the chemical composition of the material collected onto filters. Mutzel et al have found that 15 min ultrasonic agitation causes increase in PM-bound peroxides and degradation of some Secondary Organic Aerosol (SOA) compounds[12]. Despite this, sonication is still commonly used method for extraction of PM collected onto filters for subsequent chemical and toxicological analysis.

2. METHODOLOGY

Chemicals: Three molecular probes commonly used to detect Reactive Oxygen Species (ROS) were used to investigate the generation of radicals upon sonication of water, ethanol/water mixture and dimethyl sulfoxide (DMSO):dithiotreitol (DTT), dichlorofluoresceindiacetate(DCFH-DA) and 9,10-bis(phenylethynyl)anthracene-nitroxide (BPEAnit), respectively. While DTT and DCFH-DA are both commercially available, BPEAnit was synthesized in our laboratory [13]. DCFH-DA was dissolved in 50 mL 10% ethanol/90% water (v/v) to get concentration of ~10 μM and 30 min prior to sonication was treated with 5 mL of 0.01 M NaOH in order to cleave diacetate groups (i.e. to generate dichlorofluorescein (DCFH)). Just before sonication, horseradish peroxidase (HRP) was added to the DCFH solution to catalyze the reaction between DCFH and ROS species. Concentration of BPEAnit in DMSO was ~ 10 μM, while concentration of DTT in water was ~ 1 mM.

Sonication experiments: Sonication was performed by placing a reaction flask in an ultrasonic bath (ElmasonicS30(H)) with a frequency of 37 kHz and power of 80 W.

Spectroscopy measurements: Fluorescence emission of BPEAnit and DCFHwas measured using a Varian Cary Eclipse spectrofluorimeter. In case of BPEAnit excitation wavelength was set to 430 nm, whereas in case of DCFH excitation wavelength was set to 485 nm. Absorbance spectra of DTT were measured using a Varian Cary 50 UV-VIS Spectrophotometer. Fluorescence and absorbance spectra were recorded at various sonication times, ranging from t = 0 min to t = 60 min

3. RESULTS AND DISCUSSION

Sonication of BPEAnit in DMSO results in an increase of fluorescence emission of BPEAnit with increase of sonication time (**Figure 1**). The increase of fluorescence indicates that BPEAnit has reacted with radicals or ROS. Previously SO_3^{2-} was identified as the main product of the sonication of the argon saturated 75% DMSO/25% water mixture [14]. In addition, our recent study has shown that sonication of DMSO in the presence of BPEAnit results in formation of BPEAnit-S(O)CH_3 adduct [15].

a)

b)

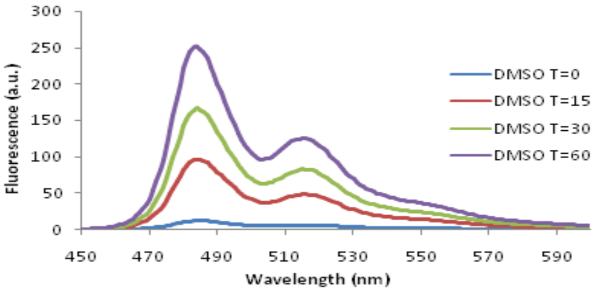

Figure 1. a) BPEAnit; b) Fluorescence spectra of BPEAnit upon sonication in DMSO.

Figure 2 shows that sonication of DCFH in 10% ethanol/90% water in the presence of HRP also results in the increase of fluorescence with increase of sonication time. What can also be seen from Figure 2 (red curve) is that the fluorescence of DCFH goes up after HRP is added in the solution. The role of HRP is to catalyse the reaction between H_2O_2 and DCFH, but it has been demonstrated previously that DCF*H* reacts with HRP even in the absence of H_2O_2 to give fluorescent DCF[16]. However, further significant increase of fluorescence upon sonication is observed, which might be explained by generation of hydrogen peroxide, which, in turn, reacts with horseradish peroxidase to initiate another oxidative cycle of DCFH. As mentioned in the Introduction, the most common reaction upon sonication of water is dimerisation of the hydroxyl radical or hydrogen-peroxyl radicals producing hydrogen peroxide. Figure 3 shows that without HRP there is still an increase of fluorescence, but that increase is ~25 times smaller than in the presence of HRP. Similar increase of fluorescence is observed when just ethanol or water were used as solvents.

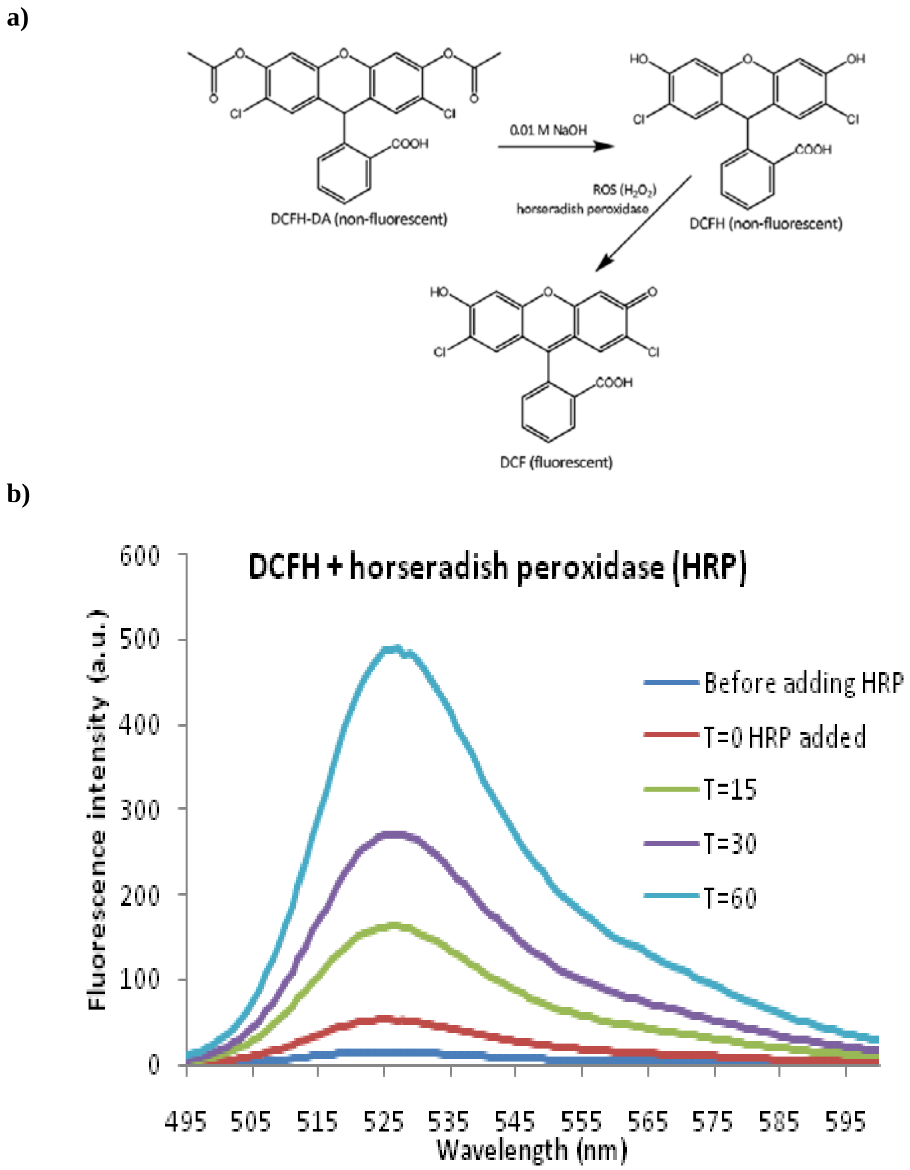

Figure 2. A) Hydrolysis of DCFH-DA and ROS-induced oxidation of DCF*H;* b) Fluorescence spectra of DCFH upon sonication in 10% ethanol/90% water in the presence of HRP.

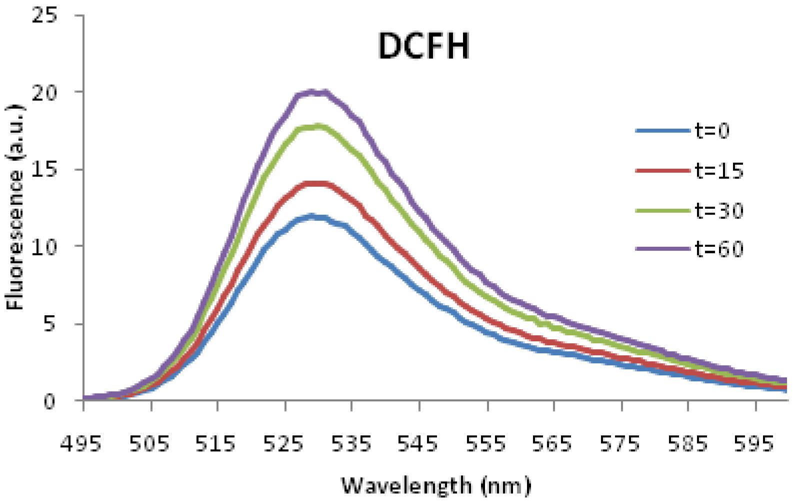

Figure 3. Fluorescence spectra of DCFH upon sonication in 10% ethanol/90% water without HRP.

Figure 4 shows absorbance spectra of oxidised DTT upon sonication in water. DTT and its oxidised form have diferent UV spectrums – oxidised DTT has an absorption peak at ~270 nm, while reduced DTT does not. It can be seen from Figure 4 that the absorbance at 270 nm increases with increase of sonication time from t= 0 min to t = 20 min and then at t = 30 min drops down to its initial value (i.e. at t = 0 min). This means that the amount of oxidised DTT increases during the first 20 min of sonication. ROS, such as OH radical and hydrogen peroxide can oxidise DTT. After that oxidised DTT either goes back to its reduced form or gets degraded.

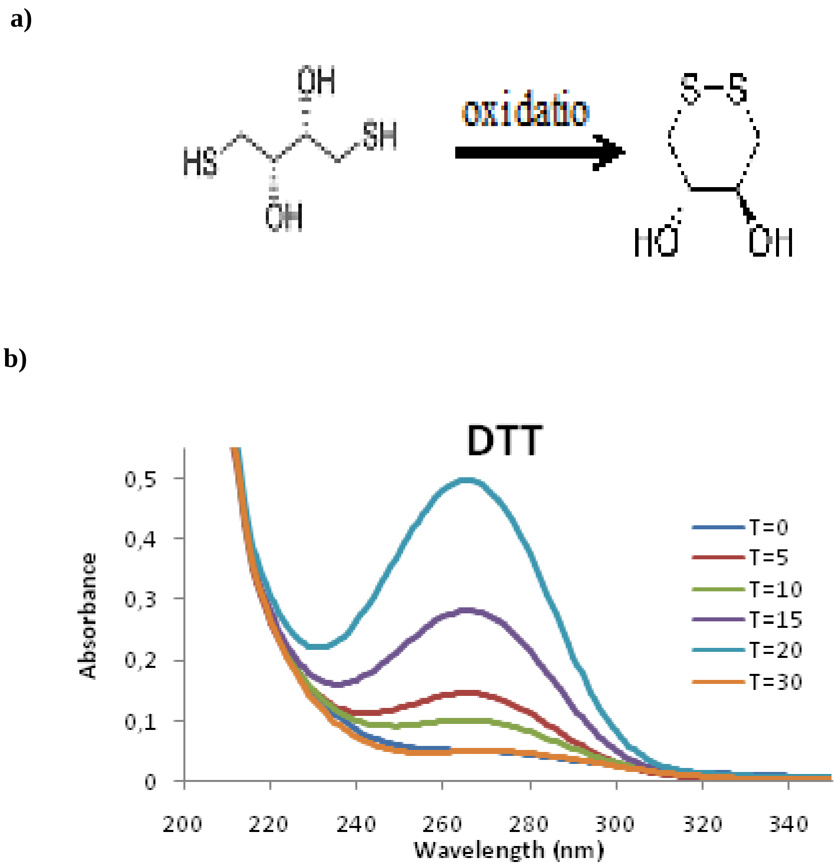

Figure 4. Absorbance spectra of oxidised DTT upon sonication in water.

4. CONCLUSIONS

Sonication of dimethyl sulfoxide, water and ethanol/water mixture leads to generation of radical species, which is in accordance with previous literature. These species can lead to changes of material collected onto filters. Therefore, the standard use of sonication for extraction of organic material from filters should be avoided. In addition, if sonication is applied in the presence of the molecular probes used in this study, sampling artifacts (e.g. fluorescence rise due to ultrasound-induced radicals) should be taken into consideration when interpreting results.

5. ACKNOWLEDGMENTS

Parts of this paper were presented at the 4thWeBIOPATR workshop, Belgrade 2-4. October 2013. This work was supported by the Australian Research Council Discovery grant (DP120100126) and Queensland University ofTechnology.

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5.6 FLUCTUATIONS OF THE NUMBER OF ADSORBED MICRO/NANOPARTICLES IN SENSORS FOR MEASUREMENT OF PARTICLE CONCENTRATION IN AIR AND LIQUID ENVIRONMENTS

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ABSTRACT

We present a theoretical model of fluctuations of the number of adsorbed micro/nanoparticles in environmental sensors operating in air and liquids, taking into account the effects of the mass transfer processes of the target particles in a reaction chamber. The presented analysis shows that the transfer processes have a significant influence on the spectrum of fluctuations. The influence is estimated at different values of target particles concentration, functionalization sites density, and adsorption and desorption rates constants. The analysis provides the guidelines for optimization of sensor design and operating conditions in order to decrease the influence of the transport processes, thus decreasing fluctuations and improving the ultimate performance of sensors for particle detection.

1. INTRODUCTION

Detection of micro/nanoparticles in the environment is very significant for environmental protection, public healthcare, agriculture and other fields. Different platforms exist for detection of particles and measurement of their concentration in a sample. The principle of operation of a large group of sensors is based on selective adsorption of target particles on a functionalized sensor surface, occurring in the sensor's reaction chamber and causing a change of some of the measured parameters (mechanical, optical, electrical) (Alvarez 2010, Homola 1999). In this paper we examine micro/nanosensors with a flow-through reaction chamber (e.g. plasmonic, FBAR - thin Film Bulk Acoustic wave Resonators, QCM - Quartz Crystal Microbalance, microcantilever sensors etc. (Anderson 2011, Gervais 2006, Myszka 1998). We also observe the case of reversible adsorption of target particles to the functionalizing surface sites. The value of the sensor's response is determined by the number of adsorbed particles. The response rate depends on the rates of adsorption and desorption, and also on the rates of transport processes (convection and diffusion) of target particles, by which they are moved to (or from) the immediate vicinity of the adsorption sites (Myszka 1998). Unavoidable fluctuations of the number of adsorbed particles cause fluctuations of the sensor's output signal and thus affect the sensor's ultimate performance (noise, minimal detectable signal).

In this paper, a theoretic model of fluctuations of the number of adsorbed micro/nanoparticles in environmental sensors will be presented. The approximations used in the model derivation are applicable for transport-reaction regimes typical for the mentioned types of affinity-based sensors with a flow-through reaction chamber. A characteristic of such regimes is the formation of a thin layer depleted of target particles, adjacent to the functionalized sensor's surface. Based on numerical calculations, the influence of the transport processes on the parameters of the spectral density of the fluctuations of the number of adsorbed particles will be considered, as well as the dependences of that influence on the concentration of target particles, on the surface density of the functionalizing sites and on the affinity of target particles for the adsorption sites on the sensing surface. Since the fluctuations of the number of adsorbed particles directly cause the fluctuations of the sensor's response, theoretic modeling and analysis of fluctuations are important for estimation of the sensor's ultimate performance (e.g. minimal detectable signal) as a function of both the relevant sensor's parameters and the measurement conditions.

2. THEORETICAL DERIVATIONS

In a large group of micro/nanosensors the principle of operation is based on the change of a measured parameter caused by the adsorption of the target particles from the environment. Therefore, the response of such sensors is determined by the number of adsorbed particles, $N(t)$. In the sensor flow-through reaction chamber the following processes occur: adsorption, desorption, convection and diffusion of target particles (Figure 1). Adsorption and desorption processes take place on the functionalized sensor surface. Adsorption can occur when a target particle is transported to the immediate vicinity of a surface adsorption site. A desorbed particle can be adsorbed again or moved away from the adsorption site by diffusion or convection.

The following assumptions are introduced: 1. the adsorption sites surface density is approximately uniform, 2. no more than one target particle can be bound to any adsorption site, 3. all the adsorption sites are equivalent, 4. there is no interaction between target particles.

The typical transport-reaction regime in plasmonic, QCM and FBAR sensors with a flow-through reaction chamber (Anderson 2011, Gervais 2006, Myszka 1998) is such that a thin layer depleted of target particles forms adjacent to the functionalized surface when the process kinetics, $N(t)$, is limited by diffusion (in the case of reaction-limited kinetics the concentration of target particles in a reaction chamber is uniform, so the problem is much simpler for mathematical analysis). In a diffusion-limited case, the distribution of the particle concentration in a reaction chamber can be approximated by a model which assumes the existence of two regions (i.e. compartments). In the first, narrow region adjacent to the sensing surface (the inner compartment), the concentration gradient exists, while in the second, encompassing the rest of the reaction chamber (the outer compartment), the concentration is uniform and equals the particle concentration in the analyzed sample, C (Figure 1). According to the two-compartment model it can be assumed that the imaginary boundary between the two compartments is parallel to the sensor's surface, the concentration at the sensor's surface, C_s, is uniform, and for all the parameters of the adsorption-desorption (AD) and transport processes the values can be used that are obtained by averaging across the surface on which adsorption occurs. The suitability of the model for the analysis of the kinetics of the process of binding of particles to a functionalized surface was experimentally confirmed (Myszka 1998). According to the model, a boundary condition valid for the functionalized surface is defined by the expressions

$$k_m A(C - C_s) = dN/dt \tag{1}$$

$$dN/dt = k_f C_s (N_m - N) - k_r N = a_{eq}(N) - d_{eq}(N). \tag{2}$$

where N_m is the total number of adsorption sites on the functionalized surface of the area A, k_m is the mass transfer coefficient of target particles, while $a_{eq}(N)$ and $d_{eq}(N)$ denote the equivalent rate of the processes that contribute to the increase of the number of adsorbed particles and the equivalent rate of the processes that decrease the number of bound particles, respectively.

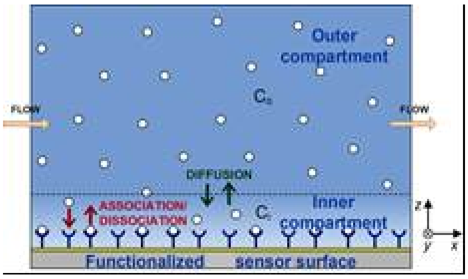

Figure. 1 Illustration of the processes in the sensor's reaction chamber, relevant for the sensor's response. Two regions of characteristic concentrations, according to the Two-compartment model, are also shown.

The number of adsorbed particles on the sensor's functionalized surface, $N(t)$, is a random process because it is a result of stochastic AD processes coupled with transport processes. Let us observe the fluctuations ΔN around the expected equilibrium value, N_e, assuming $\Delta N \ll N_e$. Based on Eqs. 1 and 2, a nonlinear differential equation is obtained for N. Its linearization around N_e yields the fluctuation equation

$$d(\Delta N)/dt = \left(da_{eq}/dN - dd_{eq}/dN\right)\Big|_{N=N_e} \cdot \Delta N = -\Delta N/\tau, \tag{3}$$

$$\tau = \left(1 + k_f k_r N_m/(k_m A)/(k_r + k_f C)\right)/(k_r + k_f C) \tag{4}$$

$$N_e = N_m k_f C/(k_r + k_f C)\ . \tag{5}$$

Eq. 3 assumes the Langevin form after addition of the stochastic term η on the right side. According to (Jokić 2012), based on the Langevin equation the expression is derived for the single-sided power spectral density of the fluctuation process

$$<\Delta N^2(\omega)> = <\eta^2(\omega)> \tau^2/(1+\omega^2\tau^2) = 4a_{eq}(N_e)\tau^2/(1+\omega^2\tau^2), \tag{6}$$

which is of the Lorenzian type ($\omega=2\pi f$). The spectral density of the number of adsorbed particles equals $<\Delta N^2(f)>^{1/2}$ [1/Hz$^{1/2}$], and the parameters by which it is fully determined are the spectral density for $f\rightarrow 0$, the so-called plateau, P, and the frequency at which the spectral density decreases by the factor $2^{1/2}$ (the cut-off frequency). This frequency equals $1/(2\pi\tau)$, where τ is given by Eq. 4. Based on Eq. 6, the plateau is determined by

$$P=\sqrt{4a_{eq}(N_e)\tau^2}=2\tau\sqrt{k_rN_e}\;. \tag{7}$$

Based on Eqs. 4 and 7 the spectral density of fluctuations of the number of adsorbed particles in micro/nanosensors with a flow-through reaction chamber can be analyzed.

3. RESULTS AND DISCUSSION

The presented theory is applied for the analysis of the influence of transport processes on the plateau value of the fluctuations spectral density of the number of adsorbed particles in sensors. It is used in order to determine how pronounced the influence is at different target particles concentrations, different surface densities of functionalization sites, and different values of adsorption and desorption rate constants. The area of the functionalized surface is typical for microsensors, $A=1\cdot10^{-9}$ m^2. On all of the given 3D diagrams (Figs. 2 a-d), the lower surface (shown in uniform gray) is obtained by assuming that the mass transfer is fast enough that it does not influence the kinetics of the process of binding the particles to the sensor's surface. It is intended for the comparison of the influence of each of the analyzed parameters on the effect the mass transfer has on the fluctuation spectrum.

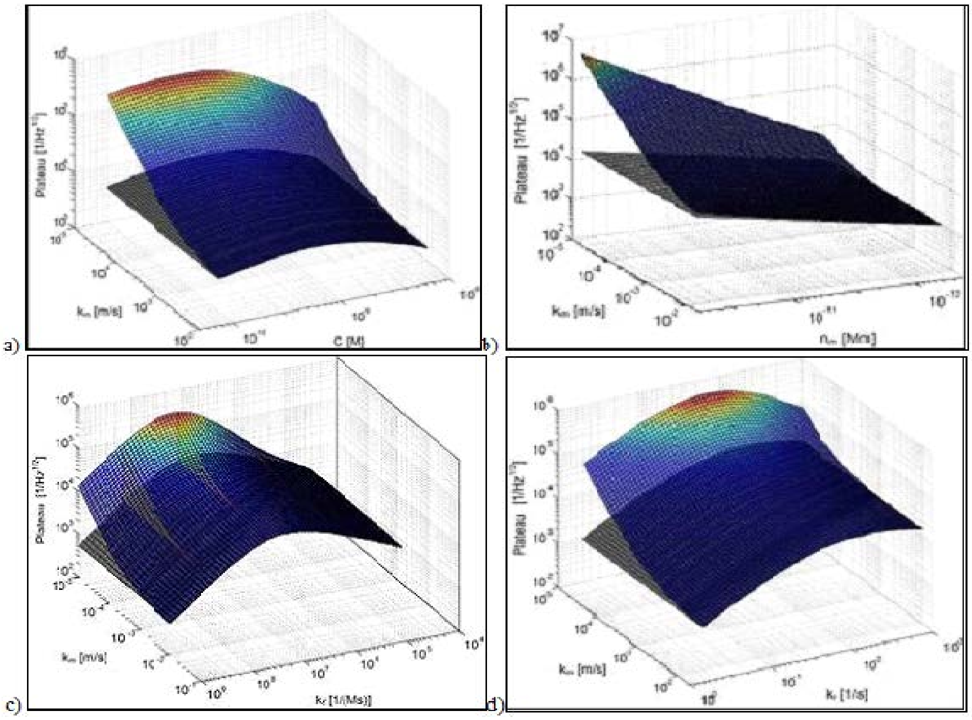

Figure 2. The influence of the transfer process coefficient on the plateau value of the adsorbed particles number fluctuations spectrum for different: analyte concentrations (a), values of the functionalization sites surface density (b), adsorption rate constants (c), and desorption rate constants (d).

Fig. 2a shows the dependence of the spectrum plateau on both the mass transfer coefficient and the target particles concentration at $k_f=5\cdot10^7$ 1/(M·s), $k_r=0.08$ 1/s and $n_m=N_m/A=1\cdot10^{-11}$ M·m. It can be seen that when the mass transfer is slow (i.e. at lower k_m), the influence of the transfer on the plateau magnitude becomes significant. The plateau magnitude can be increased by more than one order of magnitude compared to the case of fast mass transport. Fig. 2b shows the plateau magnitude as a function of both k_m and the surface density of adsorption sites on the sensor's surface ($k_f=8\cdot10^7$ 1/(M·s), $k_r=0.08$ 1/s, $C=5\cdot10^{-10}$ M). In the case of slow mass transfer and high n_m, the plateau magnitude is more than 100 times greater than it is when the mass transport is fast. As the number of functionalized sites decreases, so does the influence of the transport process speed on the plateau magnitude. In Fig. 2c the influence is shown of both the transfer process speed and the adsorption rate constant on the fluctuation spectrum plateau (k_r=0.02 1/s, C=2·10^{-9} M, n_m=2.5·10^{-11} M·m). At higher binding affinities of the target particles for the sensing surface (i.e. higher k_f), the mass transfer exhibits a higher influence on the fluctuation spectrum in the plateau range, and thus also on the corresponding sensor noise. In order for the analysis to be complete, it is also necessary to consider the dependence of the fluctuations spectrum plateau on both the k_m and the desorption rate constant (the affinity is inversely proportional to k_r). This dependence is shown in Fig. 2d for k_f=5·10^7 1/(M·s), C=2·10^{-10} M and n_m=1·10^{-11} M·m.

4. CONCLUSIONS

We presented the theoretical model of fluctuations of the number of adsorbed micro/nanoparticles in environmental sensors operating in air and liquids, taking into account the effects of the mass transfer processes of the target particles in a reaction chamber. The expression for the fluctuations spectral density, which is of Lorentzian type, yielded expressions for the parameters that determine it completely, i.e. the maximal value of the spectral density (the so-called plateau), and the frequency at which the spectral density reduces to the value $2^{1/2}$ times lower than the plateau (usually called the cut-off frequency).

The presented theory is applied for the analysis of the influence of transport processes on the plateau value of fluctuations spectral density. The analysis shows that transfer processes have a significant influence on the spectrum of fluctuations. It shows how significant this influence can be at different values of target particles concentration, functionalization sites density, and adsorption and desorption rates constants. Significant differences have been observed in the maximal value of the fluctuations of the number of adsorbed particles at different values of these parameters, chosen to correspond to real conditions. The results of the analysis provide the guidelines for optimization of sensor design and operating conditions (the flow rate of the sample through the reaction chamber, the surface density of the functionalization sites etc.) in order to decrease the influence of the transport processes, thus decreasing fluctuations and improving the ultimate performance of sensors for particle detection in the environment.

5. ACKNOWLEDGEMENTS

This work was partially funded by the Serbian Ministry of Education, Science and Technological Development within the Project TR32008 and by the Serbian Academy of Sciences and Arts within the project F150.

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6 EXPOSURE AND BIOMARKERS

6.1 THE USE OF BIOMARKERS FOR THE RISK ASSESSMENT FOR EXPOSURE TO PAHS

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ABSTRACT

Carcinogenic polycyclic aromatic hydrocarbons (c-PAHs) adsorbed onto respirable particles (< 2.5 µm, $PM_{2.5}$) are mainly derived from incomplete combustion. Health risk associated with genotoxic and carcinogenic effects of their environmental exposure is evaluated by biomarkers of exposure, effect and susceptibility. The use of these molecular methods combined with epidemiological studies became new research area termed molecular epidemiology. The first studies using biomarkers were conducted in highly polluted regions in Europe. The advantages of such approach are demonstrated on examples from the Czech Republic. This very specific situation was utilized to investigate the sensitivity of biomarkers of exposure and effect to evaluate the impact of air pollution to genetic damage in exposed populations. Simultaneously the exposure to c-PAHs was measured by personal monitoring. In vitro cell free system with CT-DNA was used to study the genotoxicity of complex mixtures of environmental pollutants adsorbed on $PM_{2.5}$. All presented studies indicate, that DNA adducts, Comet assay and DNA fragmentation in the sperm are sensitive biomarkers of exposure to c-PAHs in polluted air, chromosomal aberrations assessed by FISH and micronuclei are suitable biomarkers of effect, and 8-oxo-7,8-dihydro-2'-deoxyguanosine (8-oxodG) and 15-F_{2t}-isoprostane (15-F2t-IsoP) biomarkers of oxidative damage.

1. INTRODUCTION TO THE TOPIC

A new and evolving area of research termed molecular epidemiology aims to merge sophisticated and highly sensitive laboratory methods (many of them developed during the recent revolution in molecular biology) with analytical epidemiological methods. Molecular epidemiology bridges from basic research in molecular biology to studies of human cancer causation by combining laboratory measurement of internal dose, biologically effective dose, biological effects and the influence of individual susceptibility with epidemiologic methodologies [1]. The most common view is that the approach represents a natural convergence of molecular biology and epidemiology [2].

The number of biomarkers available for evaluating genetic and cancer risk in humans is quite large. Their utility for human biomonitoring is suggested by the well-known paradigm of environmentally induced cancer, which represents endpoints for assessing the entire spectrum of human-genotoxicant interactions [3]. These biomarkers begin with exposure and include absorption, metabolism, distribution, critical target interaction (i.e. DNA damage and repair), genetic changes and finally disease. Disease is the province of traditional epidemiology. The development of biomarkers has given rise to the field of molecular epidemiology, which uses these biomarkers rather than disease to assess the risk of environmental exposure [4, 5].

The paradigm of environmental cancer starts with exposure. A large number of biomarkers are available now, but to evaluate their sensitivity and to interpret the results obtained we need to know data on exposure. Previously, data on exposure were usually not published in studies using various biomarkers.

It is well established that ambient air pollution is related to human health. Increased exposure to respirable particulate matter (PM) correlates with increased mortality caused by lung cancer and cardiovascular diseases [6-8]. Pope et al. [9] suggested that a long term increase in $PM_{2.5}$ of 10 $\mu g/m^3$ is connected with an 8% increase in lung cancer mortality in adult men. Despite the fact that other factors related to cancer incidence, such as smoking habit or inappropriate diet, are probably stronger influences, the absolute number of cancer cases related to air pollution is high due to the high prevalence of exposure [10].

Although the quantitative health risk related to air pollution is assessed by epidemiological studies [11-14], alternative types of studies are necessary for the purposes of primary prevention. On the level of human populations, such studies are first of all molecular epidemiological studies evaluating quantitative relations between external exposure and measurable biological events (biomarkers). These biomarkers form a chain from exposure to disease [15-17]. One of the most frequently used biomarkers are DNA adducts as biomarker of exposure, quantifying the biologically effective dose of genotoxic compounds that were covalently bound to DNA as a target molecule of carcinogenesis [18-22]. If DNA adducts are not effectively repaired, they might be fixed as mutations during replication. According to the well known scheme of the multi-step process of chemical carcinogenesis, an accumulation of mutations may lead to carcinogenesis. Thus, DNA adduct levels have a direct relation to mutagenesis and carcinogenesis. Data are accumulating about the relation of DNA adducts to environmental exposure to complex mixture components such as carcinogenic polycyclic aromatic hydrocarbons (c-PAHs) [23] and to malignant tumors and other degenerative diseases [24, 25].

The Comet assay (single cell gel electrophoresis, SCGE) in its standard alkaline version allows the detection of DSB (double strand breaks), SSB (single strand breaks), alkali-labile sites and transient repair sites. DSB represent the principal lesion leading to the formation of chromosomal aberrations. The majority of chemical mutagens induce DSB indirectly via the generation of other DNA lesions such as SSB or oxidative damage that may be converted to DSB during DNA replication or repair [26]. When combined with specific bacterial repair enzymes, it identifies a broad spectrum of additional lesions including oxidized purines and pyrimidines [27]. Due to its relative simplicity, its low requirements on the number of analyzed cells as well as its capacity to detect DNA damage independently of the cell cycle, comet assay is believed to serve as an exposure biomarker assay providing information about the biologically effective dose [28].

DNA fragmentation in the mature sperm may be understood as another biomarker of exposure , measured by the sperm chromatin structure assay (SCSA) [29]. Human sperm cells can undergo DNA fragmentation or covalent modification of nucleotides. Both these types of disturbances contribute to infertility. Altered sperm chromatin structure can be significant contributing factor to subfertility that is not revealed by standard spermiogram parameters, because they can range within physiological values. Consequently, fertilization failure, impaired embryo morphology, abnormal development of blastocysts, embryo implantation failure or repeated spontaneous abortions can occur.

Chromosomal aberrations in human peripheral lymphocytes are recognized as a valuable biomarker of effect, probably the only one that has been internationally standardized and validated [30]. While classic cytogenetic analysis (conventional method) is the method of choice for determining unstable types of aberrations, the fluorescent in situ hybridization technique (FISH) seems to be a rapid, sensitive, and reliable method for the detection of stable structural rearrangements that remain undiminished over time, such as translocations [31-35]. The FISH painting technique appears to be more sensitive than the conventional technique for detecting the genomic frequency of translocations induced by various chemical agents or irradiation [36].

The measurement of micronuclei (MN) in human peripheral blood lymphocytes is one of the methods frequently used in molecular epidemiology. MN represent a measure of both chromosome breakage and chromosome loss. Therefore, an increased frequency of micronucleated cells, used as a biomarker of genotoxic effects, can reflect exposure to agents with clastogenic or aneugenic modes of action [37]. Currently, the MN assay is one of the preferred methods for assessing chromosomal damage as a result of environmental mutagen exposure as well as a tool for genotoxicity testing.

Another important aspect demonstrating the advantages of molecular epidemiology studies over classical epidemiology is the possibility of identifying the genetic susceptibility of individuals to the action of various compounds [17]. The role of genetic polymorphisms on the metabolic activation of xenobiotics (oxygenases of cytochromes P450 such as *CYP 1A1*) and also their detoxification (glutathione-S-transferases) is well known. Further biomarkers of individual susceptibility are polymorphisms in genes encoding DNA repair enzymes (*XRCC1*, *XPD, hOGG1*) [38-40]. One more factor affecting susceptibility to the genotoxic and carcinogenic effects of xenobiotics is the saturation of the organism by vitamins A, C, E, folic acid etc., which are known to play a significant role as free radical scavengers and antioxidant agents and which also affect the synthesis of DNA repair enzymes [41-44].

Inhalation of PM, particularly PM of aerodynamic diameter < 2.5 µm ($PM_{2.5}$) and smaller, leads to inflammation and subsequent production of reactive oxygen species (ROS) [45]. The production of ROS, that include e.g. the hydroxyl radical, superoxide anion, or hydrogen peroxide, is caused by both the physical effects of PM (PM is phagocyted by macrophages that consequently produce ROS), and the presence of various chemicals on the surface of PM (e.g. metals, PAHs) with pro-oxidant properties. ROS may arise from exogenous or endogenous sources. The latter are mostly physiologic and include various metabolic processes and inflammation, whereas exogenous sources are environmental factors such as smoking, diet [46, 47], ultraviolet radiation, ionizing radiation or exposure to environmental pollution [48].

ROS can attack lipids, proteins and nucleic acids simultaneously [49]. The highly reactive hydroxyl radical reacts with DNA by addition to the double bonds of DNA bases, and by abstraction of a hydrogen atom from the methyl group of thymine and C–H bonds of 2'-deoxyribose [50]. This reaction yields several modified bases but, as a biomarker of oxidative DNA damage, 8-oxodeoxyguanosine (8-oxodG) is most often studied. The oxidized base is highly mutagenic and, if unrepaired, its presence in DNA causes GC>TA transversions. If repaired, 8-oxodG is excreted in urine where it can be assessed by various techniques as a general biomarker of oxidative stress. Urinary levels of 8-oxodG are also believed to reflect the total DNA excision repair capacity of an organism [51]. Other sources of 8-oxodG, including oxidation of the nucleotide pool, may affect urinary levels of 8-oxodG. Numerous reports have indicated that urinary 8-oxodG is not only a biomarker of generalized, cellular oxidative stress, but may also imply the risk of cancer, atherosclerosis and diabetes [49, 52].

Several metabolic pathways of PAH activation have been described [53] and one of them, activation through PAH-*o*-quinones, leads to ROS generation and oxidative stress [54]. The modification of DNA molecules represents the most serious form of impact of ROS on the organism because it may lead to base changes, mutations, and/or DNA breaks. If ROS attack both DNA strands, double-strand DNA breaks may appear. These breaks may lead either to unstable chromosomal aberrations, or, if homologous or non-homologous end-joining repair seals the breaks, to stable chromosomal translocations. Translocations are more serious because they are usually fixed in the genome and may lead to rearrangements of regulatory elements and genes, including oncogenes thus increasing cancer risk [55]. Another, indirect mechanism of DNA double strand breaks induction is associated with DNA adducts formation. Adducts may cause persistent blockage of one DNA strand during its synthesis and uncoupling of the other strand which may result in the formation of double strand breaks [56].

The attack of ROS on lipids leads to lipid peroxidation. This reaction may have potentially serious consequences, as it may damage cellular membrane and inactivate membrane-bound receptors or enzymes. In addition, secondary products of lipid peroxidation, such as aldehydes, are highly reactive and may propagate oxidative stress by reacting with other cellular molecules including proteins [57]. Currently, isoprostanes are considered the most reliable markers of lipid peroxidation. These prostaglandin-like compounds, first described in the 1990s, are formed by free-radical induced peroxidation of arachidonic acid, independent of cyclooxygenase enzymes. Lipid peroxidation products, including isoprostanes, play a role in the pathogenesis of many diseases [58].

2. DISCUSSION

The average personal environmental exposure to approx. 10 ng/m^3 of c-PAHs (or 1.6 ng/m^3 of B[a]P) [59], or approx. twice as high c-PAHs concentrations by stationary monitoring – according to outdoor/indoor ratio) during winter increases DNA adduct formation and decreases repair efficiency, which may be further affected by genetic polymorphisms. This concentration of c-PAHs and its impact on increased DNA adduct formation seems to be important for re-evaluating the risk assessment of c-PAHs. PAH-DNA adduct formation represent one of the key first steps in carcinogenesis [60]. According to Phillips [61] the use of DNA adducts as a measure of exposure, several years prior to the onset (or clinical manifestation) of disease, can identify individuals at higher probability of subsequently developing cancer. Another study demonstrated significant correlations between DNA adduct levels and atherosclerosis [25]. Both examples demonstrate the potential of DNA adducts as biomarkers of risk.

DNA adducts determined by the ^{32}P-postlabeling method are sensitive biomarkers of environmental exposure to c-PAHs, if the study simultaneously includes personal and stationary monitoring, information on life style, determination of cotinine, vitamin and lipid levels, as well as genetic polymorphisms of metabolic and DNA repair genes.

Nowadays it is generally accepted that a high frequency of chromosomal aberrations in peripheral lymphocytes is predictive of an increased risk of cancer [30]. Therefore, it may be hypothesized that environmental exposure to c-PAHs that increases the genomic frequency of translocations represents a significant health risk. Surprising results were observed in the group of city policemen who were examined in January and March: the genomic frequency of translocations decreased similarly as did their exposure to c-PAHs. This reveals that these chromosomal aberrations are not so stable as originally expected [59]. When

Binkova et al. [22] studied the relationship between chromosomal aberrations and DNA adducts in the same subjects using FISH, multiple regression analysis indicated that B[a]P-like DNA adducts are a significant predictor of the genomic frequency of translocations. Whole chromosome painting using the FISH technique is more sensitive than the originally used conventional cytogenetic method, which was not affected by the studied concentrations of c-PAHs.

Studies in the Czech Republic [22, 34, 62, 63] suggest that environmental exposure to concentrations higher than 1 ng B[a]P/m^3 represent a risk of DNA damage as indicated by an increase in DNA adducts and an increase in translocations detected by FISH, increase of micronuclei as well as the increase of DNA fragmentation in the mature sperm.

A relationship between DNA adducts (biomarker of exposure) and chromosomal aberrations as determined by FISH (biomarker of effect) was observed for the first time [22].

Studies by Binkova et al. [18, 19, 22] and Topinka et al. [64] suggest that DNA adducts in the lymphocytes of subjects exposed to increased c-PAH levels are an appropriate biomarker of a biologically effective dose, directly indicating whether or not the extent of exposure to these compounds is related to an increased mutagenic and carcinogenic risk. All results indicate that molecular epidemiology studies should be done in a very complex manner, simultaneously using biomarkers of exposure, effect and susceptibility. Air pollution, and specifically c-PAHs, induce genetic damage and may significantly affect human health.

Although PAHs may induce oxidative stress during their metabolism by the formation of reactive quinones, the results of epidemiological studies on 8-oxodG levels after occupational, as well as environmental, PAH exposure are contradictory. Several authors reported a positive correlation between PAH exposure, measured by urinary levels of 1-hydroxypyrene, and 8-oxodG levels, either in lymphocytes or in urine [65-68]. Others did not see any correlation between 8-oxodG levels and urinary 1-hydroxypyrene and/or PAH levels in the air [69-71]. Similarly, Rossner et al. [72] did not find any effect of either personal or stationary c-PAH exposure on 8-oxodG levels in urine. These observations suggest that while c-PAHs may have the potential to induce oxidative DNA damage, other factors probably play a role in the response of the organism to environmental pollution.

Unlike c-PAHs and B[a]P, Rossner et al. [73] did not observe any effect of stationary $PM_{2.5}$ and PM_{10} on levels of 15-F_{2t}-IsoP when PM concentrations over a 3-day period immediately preceding urine collection were used in the statistical analysis. Only when the multivariate model was applied did the effect of PM2.5 exposure reach borderline significance. Interestingly, when concentrations of $PM_{2.5}$ and PM_{10} over various 3-day periods before sampling were included in the statistical analysis, they found significant effects of PM exposure on 15-F_{2t}-IsoP levels. This observation suggests that 15-F_{2t}-IsoP levels, unlike 8-oxodG, are not markers of immediate effect; rather, they reflect the exposure to pollutants that occurred at least 3-4 weeks before sampling. The possible explanation may be the existence of DNA repair mechanisms that remove damage to DNA shortly after it occurs. Damage to lipids is not repaired; rather the lesions accumulate and thus allow the detection of exposure to pollutants longer period before sampling.

Among other factors that seem to affect the levels of oxidative stress markers, a positive association between cotinine (considered as a marker of passive smoking) and 15-F_{2t}-IsoP levels was observed [74-76], although negative reports have also been published [77].

In vitro studies reveal that the biological activity of PM2.5 may differ according to the sources and the content of c-PAHs. The genotoxic risk may be substantially different when comparing industrial emissions vs. traffic related emissions or emissions from the local heating using coal.

Review of in vitro studies allows to propose the cell free system with CT-DNA to be used as a system to evaluate the biologic activity of organic compounds extracted from particulate matter, detecting genetic damage as DNA adducts or oxidative damage as 8-oxodG, as a first information about a possible genetic risk of air pollution, and the different quality of respirable particles according to the content of c-PAHs adsorbed on their surface as well as oxidative damage induced according to the size of PM.

3. CONCLUSION

All studies indicate, that DNA adducts, Comet assay and DNA fragmentation in sperm are sensitive biomarkers of exposure to c-PAHs in polluted air, chromosomal aberrations by FISH and micronuclei as biomarkers of effect, and 8-oxodG and 15-F2t-IsoP as biomarkers of oxidative damage.

It seems that when using these biomarkers the dose-effect is seen only in a certain range, probably up to 10 ng B[a]P/m^3.

It is important to identify simultaneously the gene susceptibility, especially the genetic polymorphisms of metabolic genes and genes encoding DNA repair enzymes. DNA damage may be further affected by life style as smoking, ETS, diet – intake of vitamins A, C, E, folic acid, oxidative metabolism by lipid metabolism (triglycerides, cholesterol, HDL, LDL) – it is therefore pertinent to analyze all these endpoints in the biological material in the course of molecular epidemiology studies.

New perspectives may be seen in using the microarray methods, e.g. studying the gene expression of genes coding DNA repair enzymes.

Summing up, molecular epidemiology studies on the environmental exposure to c-PAHs in ambient air should be very complex: determining personal exposure, DNA and oxidative damage, gene susceptibility and life style factors. It will bring new results, which may specify new information important to evaluate properly c-PAHs human health risk.

4. ACKNOWLEDGEMENT

Supported by a collaborative project CITI-SENSE funded by the EU FP7-ENV-2012 under grant agreement no.308524.

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6.2 FINE AND ULTRAFINE PM EFFECTS AND ACTION MECHANISMS ON *IN VITRO* SYSTEMS

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ABSTRACT

Particulate matter (PM) is still one of the main concerns in urban areas for its human health adverse effects. Fine (FP) and ultrafine (UFP) fractions have recently received great attention for their role in eliciting pulmonary and cardiovascular diseases. Here the biological effects of such particles are investigated; FP ($PM_{2.5}$) were sampled during summer and winter in Milan (Italy), while samples of organic UFP (NOC), derived from experimental combustion processes, were obtained in laboratory. The effects of these particles have been tested on in vitro systems representative of the human lung epithelia (A549 and BEAS-2B cell lines).

Winter FP generated ROS, DNA damage and cell cycle alteration. NOC derived by different fuels differently affected the biological outcomes. These results outline that the compounds adsorbed on FP and the chemical composition of organic UFP are crucial for the induction of the cellular effects.

1. INTRODUCTION

According to WHO air quality guidelines (global update, 2005) each year more than 2 million premature deaths can be attributed to the effects of urban outdoor and indoor air pollution. One of the most dangerous air pollutants is particulate matter (PM). For PM, a quantitative relationship between the concentration of the pollutant monitored in ambient and specific health outcomes as mortality and hospitalizations for respiratory and cardiovascular diseases has been reported (Brunekreef and Forsberg, 2005; Pope and Dockery, 2006). Moreover the IARC (press release n° 221, 17 October 2013) has classified outdoor particulate matter as “carcinogenic to humans (Group 1)”. Despite these evidences and the intensive researches to explain these associations, there are still unresolved issues, regarding the biological mechanisms inducing the different adverse effects, and which PM components (metal, organic compounds etc..) are more significant in determining the biological responses. This information is of primary importance for the individuation of the most impacting sources, which should be specifically regulated.

PM is defined as an air-suspended mixture of solid and liquid particles that vary in number, size, shape, surface area, chemical composition, solubility, and origin (Pope and Dockery, 2006); among these characteristics, the size is the one used for classification due to its intrinsic importance, as the atmospheric deposition rates of particles, their residence times in the atmosphere and deposition patterns within the lung are strongly influenced by this parameter. Recently, more and more attention has been reserved to the fine (FP) and ultrafine (UFP) fractions for the toxic potential related to the small size (WHO, 2013), as these particles have enhanced ability to penetrate the lung and possibly also systemic circulation (Li et al., 2003, Furuyama et al., 2009). Besides the high number concentration and large surface area per unit mass of this class of PM determine peculiar behaviours, as increased adsorption of organic molecules.

FP and UFP are mainly generated by combustion sources and are composed by aggregates of small round-shaped particles; these nanoparticles are formed by an inner core constituted by elemental carbon (EC) or soot, that is generated during the combustion process and functions as a condensation nucleus for a very heterogeneous group of components; inorganic ions, metals and organic compounds, as polycyclic aromatic hydrocarbons (PAHs), that are emitted from traffic and biomass combustions, are thus highly represented in fine particles (Pope and Dockery, 2006). All these compounds are notorious genotoxic elements (Mehta et al., 2008); in particular, the presence of PAHs might be very important in determining a high genotoxic potential of fine and ultrafine particles. The metabolic activation of PAHs by cytochromes P-450 (CYP1A1/1B1) forms reactive species, epoxides, that may form bulky adducts on the DNA (Billet et al., 2008). The formation of such kind of adducts is a well known process in cells and animals exposed to PAHs, such as benzo[a]pyrene (BaP) (Park et al., 2009; Jiang et al., 2006). BaP is indeed one of the organic molecules present in fine PMs and it is thus likely that the organic fraction released from particles could activate such processes.

The difficulty of investigating PM toxicity partly lies in the variability and complexity of this pollutant, whose heterogeneity in structure and composition can lead to different biological outcomes. In order to understand the epidemiological findings, the toxicological studies have an important role, providing controlled and simplified models that can help to clarify the mechanisms of PM toxicity and the molecular pathways involved, and to associate a specific biological effect to physico-chemical properties of the particles. *In vitro* models are of fundamental importance in understanding the molecular pathways activated by PM exposure at cellular level, which in turn might explain the biological outcomes observed in humans.

Here we used alveolar and bronchial epithelial cell lines (A549 and BEAS-2B) to study the biological effects of FP and UFP; FP (PM2.5) were sampled during summer and winter in Milano, in a representative background site for air quality, while samples of organic UFP (NOC), derived from experimental combustion processes, were obtained in laboratory. The effects on ROS and DNA damage formation and cell cycle alteration have been investigated by means of common biochemical and microscopy techniques. The results outlined that the compounds adsorbed on FP and the chemical properties of UFP have a great significance in the induction of the different cellular effects. Moreover the results on NOC toxicity underline the need of further investigation to improve the knowledge of the biological effects produced by UFP generated by combustion processes.

2. METHODOLOGY

2.1. FP and UFP Sampling and Chemical Characterization

FP (PM2.5) were collected daily, in summer and winter season, in a representative urban site of Milano influenced by vehicular traffic. A low volume gravimetric sampler (EU system, FAI Instruments, Rome, Italy) was used to collect PM samples on Teflon or quartz filter for biological analysis and chemical characterisation respectively. Particles were characterised for elements (mineral dust and trace elements), polycyclic aromatic hydrocarbons (PAHs), inorganic ions and total carbon as previously described (Perrone et al., 2010; Gualtieri et al., 2009). To obtain particles for in vitro exposures, particles were extracted from filters using a Sonica ultrasound bath (Soltec) by replicating four 20 minute cycles using 2 ml of sterilized water for each filters' pool. Detached particles were then dried in a desiccator, weighed and stored at -20 °C until further use. The resulting pellets were resuspended in sterile water (2 μg/μl) just before use for biological analysis (Longhin et al., 2013).

UFP sampling was performed at the exhaust of an engine propelled with different kind of diesel fuels, by condensing the exhaust in a sterile tube immersed in an ice bath. Part of the exhaust was directed to a Scanning Mobility Particle Sizer (SMPS), provided of a DMA column and of a diluter to avoid saturation, for particle numerical concentration and particles size distribution (Gualtieri et al. 2013, submitted).

2.2. Cell Culture and Treatments

Human alveolar epithelial cells, A549 (American Type Culture collection), were routinely maintained in OptiMEM medium at pH 7.2, supplemented with 10% inactivated foetal bovine serum (FBS) and 1% penicillin/streptomycin and were grown at 37 °C, with 5% CO_2. The SV40 hybrid (Ad12SV40) transformed human bronchial epithelial cell line BEAS-2B was purchased from European Collection of Cell Cultures (ECACC, Salisbury, UK). The cells were maintained in LHC-9 medium at 37 °C with 5% of CO_2, split every three day and the medium was changed the day after. Cells were seeded at a concentration of 1.5×10^5 in 6-well plate. After 24h from seeding, cells were treated with FP and UFP at different concentrations.

2.3. ROS production

Cells were incubated at 37 °C with 5 μM of 2'7'-dichlorodihydrofluorescein diacetate (DCFH) in PBS for 20 min, washed in PBS, and treated with FP and UFP for 1 h. At the end of this period, cells were harvested and suspended in PBS. The ROS production, detectable by the oxidation of DCFH to dichlorofluorescein (DCF), was quantified by measuring the fluorescence intensity of 10,000 events with the cytometer EPICS XL-MCL (Beckman-Coulter) using 525 nm band pass filter. Data were analysed using the EXPO32 ADC software.

2.4. DNA Damage

γH2AX was used as marker of DNA damage and measurements were performed by flow cytometry. Cells were harvested after 24 h of treatment, fixed with 1% paraformaldehyde on ice for 15 min, re-suspended in cold methanol 90% and stored overnight at -80 °C. After discharge of methanol, cells were washed once in PBS 0.5% BSA and incubated 4 h with an Alexafluor-488 conjugated γH2AX antibody (1:100 dilution, Cell Signaling) in PBS 0.5% BSA, 0.2% Triton X-100 at room temperature. Finally, cells were washed once in PBS 0.5% BSA, resuspended in PBS and analysed on the Beckman Coulter EPICS XL-MCL flow cytometer. Fluorescence of 10,000 events was detected using 525 nm band pass filter.

2.5. Cell Cycle

Cell cycle was investigated by flow cytometry. After the exposure, the cells were harvested, fixed in 70% ethanol at -20 °C and stored until analysis. After discharge of ethanol, cells were resuspended in PBS and RNAse DNAse-free (Sigma-Aldrich, Italy) was added for 30 min at 37 °C. The fluorescent dye propidium iodide (PI) was used to stain DNA of cells and fluorescence was measured by flow cytometer using 575 nm band pass filter.

2.6. Statistical Analyses

The data here presented are reported as mean values of independent experiments ± SEM. Statistical differences between samples were tested with one-way ANOVA and post hoc comparisons performed with Dunnett’s method, by using SigmaStat 3.1 software. Statistical differences were considered to be significant at the 95% level ($P < 0.05$).

3. RESULTS AND DISCUSSION

3.1. Particles Composition

The chemical composition of FP sampled in summer and winter has been previously reported (Longhin et al., 2013; Perrone et al., 2013, Mantecca et al., 2012). In Fig 1 are reported the main results from our previous analyses. The data showed that total carbon is similar in both the samples, although differences are clear comparing elemental (EC) and organic carbon (OC) (Fig 1A). Winter particles are richer in OC while summer in EC. Total inorganic ions were similar in the FP samples although some differences were evident. Interestingly summer FP were characterized by higher amount of metals (FIG. 1B) while winter FP by the higher amount of PAHs (FIG. 1C).

UFP characterization showed that the chemical composition was strictly related to the diesel blend (Gualtieri et al., 2013 submitted). So far few data have been reported on the characterization of these organic carbon ultrafine particles, however the data obtained are in agreement with the aromatic nature of the emissions and with the different additives used to dope the pristine diesel fuel (Karlitschek et al., 1998).

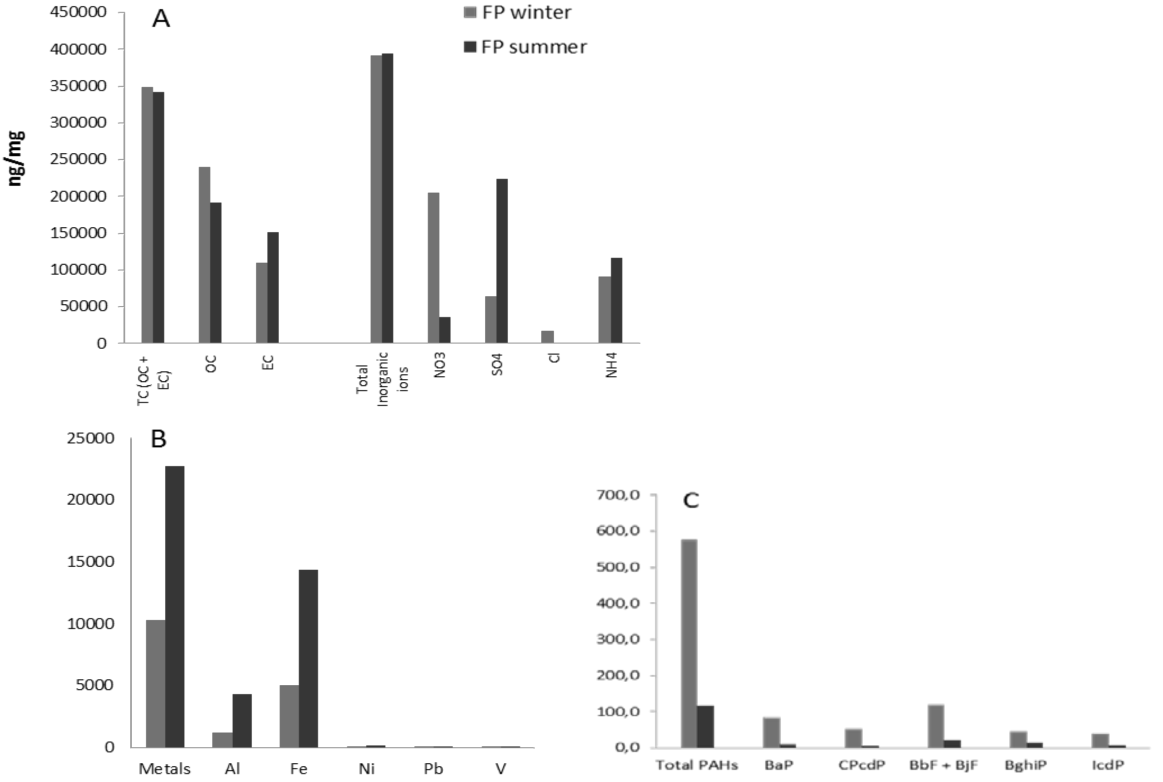

Figure 1. Chemical characterization of summer and winter PM2.5. The main organic and inorganic pollutants are reported. Total carbon (TC), elemental and organic carbon (EC and OC), total inorganic ions NO_3^-, $SO_4^=$, Cl^- and NH_4^+ (Fig 1A), total metals contribution, aluminium (Al), iron (Fe), nickel (Ni), lead (Pb) and vanadium (V) (Fig 1B), total PAHs and different contribution of five main PAHs (Fig. 1C) are reported.

3.2. ROS Formation

BEAS-2B exposed to winter fine PM showed a significant increase of intracellular ROS (Fig 2). Summer PM did not altered the oxidative equilibrium. These results are in agreement with the toxicological literature (Binkova et al., 2003; Chakra et al., 2007) and can be explained by the higher PAHs content in winter fraction, leading to cytochrome P-450 (CYP enzymes) activation, which we previously observed in cells exposed to winter FP (Gualtieri et al., 2012). Cytochrome P-450 is known to induce ROS formation catalyzing the oxidation of PAHs to quinones, electrophilic metabolites that enter redox cycles and amplify ROS (Burczynski and Penning, 2000).

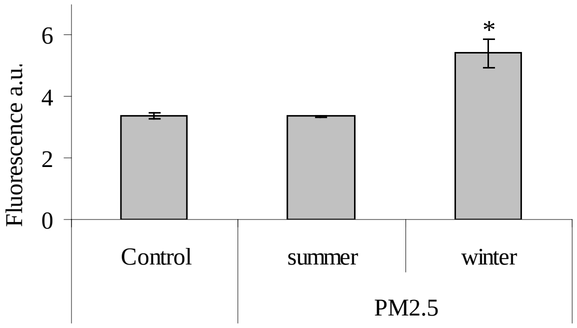

Figure 2. ROS formation in BEAS-2B exposed to summer and winter PM2.5. Winter particles induced a significant increase of intracellular ROS in exposed cells. * statistically significant $p < 0.05$

Preliminary data on UFP showed that ROS formation was increased by all the diesel blends tested (Fig 3). No data are available in the literature for these particles however Helfenstein et al. (2008) compared the effects of diesel soot UFP with those of other nanoparticles, such as single walled nanotubes and TiO2, evidencing a higher potency of diesel UFP to induce ROS. Further research are however needed to determine why organic UFP can induce reactive oxygen species and if this event is related to an actual oxidative stress condition.

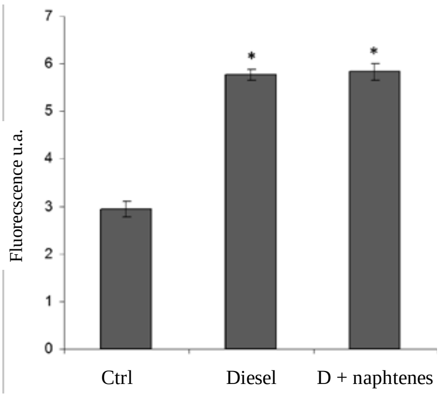

Figure 3. ROS formation in BEAS-2B exposed to UFP deriving from different diesel blends. All the blends tested were able to increase the intracellular ROS levels. * statistically significant $p < 0.05$

3.3. DNA Damage

Winter FP are able to induce DNA damages in exposed BEAS-2B. Our data (Table 2) demonstrate the ability of PM2.5 to induce significant damages at DNA level in exposed cells. The genotoxic potential of winter FP is in agreement with our previous results, showing that this fraction induces ROS formation and cytochromes P-450 activation; in fact, ROS and the reactive electrophilic PAHs intermediates produced by the CYP enzymes are known to induce oxidative DNA damages and DNA adducts (Park et al., 2009).

3.4. Cell Cycle

BEAS-2B cells exposed for 24 hour to 10µg/cm^2 of winter PM2.5 showed an altered cell cycle progression. The data (summarised in Table 2) obtained showed a significant increase of cell in G2/M phase. Furthermore, as reported in Gualtieri et al. (2011), winter fine PM is able to disrupt the mitotic process inducing an sustained arrest in metaphase, which explain the results observed at flow cytometer.

Several data have been reported on the ability of particulate matter to alter the cell cycle of exposed cells, however few data have been reported on the ability of particles to alter the mitotic tuning. Additional research will be focused to uncover the mechanisms of such alteration as it may be an outcomes with significant impact on human health. Abnormal mitosis might determine an incorrect chromosomes division between the daughter cells and promote DNA instability. The IARC definition of PM as carcinogen in humans open an important issue i.e. the definition of which molecular mechanisms are at the basis of the cell transformation.

Preliminary data on UFP from different diesel blends indicate their ability to induce significant cell cycle alteration. These data moreover suggest that the reference diesel is more potent in inducing such alteration while the doped blends resulted less effective (data not shown). The role of UFP on human health is under investigation however some evidences determined negative association between daily mean number concentrations of urban PM (dominated by UFP) and the lung function (Penttinen et al., 2001).

Table 2. DNA damage and cell cycle alteration induced by summer and winter PM2.5 as reported in our previous studies.

	Winter PM2.5	Summer PM2.5	References
DNA damage (γH2AX positive)	+ (flow cytometry, immunocytochemistry)	-	Gualtieri et al. (2011), Longhin et al. (2013)
Cell cycle	+ (G2/M arrest)	- (tested in THP-1 cells)	Gualtieri et al. (2011) Longhin et al. (2010)
Comet assay	+	Not tested	Gualtieri et al. (2011)
8-OxodG	+ (immunocytochemistry)	Not tested	Gualtieri et al. (2011)

4. CONCLUSIONS

Air quality is a matter of concern in several Countries for the well-known adverse health effects related. PM is one of the most important causes of degradation of air quality all over the world and several efforts have been posed to determine the causal relation between PM exposure and negative health outcomes.

The decision of IARC to include PM among the Group 1 carcinogens confirm the seriousness of this environmental issue. While epidemiological studies are in agreement in the definition of the risks associated with PM exposure, toxicologist are still uncovering different aspect of the mechanisms by which PM alter the cells homeostasis. Differences in the lab models used are likely an important issue in determining the different results reported but a parameter of major importance is the chemical composition of PM. Uncovering which PM associated compounds are responsible for the biological effects reported is a matter which can help in the future to adopt limitation to those sources with higher emission levels for the selected chemicals. In this respect the research is still far to score the decisive point, although a lot has been done. In the next future the toxicological research will need to pinpoint the causal relation composition-effect and pose the scientific basis for more focused air quality thresholds.

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6.3 PERSONAL EXPOSURE TO CARCINOGENIC POLYCYLIC AROMATIC HYDROCARBONS BOUND TO PM2.5 IN THE CZECH REPUBLIC

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ABSTRACT

Personal exposures to carcinogenic polycyclic aromatic hydrocarbons (c-PAHs) boud to airborne PM2.5 (particulate matter ≤ 2.5 µm) were measured. Sampling was carried out in 3 industrial cities in the Czech Republic: Ostrava, Karvina and Havirov. The city of Prague, served as a control. The first monitoring campaignes were held in winter and summer 2009. The active personal monitors PV1.7 for PM2.5 bound c-PAHs were used. Only adult non-smokers participated in the study (N=160).The average personal winter exposures to c-PAHs was highest in Karvina, 39.1, followed byOstrava at 15.1 and Prague at 4.3 ng/m^3. The winter levels were significantly higher than the summer values ($P<0.001$). We found outdoor concentration, environmental tobacco smoke exposure,home heating fuel of coal, wood or gas, frequency of exhaust fan use, cooking and commuting by a car to be the maindeterminants of personal exposure.

1. INTRODUCTION

The adverse effects of air pollution on human health have been well documented in many studies (Brunekreef and Holgate, 2002; Brunekreef et al., 2009; Künzli and Tager, 2005; Peng et al., 2009; Pope et al., 2002; Pope et al., 2004; Sorensen et al., 2003; Sram et al., 2005). The main sources of air pollution in the Czech Republic are industry, traffic and local heating (CENIA, 2009). The most important biologically effective components of air pollution are fine aerosol particles and compounds bound to them, particularly carcinogenic polycyclic aromatic hydrocarbons (c-PAHs) (Binkova et al., 1999). The aerosol particles having a diameter smaller than 2.5 µm ($PM_{2.5}$) are most important because of their ability to reach the lower respiratory tract in humans. From the retention point of view and the deposition of aerosols in the lungs, fine particles are the most dangerous because of their penetration through the bronchioles to the air sacks (Sugita et al., 2004).High $PM_{2.5}$ air pollution can have acute effects on human health from short-term exposure contributing to acute coronary events, especially among patients with underlying coronary artery disease. It may also contribute to complications of atherosclerosis and may play a role in triggering acute ischemic heart disease events. Higher long-term exposures of $PM_{2.5}$ contributes to pulmonary and systemic oxidative stress, inflammation, progression of atherosclerosis, risk of ischemic heart disease, could increase total mortality as well as lung carcinoma (Brunekreef and Holgate, 2002; Künzli and Tager, 2005; Peng et al., 2009, Pope, et al., 2006). Along with B[a]P and other c-PAHs, other toxic substances (such as nitro- and alkyl PAH derivatives) could be bound on $PM_{2.5}$ and could change their composition, toxicity and impact on human health (Lewtas, 2007; Nishioka and Lewtas 1992). However, recent data suggest that the most biologically important $PM_{2.5}$ components are PAHs (Topinka, et al., 2011). Some of these are classified as mutagenic and carcinogenic (compounds with 4 and more aromatic rings) (Binkova and Sram, 2004, Lewtas, 2007). We measured eight most often reported (carcinogenic) 4-6 ring PAHs which are only a subset of the group of potentially carcinogenic polycyclic aromatic compounds (4-6 ring PAHs, their sulfur- and nitrogen-containing analogues and their alkylated homologues). But selected eight c-PAHs can be used as a marker of exposure for the whole set because generally the concentrations of heterocyclic PAHs show proportionality to the concentrations of the corresponding PAHs (Brandt and Watson, 2003). The International Agency for Research on Cancer (IARC) classifies 8 compounds that were monitored as carcinogens in group 1 – carcinogens to humans (benzo[a]pyrene), group 2A – probable carcinogens to humans (dibenz[a,h]anthracene), group 2B – possible carcinogens to humans (benz[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, indeno[c,d]pyrene) and group 3 - not classifiable as to its carcinogenicity to humans (benzo[g,h,i]perylene) (IARC, 2009).

Previous studies have demonstrated that indoor air contains 50-70% of the pollution present in the outdoor air (Monn et al., 1997), but this depends strongly on the extent of ventilation and the type of housing. When assessing personal exposure, we need to consider that people spend on average 80-90% of their daily time indoors (Adgate et al., 2004; Brunekreef and Holgate, 2002; Jedrychowski et al., 2007). Personal exposure to air pollution is substantially affected by the distance from the source of pollution (proximity of busy roads, industrial sources), environmental tobacco smoke (ETS), oven cooking or frying. Personal exposure to air pollution depends strongly on individual activities (Devi et al., 2009; Gerharz et al., 2009). Together with a long-term increase in carcinogenic risk, human exposure to $PM_{2.5}$ can have significant adverse effects on the respiratory and cardiovascular systems (Pope et al., 2002; Pope et al., 2004).

In the context of a large-scale molecular epidemiology study, we analyzed the impact of air pollution on the population of industrial cities within the Moravian-Silesian region (MSR) of the Czech Republic: Ostrava, Karvina and Havirov. The capital city of Prague served as a control. We investigated personal exposure to c-PAHs and the impact on biomarkers of exposure, effect and susceptibility that could demonstrate possible damage to important biomolecules (DNA, proteins, lipids) and changes in the human transcriptome. This paper describes individual exposures to c-PAHs and their relationships to some exposure-modifying parameters.

2. METHODOLOGY

Sampling Localities

The MSR is an industrial and heavily populated area situated in the easternmost part of the Czech Republic. The region has been characterized by coal-mining, the processing of coal and metallurgy from the second half of the 18th century. It is bordered on the west, east and partially the south by mountains, forming a basin with frequent temperature inversions in winter. The MSR covers 5 427 km^2 with 1.25 million inhabitants (Czech Statistical Office, 2010). The MSR administrative structure consists of six districts (from the west: Bruntal, Opava, NovyJicin, Ostrava city, Karvina and Frydek-Mistek). The Karvina district is one of the most densely populated districts of the Czech Republic (789 inhabitants/km^2). There are approximately 30 thousands industrial facilities in the MSR. The most important industrial sources of air pollution are metallurgy, steel, coke ovens, coal-mining and power generation facilities. The population density in the MSR increases vehicle emissions and energy consumption, which are important factors decreasing air quality in this area. Fifty percent of the inhabitants use central heating, 34% natural gas, 10% coal, 3.3% electricity and 3% wood (Czech Hydrometeorological Institute, CHMI, 2008). With respect to the rising prices of energy, there could also be a “supplemental” kind of fuel that could significantly contribute to the air pollution in winter.

Prague is the capital and largest city in the Czech Republic, situated in central Bohemia. The city is spread over nine hills with 1.3 million inhabitants (Czech Statistical Office, 2010). Traffic and home heating are considered to be the most important sources of air pollution in winter. Most of the households (51.5%) use central heating, 40% natural gas, 5.7% electricity, 2.4% coal and 0.2% wood (CHMI, 2008).

Study Population

The study was planned to include three monitoring campaigns: winter 2009, summer 2009 and winter 2010. We are presenting the results from the first two campaigns. Non-smoking city policemen from Prague, Karvina and Havirov, and office workers from Ostrava, 22-63 years old, participated in the study. The same subjects participated in both campaigns. In an attempt to exclude unreported smoking, cotinine levels (a major nicotine metabolite) were measured in urine samples. Participants were informed prior to the field study that their smoking status would be checked biochemically (Langone and Van Vunakis, 1982). All participants completed a personal history questionnaire giving information on their place of residence, dietary habits, health history, and activities that might influence their exposure to the agents of interest for the study. In addition, during a 2-day observation period, when they carried the personal monitors, they kept a detailed time-location-activity diary (TLAD) in which they recorded information about their location and activities every hour. All the volunteers received information about the purpose of the study and signed an informed consent form prior to entering the study. The ethical committee of the Institute of Experimental Medicine AS CR in Prague approved the study.

Personal Exposure Monitoring

Personal exposure to 8 c-PAHs was measured by personal monitors used by the study subjects during two consecutive days (48h). The active PV 1.7 monitors (URG Corp, Chapel Hill, NC, USA) were equipped with Teflon-impregnated glass fiber filters T60A20 (Pallflex) collecting $PM_{2.5}$ particles (Binkova et al., 1995). The sampler was connected to a pump operating at 1.7 L/min. powered by batteries with inlet attached to the individual’s breathing zone and was located by his bed during the night (total weight of the sampler 1kg) (Williams, et al., 1999). Quantitative chemical analysis of 8 c-PAHs (benz[a]anthracene (B[a]A), benzo[a]pyrene (B[a]P), benzo[b]fluoranthene (B[b]F), benzo[g,h,i]perylene (B[ghi]P), benzo[k]fluoranthene (B[k]F), chrysene (Chry), dibenz[a,h]anthracene (DB[ah]A), indeno[1,2,3-c,d]pyrene (I[cd]P) was performed using a High Performance Liquid Chromatograph (HPLC) instrument with fluorescence detection in the laboratories of the certified company ALS Czech Republic, Prague (EN ISO CSN IEC 17025).

Statistical Analysis

Statistical analyses were done using Statistica 7.1 (StatSoft, OK, USA), SAS 9.1.3. (SAS Institute, NC, USA) and SPSS 17.0 software. The nonparametric method for bivariate analyses was used for data that did not follow a normal distribution: the Mann–Whitney Rank Sum U-test for comparison of two groups. The impact of TLAD activities to individual exposition values was estimated by splitting up all cases according to activity lengths into two groups by medians: below median (BM) and above median (AM) values of activity length. If in some cases median of distribution of individual TLAD activity was equal to zero, instead of median was used as splitting criterion condition equal to zero (BM) respective greater than zero (AM). Relations to personal exposure of this AM vs. BM group were tested by U-test. Multivariate models of estimating impact to personal exposures were completed by multivariate linear regression using forward stepwise mode building option.

3. RESULTS AND DISCUSSION

Personal Exposure to c-PAHs

The average winter c-PAHs and B[a]P personal exposure values were 15.2 and 2.5 ng/m^3 in Ostrava, 39.1 and 6.9 ng/m^3 in Karvina and 4.3 and 0.8 ng/m^3 in Prague, respectively ($p<0.001$). There was a similar rank in the concentrations of all monitored c-PAHs in the winter period – the highest concentrations in Karvina, followed by Ostrava and the lowest in Prague. A seasonal variation was clearly evident, as the values of c-PAHs and B[a]P exposure were significantly higher during the winter than during the summer period in all locations ($p<0.001$). The highest exposures were confirmed in Karvina city where the levels in summer were similar to the winter levels of c-PAHs in Prague.

The Environmental and Life Style Factors Affecting Personal Exposure

There were higher concentrations of c-PAHs in households that used coal and wood indoors for heating, but only 15% of respondents used this type of heating and the results were not significant. There were significantly higher concentrations of c-PAHs ($p<0.001$) when using a gas stove instead of an electric stove for cooking. Also, significantly higher concentrations of c-PAHs were found for subjects that cooked frequently. Using an exhaust fan in the kitchen decreased the cooking fumes and thus the concentration of pollutants.

The smoking status (tobacco smoke exposure) is always very important in the case of personal exposure. The effect of passive smoking reported in the questionnaires was an important factor contributing to the personal exposure to c-PAHs. Being in the company of smokers outdoors appeared as a significant factor for c-PAHs exposure in winter ($p<0.05$) and summer ($p<0.01$). Being in the company of smokers indoors also elevated exposure. Smoking at home increased personal exposure (significant in the summer season, $p<0.05$).

The results from the time activity questionnaire (TLAD) reflected the period of personal exposure monitoring during 48 hours. The results from bivariate analyses indicated that using public transport lowered personal exposure to c-PAHs (significant in winter $p<0.01$), while using a car increased exposure to c-PAHs in winter ($p<0.05$). The results also showed that time spent at home significantly increased exposure to c-PAHs. Passive smoking as well as activities performed with smokers increased personal exposure. Travelling significantly decreased exposure (probably connected with travelling by public transport). It seemed that using windows for ventilation increased exposure to c-PAHs mainly in the summer. Time spent indoors significantly increased exposure, while time spent at work decreased c-PAHs exposure. Time spent outdoors decreased exposure to c-PAHs, significantly in winter period ($p<0.01$). Linear models of relation between outdoor concentrations and personal exposures revealed strong correlation of c-PAHs ($p<0.001$) in all groups together ($B=0.31$, $p<0.001$), also in Prague ($B=0.48$, $p<0.001$) and in Ostrava ($B=0.29$, $p<0.001$). Multivariate regression model estimates strong significant relation between outdoor concentration of c-PAHs and personal exposures ($B=0.31$, $p<0.001$) in winter period. Many confounders from questionnaires were tested and as significant were found: being in work, at home or elsewhere (indoor) estimated as significant decreasing of relation outdoor concentration and personal exposure ($B=-0.56$, $p<0.001$, $B=-0.34$, $p<0.05$, $B=-0.59$, $p<0.05$ per hour of activity) for the Prague and Ostrava group together. When controlled for the individual locality, data had the same trend but were not significant.

Previous studies (Peluso, et al., 1998, Taioli, et al., 2007, Topinka et al., 2007) have shown that city policemen are a representative group reflecting the extent of air pollution in cities. They spend most of their work-time moving through the city, breathing its ambient air. In our study, city policemen from Prague, Karvina and Havirov were employed. The office workers enrolled in the study in Ostrava represented the majority of the population who spend most of their time indoors. Considering the high air pollution levels in Ostrava, personal exposure in this city is increased even in the population of subjects spending most of their time indoors.

Since 2004 (as we had data for B[a]P) Ostrava-Bartovice has been the most polluted locality in the Czech Republic (annual average 9.2 ng/m^3 in 2009, CHMI 2010). These concentrations are much higher by far than the EU (WHO standard) limit of 1 ng/m^3 of B[a]P, which is expected to be reached by the end of 2012 (DIRECTIVE 2004/107/EC). It is very likely that the more than nine-fold higher B[a]P levels pose a long-term increased health risk for the local inhabitants (Hertz-Picciotto et al., 2007, Rossner et al., 2010, Sram et al., 2007, Svecova et al., 2009, Topinka et al., 2007). In comparison to other studies dealing with personal exposure to B[a]P, Prague levels (winter/summer 0.8/0.1 ng/m^3) are similar to the levels observed in pregnant women in New York City - winter/summer 0.63/0.2 ng/m^3 (Tonne et al., 2004). Zmirou et al. (2000), measured the personal exposure of adult non-smoking volunteers in the Grenoble, France, metropolitan area and found an average B[a]P value of 0.67 ng/m^3, even though the winter exposures were indicated to be 3 to 25 times greater than summer exposures. Both occupational and environmental personal exposures to B[a]P were measured in taxi drivers in Genoa, Italy (Piccardo et al., 2004). The summer 1998/winter 1999/summer 1999 mean exposures were 1.4/1.23/1.22 ng/m^3, respectively, with significantly lower values in controls (0.16 ng/m^3). The personal B[a]P exposures in Ostrava city (winter/summer 2.5/0.4 ng/m^3) were highest for a non-occupationally exposed urban population.

Based on the questionnaire data, more than half of the study participants in Ostrava city used public transport and less than half used a car. According to bivariate analyses subjects using public transport had significantly lower exposure to c-PAHs in the winter season than the other groups ($p<0.05$), but this finding was not observed in the Prague participants. Bivariate models also showed being indoor as increasing personal exposure, but multivariate models of relation between outdoor concentration and personal exposure revealed being indoor as decreasing confounder indicating outdoor concentration as more important factor. Personal exposure is also determined by other factors such as ETS, the type of home heating, fumes encountered in the cooking process (e.g. frying or broiling), time spent in restaurants, and other activities. Detailed information about the subject`s life style and activities during the period of personal monitoring was obtained through a personal history questionnaire and TLAD. Statistical analyses suggest that factors increasing personal exposure include: outdoor concentration, ETS exposure, home heating fuel of coal, wood or gas, frequency of exhaust fan use, cooking, and commuting by car. In a study of personal exposures to PAHs in Krakow, the authors considered the following variables as short-term predictors of personal exposure to c-PAHs: residence in the city center, ambient temperature, wind speed, ETS exposure, frequency of exhaust fan use, residence near an industrial plant, commuting by tram, apartment height (floor), home heating fuel of coal or wood, time spent outdoors (hour/day), and simultaneously monitored outdoor concentration of c-PAHs (Choi et al., 2008).

The personal exposures to c-PAHs in Ostrava and Karvina show high levels in the winter period. This region, together with the Polish part of Silesia, is probably one of the most polluted areas in the EU by c-PAHs. B[a]P poses one of the major health risks from polluted air in urban and industrial areas. The Ostrava region is, due to its composition of sources, especially coke production and metallurgy, the most polluted region in the Czech Republic. Development over the last 12 years has resulted in a lasting adverse situation in this region that poses a long-term health risk for local residents.

4. CONCLUSIONS

The main determinants of exposure were observed outdoor concentration, ETS exposure, home heating fuel of coal, wood or gas, frequency of exhaust fan use, cooking, and commuting by car. The high biological activity and adverse effects of c-PAHs on human health are major reasons to monitor, regulate and decrease the prolonged and unsustainable high levels of these air pollution components in the Moravian-Silesian region and other polluted areas. This goal might be reached by the use of the latest technology for major industrial sources and home heating.

5. ACKNOWLEDGEMENTS

The study was supported by the Ministry of the Environment of the Czech Republic (CZ:MZP CR:SP/1b3/8/08), the Ministry of Education, Youth and Sports of the Czech Republic (CZ:MSMT CR:2B08005)and FP7/ENV-2012-308524-2/CITI-SENSE EC.

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6.4 HELATH RISK ASSESSMENT OF POLLUTANTS (PAHS AND HEAVY METALS) ASSOCIATED WITH PM_{10} IN URBAN PARKING GARAGES

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ABSTARCT

Traffic-related airpollutants are considered to have negative effects on human health. There is a premise about elevated pollutant concentrations in parking garages due to intensive vehicle emissions. In this study, twenty-four hour air samples of PM_{10} were collected from two Belgrade parking garages. Concentrations of 16 US EPA priority PAHs and Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sr and Zn were determined in PM_{10} samples. The carcinogenic health risk of employees' occupational exposure to four heavy metals (Cd, Cr, Ni and Pb) and six PAHs (B[a]A, Cry, B[b]F, B[k]F, B[a]P and DB[ah]A) was estimated. The concentrations of PM_{10}, Cd, Ni and B[a]P exceeded the EU Directive target values. The obtained carcinogenic health risk values were in a range of acceptable US EPA Incremental Lifetime Cancer Risk value of 10^{-4}–10^{-6}. These results indicate the need for setting indoor air quality guidelines.

1. INTRODUCTION

Under heavy traffic conditions, particulate matter (PM) concentrations were found to be about 10% higher indoor than outdoor (Fischer et al., 2000). Thus, like tunnels or tollbooths, parking garage facilities are interesting for air quality assessment.

Parking garages represent pollution hotspot microenvironments where employees and attendants are usually exposed to elevated concentrations of traffic-related air pollutants due to very intensive vehicle activities and poor air conditions in semi-enclosed space. Both diesel and gasoline engine emissions have been considered as significant sources of PM. Additionally, wearing of brake linings and tires together with dust resuspension are the uppermost contributors to the increased PM concentrations during parking process (e.g. Birmili et al., 2006). PM is highly chemically complex mixture, consisting of various organic and inorganic compounds. Some heavy metals and polycyclic aromatic hydrocarbons (PAHs), adsorbed on the particle surface, determine its toxicological characteristics and have adverse effects on human health (Kelly and Fussell, 2012). Nevertheless, only a few studies have been carried out in parking garages including measurements of CO, VOCs and pPAH concentrations (Kim et al., 2007) as well as PM mass concentrations and element content (e.g. Yaxuan and Xiang, 2013). However, according to our knowledge, this would be the first time that evaluation of pollution comprising measurements of both elements and PAHs content in PM_{10} was conducted in parking garage.

The current study was designed to provide a multi-pollutant assessment of air contaminants (PM_{10}, trace elements and PAHs) and to estimate the carcinogenic health risk assessment of employees' occupational exposure in parking garages in Belgrade.

2. METHODOLOGY

2.1. Experimental Set-up

The study was performed in two parking garages – Pionirski park (PP) and Masarikova (M) in the centre of the Belgrade city, for 10 weeks during the autumn-winter 2011. The studied parking garages are situated in heavy traffic area. They differ in size and conception: PP is an underground garage, whereas M has three underground and six elevated, semi-enclosed levels.

In both garages, MiniVol air samplers, provided with PM_{10} cut-off inlets with a flow rate of 5 L min^{-1}, were positioned near the tollgate. The site was chosen intentionally since the traffic intensity near the tollbooth is very high. PM_{10} were collected on preconditioned and pre-weighed Teflon-coated Quartz filters (Whatman, 47 mm diameter, 2 µm pore size). The sampling time was 24 hours, from 2 p.m. one day to 2 p.m. the next day. The PM_{10} mass concentrations were measured by gravimetric method.

2.2. Chemical Analysis

After the exposure periods, a half of each air filter was digested for 45 min in a microwave digester with 7 ml of 65% HNO_3 and 1 ml of 30% H_2O_2. The concentrations of 16 elements: Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sr and Zn were determined by ICP-OES. The quality control was performed using the standard reference material lichen-336 (IAEA).

For the purpose of PAH determination, the other halves of the filter samples were stored in the fridge, at 4 ºC until three subsequent extractions by ultra-sonifications, each in 50 ml of dichloromethane for 5 min. The extracts were filtered and merged into one which was vacuum rotary evaporated to 1 ml. Analysis was performed by GC-MS. The US EPA 16 priority PAHs were determined: naphthalene (Nap), acenaphthylene (Acy), acenaphtene (Acp), fluorene (Fl), phenantrene (Phen), anthracene (Ant), fluoranthene (Fl), pyrene (Pyr), benzo[a]anthracene (B[a]A), chrysene (Chr), benzo[b]fluoranthene (B[b]F), benzo[k]fluoranthene (B[k]F), benzo[a]pyrene (B[a]P), indeno[1,2,3-c,d]pyrene (I[cd]P), dibenzo-[a,h]anthracene (DB[ah]A) and benzo[ghi]perylene (B[ghi]P).

2.3. Health Risk Calculation

We used the US EPA health risk assessment model for carcinogenic risk estimation associated with exposure to some analyzed pollutants (US EPA, 1989, 1991). The assessment of carcinogenic health risk due to exposure to PM_{10}-bound elements and PAHs was conducted by calculating the incremental lifetime cancer risk (*ILCR*) value, according to:

$$ILCR = CDI \times \mathrm{SF}$$

Exposure to carcinogenic compounds, described by chronic daily intake (*CDI*), was calculated as follows:

$$CDI = \frac{C \times IR \times ET \times EF \times ED}{BW \times AT}$$

Here *C* is concentration of the chemical in the air (µg m^{-3}), *IR* is the inhalation rate (20 m^3 day^{-1}), *ET* is the exposure time (8 hours day^{-1}), *EF* is the exposure frequency (235 days $year^{-1}$), *ED* is the exposure duration (30 years), *BW* is the body weight (70 kg), and *AT* is the period over which the exposure is averaged (70 years for carcinogenic effects).

Slope factor (*SF*), as a parameter used to describe the toxicity of a carcinogenic chemical (i.e. the capacity of a chemical to cause negative health effect), was calculated from inhalation unit risk (UR), following the equation:

$$SF = \frac{UR \times BW}{IR}$$

The parameters used in this study were obtained from US EPA Integrated Risk Information System (IRIS) and Risk Assessment Information System (RAIS) chemical toxicity databases (data are given in Table 2 shown in section Results and Discussion).

3. RESULT AND DISCUSSION

3.1. Multi-pollutant Assessment in PM_{10} Samples

According to the obtained results, in 93% and 77% samples in PP and M, respectively, daily PM_{10} mass concentrations exceeded the air quality set value of 50 µg m^{-3} (Directive 2008/50/EC) (Table 1). Although prescribed value is related to outdoor air quality, it could also be applicable to indoor air quality assessment (WHO, 2010).

Nowadays in Serbia, there are no standards or guidelines for air element concentrations in parking garages, as well as in other indoor areas. However, for outdoor air, Directive 2004/107/EC and WHO guideline (2000) recommended target values for several carcinogenic elements: As, Cd, Hg, Ni and Pb. Aiming to estimate possible effects of the exposure of employees and attendants to those elements, concentrations of Cd, Ni and Pb, determines in this study, were compared with their target values (Table 1). In all the samples analysed, Ni concentration exceeded the set daily value − 20 ng m^{-3}. Nickel is used as main additive in fuels and can be emitted from vehicle exhaust in traffic (US EPA, 2000). Additionally, geological origin of Ni was also reported in Serbia (Environmental quality in the city of Belgrade, 2011). So, its origin could be also explained by soil/road dust resuspension. Lead is still present in the urban environment notwithstanding the leaded gasoline was legally banned in Serbia in 2011. However, Pb concentrations did not exceed the daily air quality value.

In general, the total PAH daily concentrations varied from 13 to 42 ng m^{-3} and from 10 to 29 ng m^{-3}, in PP and M, respectively. High molecular weight PAHs were dominated in PM_{10} samples. B[a]P is one of the most important studied PAHs because of its carcinogenic effect. Also, it is the only one regulated by the Directive 2004/107/EC. For B[a]P, the target value of 1.0 ng m^{-3} for the total content in PM_{10} fraction, averaged over one year is established. In our study, obtained average B[a]P concentrations exceeded the target value in both garages (Table 1).

Table 1. Average concentrations of PM_{10} and Cd, Ni, Pb and B[a]P measured in PM_{10} for 10 weeks in two parking garages (Pionirski park - PP and Masarikova - M) and the air quality target values.

Pollutant	PP	M	Target value	Unit
PM_{10}	104	117	$50^{a,b}$	µg m^{-3}
Cd	5.1	3.7	5.0^{a}	ng m^{-3}
Ni	66	72	20^{a}	ng m^{-3}
Pb	145	77	500^{b}	ng m^{-3}
B[a]P	1.6	1.3	1.0^{a}	ng m^{-3}

[a]EU Directive 2004/107/EC, annual average
[b]WHO 2000, annual average

In order to compare pollutant concentrations measured indoor and outdoor, we used data from two local monitoring stations- Slavija and Bulevar Despota Stefana, situated in the surrounding of the studied parking garages. It was possible to compare the results from this study only with outdoor levels of PM_{10} and Pb, reported in Ecological Bulletin, October – December, 2011. During the experiment, average outdoor concentrations of PM_{10} and Pb were about 99 µg m^{-3} and 400 ng m^{-3}, respectively. Higher PM_{10} indoor concentrations are expected having in mind that parking garages are enclosed microenvironments, characterised with poor air conditions and intensive vehicle activities causing dust resuspension. Remarkably lower indoor Pb levels could be explained by absence of exhaust emissions enriched with Pb additives in leaded gasoline. On the other side, Pb is still present in different medium of environment, predominantly in soil.

3.2. Health Risk Assessment

According to US EPA IRIS (2013), some of the determined pollutants (Cd, Cr, Ni, Pb, B[a]A, Cry, B[b]F, B[k]F, B[a]P and D[ah]A) have been classified as known and possible human carcinogens. Due to the most intense vehicle activities, there are elevated pollutant concentrations in vicinity of tollgate, where employees spend the working days. Thus, the carcinogenic risk of employees' occupational exposure to these pollutants was characterised. On the other side, health risk for visitors was not estimated having in mind that they occasionally and for short period stay in garages.

The calculated ILCR values and cumulative cancer risks for PM_{10}-bound heavy metals and PAHs are shown in Table 2. ILCR value represents an incremental probability of an individual developing cancer over a lifetime as a result of exposure to these pollutants through inhalation. In this study, the individual ILRC values obtained for Cd, Cr, Ni and Pb as well as PAHs was below the lower limit value of the acceptable ILCR range of 10^{-4} to 10^{-6} (US EPA Cancer Risk Guideline, 2005). On the other side, cumulative cancer risk obtained as sum of ILCR values for the individual chemicals was in the acceptable range. Trace elements can be considered as the major contributors to the assessed cancer risks (about 98% of the total cumulative cancer risk in both PP and M). Hence, the risk evaluated for PAHs deemed to be insignificant in comparison with trace elements.

Comparing the results obtained in two garages, it becomes apparent that cumulative cancer risk values are quite similar, with slightly lower value in PP. Although PP is completely underground garage as opposed to M, the lack of appropriate ventilation system with filters in M is a possible cause of this result.

ILCR = 4.41 ·10-7 , ET = 8 h per day, EF = 5 days per week, 235 per year
ILCR = 1.97 ·10-6 , ET = 24 h per day, EF = 7 days per week, 350 per year

Table 2.Values of average concentration (C), chronic daily intake (CDI), slope factor (SF) and calculated incremental cancer risk (ILCR) for different heavy metals and PAHs in PM_{10} samples collected in two parking garages

	Masarikova			**Pionirski park**				
	C ($\mu g\ m^{-3}$)	**CDI ($\mu g\ kg^{-1}\ day^{-1}$)**	**ILCR**	**C ($\mu g\ m^{-3}$)**	**CDI ($\mu g\ kg^{-1}\ day^{-1}$)**	**ILCR**	**Unit Risk ($\mu g\ m^{-3})^{-1}$**	**SF ($\mu g\ kg^{-1}\ day^{-1})^{-1}$**
Cd	$3.70\ 10^{-3}$	$9.75\ 10^{-5}$	$6.13\ 10^{-7}$	$4.60\ 10^{-3}$	$1.21\ 10^{-4}$	$7.62\ 10^{-7}$	$1.80\ 10^{-3}$[a]	$6.30\ 10^{-3}$[a]
Cr	$3.66\ 10^{-2}$	$9.62\ 10^{-4}$	$4.04\ 10^{-5}$	$3.00\ 10^{-2}$	$7.88\ 10^{-4}$	$3.31\ 10^{-5}$	$8.40\ 10^{-2}$[b]	$1.20\ 10^{-2}$[b]
Ni	$7.25\ 10^{-2}$	$1.95\ 10^{-3}$	$3.27\ 10^{-6}$	$6.28\ 10^{-2}$	$1.69\ 10^{-3}$	$2.83\ 10^{-6}$	$4.80\ 10^{-4}$[a]	$1.68\ 10^{-3}$[a]
Pb	$4.51\ 10^{-2}$	$1.21\ 10^{-3}$	$5.09\ 10^{-8}$	$1.13\ 10^{-1}$	$3.04\ 10^{-3}$	$1.28\ 10^{-7}$	$1.20\ 10^{-5}$[a]	$4.20\ 10^{-5}$[a]
B[a]P	$1.30\ 10^{-3}$	$3.42\ 10^{-5}$	$1.32\ 10^{-7}$	$1.60\ 10^{-3}$	$4.20\ 10^{-5}$	$1.62\ 10^{-7}$	$1.10\ 10^{-3}$[a]	$3.85\ 10^{-3}$[a]
B[a]A	$2.40\ 10^{-3}$	$6.31\ 10^{-5}$	$2.43\ 10^{-8}$	$3.10\ 10^{-3}$	$8.15\ 10^{-5}$	$3.14\ 10^{-8}$	$1.10\ 10^{-4}$[a]	$3.85\ 10^{-4}$[a]
Cry	$1.10\ 10^{-3}$	$2.89\ 10^{-5}$	$1.11\ 10^{-9}$	$1.40\ 10^{-3}$	$3.68\ 10^{-5}$	$1.42\ 10^{-9}$	$1.10\ 10^{-5}$[a]	$3.85\ 10^{-4}$[a]
B[b]F	$2.50\ 10^{-3}$	$6.57\ 10^{-5}$	$2.53\ 10^{-8}$	$3.10\ 10^{-3}$	$8.15\ 10^{-5}$	$3.14\ 10^{-8}$	$1.10\ 10^{-4}$[a]	$3.85\ 10^{-4}$[a]
B[k]F	$2.30\ 10^{-2}$	$6.04\ 10^{-4}$	$2.33\ 10^{-7}$	$2.90\ 10^{-3}$	$7.62\ 10^{-5}$	$2.93\ 10^{-8}$	$1.10\ 10^{-4}$[a]	$3.85\ 10^{-4}$[a]
DB[a,h]A	$2.80\ 10^{-3}$	$7.36\ 10^{-5}$	$3.09\ 10^{-7}$	$3.40\ 10^{-3}$	$8.93\ 10^{-5}$	$3.75\ 10^{-7}$	$1.20\ 10^{-3}$[a]	$4.20\ 10^{-3}$[a]
Cumulative cancer risk			$4.51\ 10^{-5}$			$3.75\ 10^{-5}$		

[a] RAIS
[b] IRIS

4. CONCLUSIONS

The survey of air quality assessment in two Belgrade's parking garages showed elevated PM_{10} mass concentrations and increased content of some heavy metals (Cd, Ni and Pb) in air of semi-enclosed parking spaces with intensive vehicle activities. Due to poor air conditions, particles, as well as pollutants bound to them, remain longer inside the garage depending predominantly on ventilation effectiveness. Their idividual ILRC values calculated for Cd, Cr, Ni and Pb as well as PAHs was below the lower limit value of the acceptable range. However, cumulative cancer risk value obtained for Cd, Cr, Ni and Pb was 98 % of the total cumulative cancer risk. Contrary, cumulative cancer risk value calculated for carcinogenic PAHs (B[a]A, Chr, B[b]F, B[k]F, B[a]P and D[ah]A) was only 2 %. Therefore, heavy metals can be considered as the dominant contributors to the assessed cancer risks. According to the instrumental measurements and health risk assessment, the need for setting indoor air quality guidelines is apparent.

ACKNOWLEDGEMENTS

This paper was realized as a part of the project No III43007 financed by the Ministry of Education and Science of the Republic of Serbia.

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6.5 EFFECTS OF ARSENIC ON PHOSPHORUS CONTENT IN DIFFERENT ORGANS AND CHLOROPHYL FLUORESCENCE IN PRIMARY LEAVES OF SOYBEAN

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ABSTRACT

The effect of arsenic (32 - 96 µM) on the phosphorus content and Chl fluorescence was studied in soybean (*Glycine max*Merril) grown in the nutrient solution with and without phosphorus. The increased concentration of As led to the decrease in P content in plant organs. Parameters of Chl fluorescence of soybean leaves in the presence of these As concentrations did not show significant changes.

Additional key words: Glycine max, photosystem 2, quantum yield.

INTRODUCTION

Pollution of the soil and atmosphere by arsenic (As) is conditioned by the industry development. Copper smelters and thermal plants are great pollutants of the atmosphere. According to Smirnov and Muravin (1977) natural As content in the soil is 5 mg (As) kg^{-1}(soil). As, an analogue to phosphorus, is absorbed from the soil by P transporters. As inhibits P uptake in barley (Asher and Reay 1979) and *Arabidopsis* (Dunlop *et al*. 1997). In many of plant species, arsenates and arsenites have an affinity for thiols, such as glutathione. Furthermore, phytochelatins are formed as a response to As (Schmöger *et al*. 2000). Hartley-Whitaker *et al*. (2000a, 2000b) confirmed that As-tolerant *Holcus lanatus* L. had higher phytochelatins concentrations than As-intolerant species. Hence, similar to heavy metals, As also mobilises the socalled nonenzymic antioxidants, such as glutathione, ascorbates, and phytochelatins.

MATERIAL and METHODS

In order to find which plant species was suitable for environmental remediation, we investigated the effect of different As concentrations (2.4, 4.8, 6.0, and 7.2 g (As) m^{-3}, corresponding to 32, 64, 80 and 96 µM As) on the uptake and distribution of phosphorus (P) in plant organs and chlorophyll (Chl) fluorescence in the soybean leaves. After the 5 days of germination in the dark, plants of soybean (*Glycine max* Merril. cv. ZPS 015) were transferred into pots with the nutrient medium of pH 7.0 (Hoagland and Arnon 1950). Plants were grown in growth chambers at a 12-h photoperiod, irradiance of 300 µmol m^{-2} s^{-1} (*Sylvania* cool white lamp *P9GT12-CEW-VHO*, Danvers, USA) and day/night temperature of 24/20 °C. Plants grown on the complete medium were the control ones. The P content in the other three variants was half or double of that in the control or zero. Plants grown with and without P were exposed to 32, 64, 80 and 96 µM Na_2HAsO_4 for 5 d. Roots, stems, cotyledons, and leaves was finally dried to the constant mass and homogenised by grinding. The P amount was determined by the official method of A.O.A.C. (Horwitz 1960). Chl fluorescence of soybean primary leaves was measured by the *PAM 101/103* fluorimeter (*Walz*, Effeltrich, Germany). Parameters of Chl fluorescence were defined after Maxwell and Johnson (2000). The analysis of variance (*ANOVA*) for all variables was carried out by the *MStatic* programme.

Abbreviation: Chl - chlorophyll; Fm - maximum fluorescence; F_0 - initial fluorescence; Fv - variable fluorescence; NPQ – nonphotochemical quenching, PS_2 - photosystem 2; qP - photochemical quenching.

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RESULTS AND DISSCUSION

The applied concentrations of As, especially from 64 to 96 μM, decreased the P content in all plant organs of soybean with different P amounts in the nutrient solution (Table 1). Higher molar P/As ratios reduced Astoxicity in all plant organs of soybean. The P content in leaves and cotyledons of P-deficient soybean plants significantly decreased in the presence of As, indicating the P stored in these organs was used for building plant biomass. A statistically highly significant P decrease in the presence of As in plants with 0.05, 0.1 and 0.2 M KH2PO4 in the nutrient solution in relation to P-deficient plants pointed out that the As uptake was similar to the P uptake. In the studies with As and Al (Milivojević *et al.*, 2000) the deficiency and decrease of P content in the medium led to the increase in toxicity of these elements. Investigations of the effect of As on some physiological parameters of maize in the early growth stage showed that applied As decreased the growth, leaf and biomass accumulation, induced lipid peroxidation and increased peroxidase activity. It also decreased the Chl, carotenoid, and protein contents and Fv/Fm ratio indicated lower photosynthetic efficiency (Stoeva *et al*. 2003/4). The study of growth parameters, ATP and chlorophyll contents in *Pisum sativum* seedings after 9-d exposure to sodium arsenate showed that the low concentration of arsenate elevated the ATP content per fresh matter of the cotyledons and shoot, but the higher concentrations were without any significant effect (Paivoke 2003). The observed negative correlation between growth and ATP concentration may imply that the arsenate impacted indirectly via ATP on the growth of seedlings. The measured parameters of Chl fluorescence (Table 2) did not vary significantly under As treatments. Changes of maximum quantum yield of photosystem 2 (Φ) and photochemical quenching of fluorescence (qP) under the highest As concentrations point out to the changes of the redox state of the plastoquinone pool. Non-photochemical quenching (NPQ) of fluorescence (related to photoprotective processes in antennae of chloroplast thylakoids) was not significantly modified by As application. Since As in higher concentrations in the nutrient solution significantly reduced the P accumulation in root, leaf and stem, in certain cases even below 0.3 %, it can be spoken about the deficiency of the phosphorus.

The measured parameters of Chl fluorescence did not significantly change in primary leaves of soybean, pointing out that there were no effects of As on the photosynthetic electron transport. Abadia *et al*. (1987) found out that a low phosphorus content in the leaf had only small effects on the content of pigment-protein complexes of the thylakoids and electron transport in the light reactions of photosynthesis, while Rao and Terry (1989) detected that the P deficiency in soybean reduced the photosynthetic assimilation of CO_2. We assume that certain concentrations of As caused P-deficiency without affecting the photochemical reactions in soybean leaves during the trial. This is in accordance with the conclusions of Abadia *et al*. (1987) about a weak influence of low leaf P content on light reactions of photosynthesis.

CONCLUSIONS

Our opinion is that the observed phenomenons indicates an early phase of As-induced P-deficiency in soybean.

ACKNOWLEDGEMENTS

The study was funded by the Ministry of Education, Science and Technological Development of the Republic of Serbia, projects No. TR 31037 and TR 31018.

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Table 1. Amount of phosphorus [% (d.m.)] in organs of 11-d- old soybean plants grown under different As concentrations (0 - 96 µM) in phosphate-sufficient (+P), half of control phosphate (1/2P), double of control (2P) and phosphate-deficient (-P) nutrient solution. Values are means of three determinations from 2 - 3 plants.

As [µM]	Leaf				Stem				Cotyledon				Root			
	+P	1/2P	2P	-P	+P	1/2P	2P	-P	+P	1/2P	2P	-P	+P	1/2P	2P	-P
0	1.50	1.39	2.05	0.82	0.95	0.72	1.85	0.72	0.97	0.86	1.13	0.83	1.30	1.29	1.95	0.81
32	0.84	0.88	1.57	0.54	0.94	0.77	1.00	0.48	0.75	0.72	1.00	0.65	1.25	0.88	0.92	0.83
64	0.29	0.83	0.87	0.50	0.56	0.72	0.78	0.46	0.42	0.43	0.31	0.45	0.65	0.38	0.91	0.50
96	0.29	0.46	0.50	0.56	0.15	0.10	0.46	0.54	0.31	0.59	0.46	0.33	0.28	0.29	0.46	0.52
LSD $_{0.05}$	0.31				0.29				0.44				0.32			
LSD $_{0.01}$	0.43				0.41				0.62				0.44			

Table 2. Effects of arsenic in phosphate-sufficient nutrient medium on parameters of induction and quenching of fluorescence. Fv/Fm or Fv/Fo (maximum quantum yield of PS2 in the dark); Fv'/Fm' (maximum quantum yield of PS_2 in the light); Φ (maximum quantum yield of PS_2 at the equilibrium photosynthesis); qP (photochemical quenching of Chl fluorescence); NPQ (non-photochemical quenching of Chl fluorescence) (Maxwell and Johnson 2000).

As [µM]	Parameters of fluorescence					
	Fv/Fm	Fv'/Fm'	Fv/Fo	Φ	qP	NPQ
0	0.804	0.524	4.111	0.320	0.560	4.111
32	0.796	0.426	3.897	0.190	0.435	3.897
80	0.797	0.442	3.927	0.230	0.515	3.927
96	0.806	0.584	6.296	0.510	0.880	6.296
$LSD_{0.05}$	0.060	0.130	2.440	0.230	0.290	2.440
$LSD_{0.01}$	0.100	0.190	3.700	0.350	0.440	3.700

6.6 *IN VITRO* CO-CULTURE MODELS FOR THE STUDY OF PM BIOLOGICAL EFFECTS

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ABSTRACT

The comprehension of PM effects on human health is still not complete, expecially regarding systemic effects and action mechanisms; in order to deepen this knowledge, there is a need of improved *in vitro* models. We have previously reported that Milan summer PM_{10} induces pro-inflammatory interleukins release in mono-cultured cells; here co-cultures models have been set up to have a further insight of such effect. Epithelial A549 cells and THP-1 monocytes have been co-cultured to simulate the interaction between alveolar cells and monocytes/macrophages in the alveoli. An air-blood barrier (ABB) model has been prepared culturing alveolar epithelial cells (NCI-H441) and endothelial cells (HPMECST1.6R) on the opposite sites of a transwell filter insert. The results obtained exposing the models to PM10 demonstrated that the cell lines used are able to cross communicate, influencing the response. These models may be thus very useful for the study of PM-induced systemic events and mechanisms.

1. INTRODUCTION

Particulate matter (PM) is known to induce effects at the pulmonary epithelia, the primary target of inhaled material; inflammation, oxidative stress and DNA damage have been observed in various lung epithelial cell lines exposed to PM (Schwarze et al., 2006). Nevertheless, particles are also able to induce systemic effects, and the relationship between PM exposure and increased rates of mortality and morbidity in the population for cardiovascular diseases has been by now assessed by numerous epidemiological studies (Brook et al., 2010; de Kok et al., 2006). PM-induced cardiovascular effects have been related to the presence of a systemic inflammatory status, evidenced by the augmented levels of pro-inflammatory cytokines in the circulating blood of the exposed population (Pope and Dockery, 2006). However, the cellular mechanisms explaining these associations have not been fully elucidated.

PM’s cardio-vascular effects likely involve alterations of the air-blood barrier (ABB); constituted by the respiratory epithelium and the underlying endothelial cells, this is the pivotal defence system from inhaled material, which prevents the entrance of particles into the blood circulation. The ABB integrity is thus essential to maintain lung functions; it has been suggested that particles might affect ABB integrity, cross through the barrier, and translocate to the blood circulation (Mills et al., 2009; Furuyama et al., 2009). Another suggested mechanism for PM systemic effects involves the release in the blood stream of inflammatory mediators by epithelium and endothelium; in fact, an inflammatory status induced by PM in the barrier epithelium might promote signal transduction to the underlying endothelium, and consequent systemic inflammation, which finally might lead to vascular diseases (Mills et al., 2009).

In order to clarify this issue, detailed *in vitro* studies are highly needed. Common mono-cultures are very useful to the study of local cellular effects but they are inadequate for the study of systemic effects, involving different types of cells. In a co-culture system at least two cell types are cultivated together and these models can mimic more closely the *in vivo* situation (Klein et al., 2011). In this study we focused on the capability of co-cultures to better clarify the biological mechanisms of PM, with particular attention to the release of inflammatory mediators by epithelium and endothelium. At this aim we used two different models; the first, consisting in a co-culture of epithelial respiratory cells (A549) and monocytes (THP-1), has been helpful to determine whether the presence of cells from the immune system may modulate the inflammatory response to PM exposure. Then we set up an ABB model constituted by epithelial cells (NCI-H441) and endothelial cells from the micro-pulmonary circulation (HPMEC-ST1.6R), cultured at the opposite sides of a transwell insert. This model allowed to investigate if the PM-induced epithelial inflammation may lead to endothelial activation and potential systemic effects.

We exposed the models to Milan summer PM10, which we previously assessed to be able to induce an inflammatory response in lung epithelial cells (A549) and monocytes (THP-1) mono-cultures (Gualtieri et al., 2010), in relation to a high endotoxin and metals content (Camatini et al., 2010).

Data here presented demonstrate that, in both co-culture models, a biochemical crosstalk between the different cell lines occurred in response to PM, demonstrating that these models are suitable systems for the study of the mechanisms of PM-induced systemic effects.

2. METHODOLOGY

2.1. PM Sampling

PM was collected at Milan Torre Sarca, a representative background site for air quality, during summer (June and July). A low volume gravimetric sampler (EU system, FAI Instruments, Rome, Italy) was used to collect PM samples on Teflon filters for biological analysis. Particles were extracted from filters by sequential sonications in a Soltec water-bath (SONICA, four cycles of 20 min each) in sterile water. Particle suspensions were dried into a desiccator, weighed and stored at -20 °C, and re-suspended in sterile water at a final concentration of 2 µg/µl, just before use.

2.2. Cells Cultures

The human lung type II pneumocytes, A549, and the human monocytes, THP-1 (ATCC, Rockville, MD, USA), were maintained in Opti-MEM medium (Invitrogen) supplemented with 10% foetal bovine serum (FBS), 100 µg/ml penicillin and 100 U/ml streptomycin, in a humidified atmosphere with 5% CO_2 at 37 °C. Human pulmonary microvascular endothelial cell line HPMEC-ST1.6R was received from Dr. Ronald E. Unger (Institute of Pathology, Medical University of Mainz, Johannes Gutenberg University, Mainz, Germany) and cultured in 0.2% gelatine coated flasks, in M199 medium supplemented with 15% FBS, 2 mM Glutamax I, 25 µg/mL sodium heparin, 25 µg/mL endothelial cell growth supplements, and 100 U/100 µg/mL Pen/Strep, at 37 °C and 5% CO_2. The human lung adenocarcinoma cell line NCI-H441 (ATCC, USA) was maintained in OptiMEM medium (Gibco) supplemented with 10% FBS and Pen/Strep (100 U/100 µg/mL), at 37 °C, 5% CO_2.

2.3. A549/THP-1 Cells Co-culture

Epithelial cells/monocytes co-culture was set up in 12 well-plates; A549 were seeded at a concentration of 70,000 cell/well and after 24 h THP-1 cells were added at a concentration of 150,000 cells/well. Treatment with 10 µg/cm^2 of PM was performed afterwards; for each experiment, untreated control cells were carried together.

Experiments on mono-culture were preformed for comparison; A549 were seeded at a concentration of 70,000 cell/well in 12 well-plates, and the next day 80% sub-confluent cells were treated with 10 µg/cm^2 of PM. THP-1 cells (150,000 cells/well) were seeded in 12 well-plates and immediately treated with 10 µg/cm^2 of PM.

2.4. Air-Blood Barrier Model

For the onset of air-blood barrier model, HPMEC-ST1.6R (9×10^4/cm^2) cells were seeded on the lower surface of transwell filter membranes (polyester; 0.4 µm pore size; Costar) coated with 0.2% gelatine, and incubated for 2 h at 37 °C and 5% CO_2. The filter membranes were then turned upside down and placed in a 12-well plate filled with 1.5 mL HPMEC-ST1.6R medium and incubated for 24 h. The day after NCI-H441 (2×10^4/cm^2) cells were seeded on the top surface of the transwell filters and cultured to confluence simultaneously with the HPMEC-ST1.6R seeded on the lower surface, for 11 to 13 days. To induce differentiation, the NCI-H441 cell line in co-cultures was treated with 1 µM Dexamethasone from day 3 of cultivation.

Summer PM10 (10 µg/cm^2) was added to the apical compartment of the transwell at the 11th/12th day of co-culture, for additional 24 h.

2.5. Transepithelial Electrical Resistance (TEER) Measurements

In order to determine the integrity of the *in vitro* barrier, the transbilayer electrical resistance (TEER) was measured with an EVOM Volt Ohm Meter (World Precision Instruments, Berlin, Germany) equipped with a EndOhm Chamber (World Precision Instruments, Berlin, Germany). After PM exposure, before TEER measurements, transwell filters were washed with PBS and incubated with M199 medium for 10 min in order to avoid alteration in TEER values due to cellular debris and to insert handling. The TEER of polyester transwell filter membranes coated with gelatine 0.2%, without cells, was measured and set as blank. Barrier resistance readings ($\Omega \times$ cm^2) were made by subtracting the resistance of the blank filter membrane and by multiplying the area of the insert (1.12 cm^2). Resistance was reported as mean ± SE of at least three independent experiments.

2.6. Immunostaining

After 11-12 days of cultivation the apical compartment of co-culture was washed in PBS and then fixed with paraformaldehyde (1%) for 20 min at room temperature. Cells were then permeabilized with Triton X-100 1%, TWEEN 1% in PBS + BSA 3% for 20 min at 4 °C. The cells were then washed in PBS and incubated overnight at 4 °C with rabbit anti-human zonula occludens-1 (ZO-1) antibody (Cell signaling; 1:100) in PBS + BSA 1%. Cells were then washed three times in PBS and then incubated with the secondary antibody goat anti-rabbit Alexa Fluor-488 (Invitrogen Molecular Probes; 1:1000) for 1 h. For actin staining cells were incubated 1 h with phalloidin-TRIC (Sigma Aldrich, 1:750). Samples were mounted on a glass slide with ProLong mount (Invitrogen) and observed by an AxioScope reverted microscope (Zeiss, Germany).

2.7. Cytokine Release

After 24 h of treatment, cell culture media were collected and centrifuged for 10 min at 250 g to remove cell debris and floating particles. The final supernatants were stored at -80 °C until use. IL-6, IL-8 and IL-1β protein levels were determined by ELISA (Cytosets, BioSource International) according to manufacturer's guidelines. Absorbance was measured and quantified by a plate reader (Multiskan Ascent, Termo Scientific Instruments) at wavelengths of 450 and 570 nm.

3. RESULTS AND DISCUSSION

3.1. Inflammatory Response in the A549/THP-1 Co-culture System

The modulation of inflammatory response after PM10 exposure was analyzed measuring the release of the pro-inflammatory interleukins IL-6 and IL-8 and of the systemic cytokine IL-1β in A549/THP-1 mono- and co-culture. As we previously reported (Longhin et al., 2010), the results showed that all the proteins investigated were significantly released by the A549/THP-1 co-culture system treated with summer PM10, at higher levels in comparison to A549 and THP-1 mono-cultures; this can be expecially observed for IL-6 (Figure 1). A549 cells in mono-culture showed a low inflammatory response. These results are in agreement with other authors who showed a large increase in IL-6 and IL-8 levels in A549/THP-1 and A549/Monomac6 co-cultures exposed to hematite and silica sol particles. This higher release in co-culture system may depend on the contact between monocytes and epithelial, which can induce THP-1 to express macrophages-like properties (Wottrich et al., 2004; Striz et al., 2001).

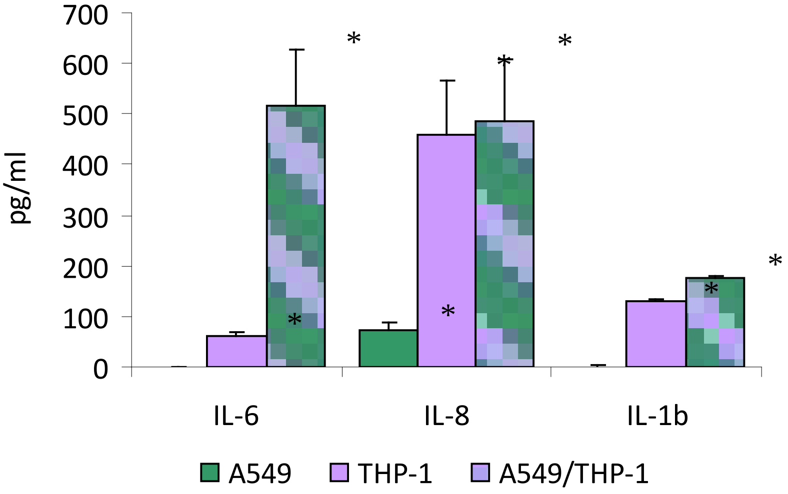

Figure 1: Release of pro-inflammatory proteins. The release of pro-inflammatory proteins IL-6 and IL-8 and IL-1β has been evaluated in A549 and THP-1 mono-cultures, and in the A549/THP-1 co-culture model, exposed for 24h to summer PM10 (10 µg/cm^2). * Statistically different from control, $P<0.05$, ANOVA.

3.2. Formation of the Alveolar-Capillary Barrier

The formation of tight junctions (TJs) and an high transepithelial electric resistance (TEER) are two pivotal parameters that permit to estimate the integrity of the *in vitro* ABB. The TJs formation was assessed by the staining of the tight junctional cytoplasmic plaque Zonula occludens-1 (ZO-1). ZO-1 is a cytoplasmic proteins that forms the TJs and it also links the transmembrane protein occludin to the actin-based cytoskeleton (Fanning et al., 1998). Data showed that after 11–13 days of co-cultures and stimulation with Dexamethazone (1 µM), ZO-1 junctions were localized at the periphery of NCI-H441 cells as a continuous line delineating the limits of each cell (Figure 2). The formation of junctions between adjacent alveolar cells (NCI-H441) was also evident by transmission electron microscope analysis (Bengalli et al., 2013).

The integrity of the barrier was assessed by measuring the TEER, expressed as Ohm × cm^2. Data showed that NCI-H441 and HPMEC-ST1.6R cocultures reached the maximum TEER at 703 ± 118 Ω × cm2 (N=7) after 11–13 days of cultures. These TEER value are reached thanks to the tight junctions (TJs) and adherens junctions (AJs) formation between epithelial cells via highly regulated events that establish cell differentiation (apical-basolateral membrane polarity) (Yonemura et al., 1995).

3.3. Summer PM10 Effects on the Barrier Integrity and Inflammatory Response

As reported by Bengalli et al., (2013), the treatments with PM10 did not produce significant changes in the TEER values. However, the apical treatment of the ABB with summer PM10 induced a significant increase in IL-1β release from basolateral compartment (158 pg/mL versus 28 pg/mL of the control group) while the apical compartment did not produce IL-1β release (Bengalli et al., 2013). Our data are in accordance with Kasper et al. (2011), who obtained a basolateral activation of endothelial cells after treatment of the epithelial cells at the apical side; these results confirm the biochemical crosstalk between the two sides of the membrane, supporting the functionality and representativeness of this ABB model. The ability of PM in triggering the release of a potent inflammatory mediator as IL-1β, has to be carefully taken into account. In fact, a significant increase of circulating IL-1β in a population exposed to high level of PM has been demonstrated (Van Eeden et al., 2001), and can be of great importance when explaining the onset of PM systemic effects.

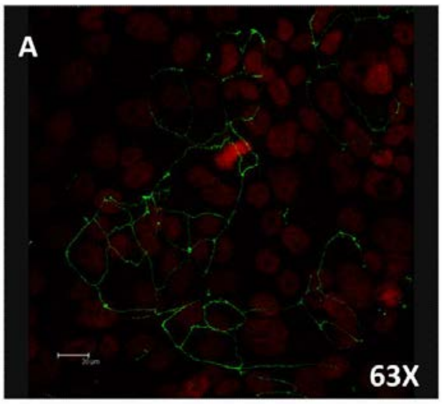

Figure 2: Tight junction formation. Immunofluorescent staining of the TJ cytoplasmic plaque protein ZO-1 (green) of the NCI-H441 monolayer on day 12; NCI-H441 differentiated with 1 µM Dexamethasone after day 3 of culture were positively stained for ZO-1 at the cell-cell interface confirming the formation of functional TJs. Nuclei were stained with DRAQ-5 (red).

4. CONCLUSION

Particulate matter (PM) exposure has been related to systemic adverse outcomes, such as cardio-vascular diseases, but the mechanisms leading to these effects have not been fully elucidated; in order to gain more insight in this issue, there is a need of improved *in vitro* models. Here we have used two models of co-cultured cells to deepen the knowledge on the effects induced by ambient particles. Our results showed that in both co-culture models, a biochemical crosstalk between the different cell lines occurred in response to PM. In particular the results obtained on the ABB model suggest that PM is likely able to induce endothelial dysfunctions, which might concur to cardio-vascular diseases.

The results here presented demonstrate that the co-culture models are suitable systems for the study of the lung damage mechanisms, and may be very important to get enhanced understanding of PM-induced systemic effects.

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6.7 TRAFFIC-RELATED TRACE ELEMENT CONCENTRATIONS IN PM_{10} AND IN HORSE CHESTNUT LEAVES

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ABSTRACT

In this study, airborne particulates (PM_{10}) and leaves of horse chestnut were collected at selected urban sites in Belgrade, Serbia, between September 2006 and September 2012. All samples were analysed for trace element concentrations of As, Cd, Cr, Ni and Pb. The results showed that mean PM_{10} concentration was decreasing during the first years of study (2006 til 2009), yet with another increase in the year 2012, and the highest value in that year was 54 µg m^{-3}. Highest values of trace element concentrations in leaves were observed in year 2012, with the exception of Pb. Lead concentration showed a decreasing trend during the whole studied period, in both PM_{10} and tree leaves. Since the leaded gasoline was banned in 2011, a possible reason for that could be in increasing number of vehicles using unleaded kind along the previous years.

1. INTRODUCTION

Urban environment is heavily impacted by airborne particulates originated from fossil fuel combustion, traffic, industry and other anthropogenic activities. A number of epidemiological studies (Pope and Dockery, 2006; Schwartz, 2001) have demonstrated that acute and chronic health effects are related to the inhalable PM10 exposure in the urban environment. Trace elements, attached to PM10, can be toxic and may have dangerous impacts on human health. The assessment of the trace element content of PM10 gives important information for development of risk assessment strategies.

In the past decades, biomonitoring of air quality using plants has been widely used to detect and monitor trace and other element atmospheric contamination (Bargagli, 1998; Markert, 1993). Trees are very efficient at trapping atmospheric particles, and tree leaves have been used for biomonitoring of trace elements in air quality studies (Bargagli, 1998). Previous studies in the Belgrade urban area have shown that horse chestnut leaves could be valuable tool for monitoring of trace elements in the atmosphere (Šućur et al., 2010; Aničić et al., 2011; Tomašević et al., 2011).

The objective of this study was to assess a temporal variability of PM10 mass concentrations and traffic-related trace element content in PM10 and tree leaves samples collected from year 2006 to 2012. It was a transition period when gasoline with lead-alkyl additives was replaced with unleaded kind, with the complete ban of the leaded gasoline in the beginning of 2011.

2. METHODOLOGY

All samples, PM10 and leaves, were collected from sites exposed to high traffic influence in the Belgrade city center. The PM10 measurements were done by using two automatic monitoring stations for continuous atmospheric particulate monitoring (EN 12341:1998) close to the City public health institute, and at square Slavija, the busiest roundabout in Belgrade. The trace element content in PM10 was assessed by ICP-MS, using EPA method O-3.5 (EPA, 1999).

The leaves of horse chestnut (*Aesculus hippocastanum* L.) were sampled from two representative parks (Karađorđev park and Botanička bašta) situated also in the Belgrade city center, and close to the previouse mentioned automatic monitoring stations. At Botanička bašta, leaf samples were collected from the traffic-exposed streets bordering it. The sampling was held during the multy-year period from year 2006 to 2012. Leaves were collected at the end of vegetation cycle, in September. Leaf samples were briefly washed (for 3–5 s) with bidistilled water before further analysis, in order to assess only accumulated and strongly adhered particles on the leaf surface. Microwave digestion of approximately 0.4 g leaf sample (dry weight) was performed with 3 mL of 65% HNO_3 and 2 ml of 30% H_2O_2. The concentrations of As, Cd, Cr, Ni and Pb in leaves were measured from the digested samples by ICP-MS using an Agilent 7500ce mass spectrometer equipped with an Octopole Reaction System (ORS). Quality control was performed using the standard reference material lichen-336 (IAEA).

3. RESULTS AND DISCUSSION

Temporal trend of the PM10 mass concentration in the Belgrade urban area, obtained in this study, is presented in Fig 1. The decrease of PM10 mass concentration was observed during the first years of the study (2002–2006), and with another increase from the year 2009, probably due to some new sources of airborne particulates. The most important sources of PM emission in urban areas are considered to be the incomplete combustion of fossil fuels, friction on mechanical components such as brakes and tyre rubber, increasing proportion of diesel, high weight and four-wheel drive vehicles, traffic, together with industrial and domestic combustion processes (Fuller and Green, 2006). However, another source that may exert a considerable influence on ambient level and composition of PM10 is mineral dust, which exhibits high geographical variations. Also, the concentration differences among the PM10 samples could stem from the changes in the meteorological conditions that were present during sampling.

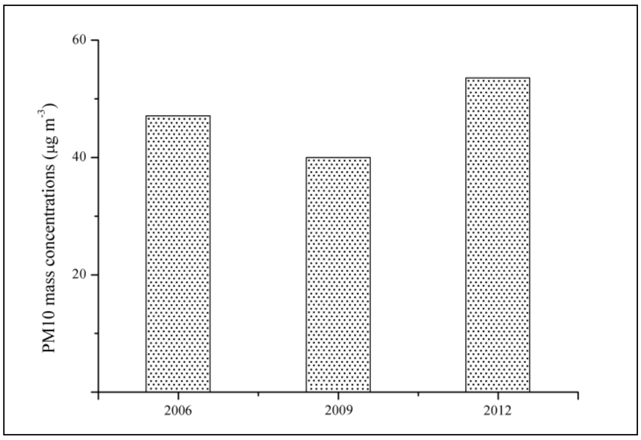

Figure 1. Temporal trend of mean PM10 mass concentrations of the years 2006, 2009 and 2012.

The mean concentration of PM10 in year 2006 was 47 µg m^{-3}, while in 2012 the concentration was 54 µg m^{-3}, which exceeded the European Union limit value of 50 µg m^{-3} (daily limit that should not to be exceeded more than 35 days in a year) (EEA, 2008). Although the PM10 concentration in 2102 was higher than at the beginning of the study, the trace element concentrations did not show this regularity (Fig 2.).

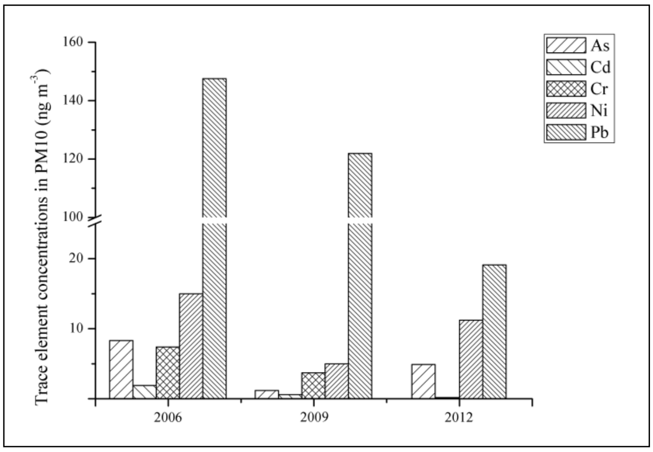

Figure 2. Annual trace element concentrations in PM10 of the years 2006, 2009 and 2012.

On the other hand, the lowest values of Cd and Pb concentrations were reported for 2012. Comparison of the study results with other studies showed higher concentration of Ni, but also lower concentration of Cd, Cr and Pb (Gaga et al. 2012; Kuzu et al. 2013). Nickel mainly originates from combustion of fossil fuels or traffic vehicle exhaust as an additive in fuels, although its relatively high geological origin in Belgrade was confirmed (Ecological Bulletin, 2008; 2011). Lead was the most abundant element in the samples, since it was still widely used as additive in gasoline, but with a strongly declining trend during the studied period as a result of increasing number of new types of vehicles using unleaded gasoline. Concentration of Cr was not measured in PM10 samples for the year 2012. Brake linings have been demonstrated to result in the release of Cd, Cr and Ni (Wiseman et al. 2013), while various vehicle electronic components and batteries of cars that contain Cd have been reported as a potential source of it (Fernandez-Espinosa and Ternero-Rodriguez, 2004).

As it was suggested from the previous studies (Šućur et al., 2010; Aničić et al., 2011; Tomašević et al., 2008, 2011), horse chestnut showed a good response as bioindicator of trace element air pollution. Trace element concentration in leaf samples showed a similar annual temporal trend in comparison to that of the PM10 trace element concentrations, with the increase in the year 2012 (Fig 3.). Also, the highest values of trace element concentrations were measured in leaves sampled in 2012, with the exception of lead, which had a decreasing trend during the whole studied period.

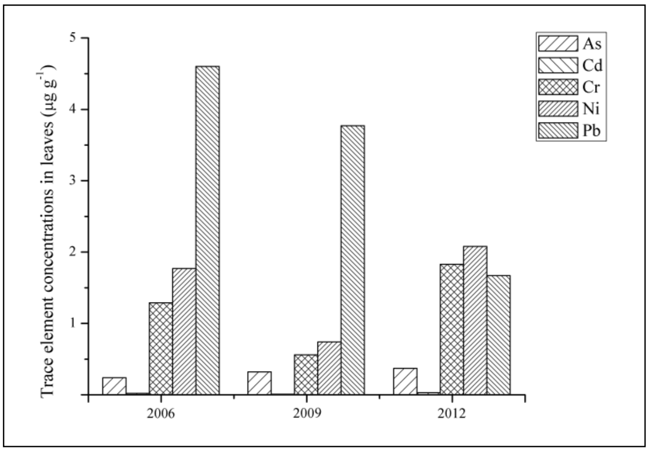

Figure 3. Temporal trend of trace element concentrations in horse chestnut leaves of the years 2006, 2009 and 2012.

Although official ban of leaded gasoline was put into effect at the beginning of 2011, a decreasing tendency of lead concentration in PM10 and in leaf samples was evident even in previous years. However, the concentration of Pb after the 7-years period was about 7 times lower in PM10 and almost 3 times lower in the leaf samples then at the beginning of the study period, indicating that during the examined period, one of most significant sources of this element was traffic.

4. CONCLUSIONS

In the study of PM10 mass concentrations and trace element concentrations in PM10 and tree leaves (*A. hippocastanum*) from the Belgrade city centre, it was shown that the PM10 mass and element concentrations had a decreasing trend in the first years of the study. On the other hand, in the subsequent study year, 2012, an increase in concentrations was recorded. Although the PM10 concentration in 2102 was higher than at the beginning of the study, the trace element concentrations did not show this regularity. The horse chestnut leaves showed good response to changes in bulk atmospheric pollution, with the similar trend in trace element concentrations as in the PM10 samples, but with the highest values in the year 2012, with the exception of Pb concentration. Lead concentration showed a decreasing trend during the whole studied period, as the result of reduced use of leaded gasoline during the studied period and with complete ban of the leaded gasoline in the beginning of 2011.

5. ACKNOWLEDGMENTS

The authors acknowledge financial support from the Ministry of Education, Science and Technological Development of the Republic of Serbia, project Nos. III 43007 and OI 172007.

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7 HEALTH EFFECTS

7.1 SUMMARY OF EVIDENCE ON HEALTH ASPECTS OF AIR POLLUTION IN SUPPORT OF THE REVIEW OF THE EU AIR QUALITY POLICIES: THE WHO REVIHAAP PROJECT

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ABSTARCT

The World Health Organization (WHO) recently coordinated an important international project to provide the European Union (EU) with information on the evidence of health aspects of air pollution, in support of the comprehensive review of EU's air quality policies scheduled for 2013. The advice provided is formulated in the form of responses to 24 key policy-relevant questions asked by the European Commission (EC). The questions cover general aspects of importance for air quality management, as well as specific topics concerning health aspects of individual air pollutants. The text in response to the questions was developed by a large group of invited experts from top institutions across the world. The first results from the evidence review conclude that a considerable amount of new scientific information on health effects of particulate matter (PM), ozone (O_3) and nitrogen dioxide (NO_2), observed at levels commonly present in Europe, has been published in the recent years. This new evidence supports the scientific conclusions of the WHO Air Quality Guidelines (AQG), last updated in 2005, and indicates that the health effects in some cases occur at air pollution concentrations lower than those serving to establish the 2005 Guidelines. It also provides scientific arguments for taking decisive actions to improve air quality and reduce the burden of disease associated with air pollution in Europe. The material developed as part of these projects is equally relevant to all Member States, in their development and implementation of effective strategies to reduce air pollution and its significant impacts on public health.

Keyword: air pollutants, air pollution – adverse effects environment and public health, evidence based practice, guidelines, health policy, WeBIOPATR

1. INTRODUCTION

Air pollution is an important determinant of health. A wide range of effects of ambient air pollution on health has been well documented by studies conducted in various parts of the world. Based on this accumulated evidence, WHO develops and issues its AQG, last updated in 2005 (WHO, 2006).

Health effects of respirable particulate matter (PM_{10}) and its fine fraction ($PM_{2.5}$) are especially well documented. There is no evidence of a safe level of exposure or a threshold below which no adverse health effects occur (WHO, 2006). Over 80% of the population in the European Region of WHO lives in cities with levels of PM exceeding WHO AQG. Only a slightly decreasing trend in average concentrations has been observed in countries in the Region over the last decade (WHO Regional Office for Europe, 2011). PM pollution creates a substantial burden of disease, reducing life expectancy by almost 9 months on average in Europe (WHO Regional Office for Europe & Convention Task Force on the Health Aspects of Air Pollution, 2006). In some more polluted cities of Europe, life expectancy could be increased by ca. 20 months if the pollution from $PM_{2.5}$ would be reduced to WHO AQG level (Medina, 2012). A recently published global burden of disease study ranked ambient air pollution from fine PM as the eight leading risk factor, contributing to 3.2 million premature deaths annually in the world (Lim et al., 2013). Since even at relatively low concentrations the burden of air pollution to health is significant, effective management of air quality aiming to achieve WHO AQG levels is necessary to reduce health risks.

Exposure to air pollutants is largely beyond the control of individuals and requires action by public authorities at the national, regional and international levels. A multi-sectoral approach, engaging relevant sectors such as transport, housing, energy production and industry is needed for the development and effective implementation of long-term policies to reduce the risks of air pollution to health. Rapidly expanding scientific evidence reveals new and significant impacts of the pollution on populations' health. Interpretation and synthesis of this evidence, in order to enable their use in policy formulation, requires special efforts from the scientific community engaged in a dialogue with the policy makers.

In that context and in the framework of 2013 EU's Year of Air (European Commission, 2013), the WHO Regional Office for Europe implemented the two projects "Evidence on health aspects of air pollution to review EU policies – REVIHAAP", and "Health Risks of Air Pollution in Europe – HRAPIE" with financial support from the EC. These projects provide scientific evidence-based advice on health aspects of air pollution in support of the comprehensive review of EU's air quality policies scheduled for 2013. The review focuses on air pollutants regulated in the EU Air Quality Directives (European Commission, 2013).

The review of accumulated scientific evidence prepared as part of these projects is equally relevant to all Member States, in their development and implementation of effective strategies to reduce air pollution and its impact on public health.

2. MATERIALS AND METHODS

The advice provided by the REVIHAAP project is formulated in the form of responses to twenty-four key policy-relevant questions asked by the EC (WHO Regional Office for Europe, 2013a). The questions cover general aspects of importance for air quality management, as well as specific topics concerning health aspects of individual air pollutants. The responses are directed at policy makers, and they are therefore short and concise in order to be useful during the policy process. Specifically, they discuss new findings regarding health effects, concentration-response functions and thresholds, as well as air pollution constituents and sources. The review also provides an integration of the evidence and present implications for future revision of the WHO AQG, as well as policy considerations for the EU. In addition, the document highlights critical data gaps.

This advice is grounded on a review of the latest scientific evidence for PM, O_3, NO_2, sulphur dioxide (SO_2), as well as emissions to the air of individual metals (arsenic, cadmium, nickel, lead, and mercury) and polycyclic aromatic hydrocarbons (PAHs), as regulated in the EU Air Quality Directives (European Commission, 2013). Even though some of the questions directly asked for the assessment of individual policies or policy instruments, the REVIHAAP discussion and answers covered only the scientific evidence underlying the policy and has not addressed political arguments.

The text in response to the questions was developed by a large group of scientists. A Scientific Advisory Committee (SAC) of eight scientists, experienced in previous reviews conducted by WHO and representing key areas relevant for the projects (epidemiology, toxicology, atmospheric sciences) was put together to guide and oversee the projects. Two meetings with the SAC members were held in December 2011 and June 2012 to provide advice and coordinate the plan of the work. The review was conducted by a group of 29 invited experts from top institutions across the world, representing various relevant scientific disciplines. These experts, working in small groups, reviewed the accumulated scientific literature, drafted succinct answers to the questions and longer rationales to the answer emerging from the research results. Furthermore, 32 invited external reviewers, as well as the SAC members, provided detailed comments on the completeness of the reviewed literature, validity of conclusions reached and the clarity of the answers. The authors used the comments to revise the text subject to further review. A full list of SAC members, expert authors, and external reviewers is provided in the project report for REVIHAAP.

In addition to the discussion conducted by electronic means of communication, direct discussion on the answers and evidence in their support was held at two WHO Experts Meetings which took place in WHO/ECEH office in Bonn, Germany on 21-23 August 2012 and 15-17 January 2013. During the second meeting, the final text for the 24 answers covered under the REVIHAAP project was adopted. The discussion solely covered scientific arguments, addressing the methodological quality of the influential studies as well as the completeness and consistency of the evidence generated by studies conducted in various areas of the world, in various populations and with various scientific methods. The conclusions reflect the collective expert judgment of specialists in the field, and the final text of the answers was adopted by consensus of experts present at the meeting.

3. RESULTS AND DISCUSSION

A summary of the main results of the evidence review of the health effects of air pollution for PM, O_3 and NO_2 is presented below, as well as evidence on sources, fractions and components of PM and proximity to roads. The implication of this evidence for the WHO AQG and EU policies is discussed. The reader is referred to the final publication presenting the results of the REVIHAAP project for the full text for all answers and evidenced-based rationales developed under this project (WHO Regional Office for Europe, 2013b).

Evidence on health effects of PM

Since the WHO AQG were issued in 2005, many new studies from Europe and elsewhere on both short and long-term exposure to $PM_{2.5}$ have been published. These studies provide considerable support for the scientific conclusions in the AQG and suggest additional health outcomes to be associated with $PM_{2.5}$. As such, there is additional support for the effects of short-term and long-term exposure to $PM_{2.5}$ on both mortality and morbidity based on several studies conducted in Europe and North America. Furthermore, an authoritative review of the evidence for cardiovascular effects, conducted by cardiologists, epidemiologists, toxicologists and other public health experts, has concluded that long-term exposure to $PM_{2.5}$ is a cause of both cardiovascular mortality and morbidity. Additional studies are now linking long-term exposure to $PM_{2.5}$ to several new health outcomes including atherosclerosis, adverse birth outcomes and childhood respiratory disease. There is also emerging evidence suggesting possible links between long-term $PM_{2.5}$ exposure and neurodevelopment and cognitive function as well as other chronic disease conditions such as diabetes.

The effects of long-term exposure are much greater than those observed for short-term exposure, suggesting that effects are not just due to exacerbations but may be also due to progression of underlying diseases. While acute and long-term effects are partly interrelated, the long-term effects are not the sum of all short-term effects. Maintaining independent short-term and long-term limit values for ambient PM_{10} in addition to $PM_{2.5}$ to protect against the health effects of both fine and coarse particles is therefore well supported. In the absence of a threshold and in light of linear or supra-linear risk functions, public health benefits will result from any reduction of $PM_{2.5}$ concentrations, whether or not the current levels are above or below the limit values.

The scientific conclusions of the AQG about the evidence for a causal link between $PM_{2.5}$ and adverse health outcomes in humans have been confirmed and strengthened and, thus, clearly remain valid. As the evidence base for the association between PM and short-term, as well as long-term, health effects has become much larger and broader, it is important to update the current AQG for PM. This is particularly important as recent long-term studies are showing associations between PM and mortality at levels well below the current annual WHO AQG level for $PM_{2.5}$ which is 10 $\mu g/m^3$.

PM sources, fractions and components

A considerable number of new studies have been published, providing evidence on the health effects of size fractions, components or sources of PM. There are three important components – black carbon, secondary organic aerosols, and secondary inorganic aerosols – for which there is substantial exposure and health research which finds associations and effects. They each may provide valuable metrics for the effects of mixtures of pollutants from a variety of sources. As well, short-term exposures to coarse particles (including crustal material) are associated with adverse respiratory and cardiovascular effects, including premature mortality. There is increasing, though as yet limited, epidemiological evidence on the association between short-term exposures to ultrafine (<0.1 µm) particles and cardio-respiratory health, as well as the central nervous system. A variety of air pollution sources have been associated with different types of health effects. Most evidence is accumulated so far for an effect of carbonaceous material from traffic. A more limited number of studies suggest that traffic-generated dust, including road, brake and tire wear, also contribute to the health effects.

Proximity to roads

Motor vehicles are a significant source of urban air pollution. Health effects of proximity to roads were observed after adjusting for socioeconomic status, and after adjusting for noise. Elevated health risks associated with living in close proximity to roads is unlikely to be explained by $PM_{2.5}$ mass since this is only slightly elevated near roads. In contrast, levels of pollutants such as ultrafine particles, carbon monoxide, NO_2, black carbon, PAHs and some metals are also more elevated near roads. Individually or in combination, these are likely to be responsible for the observed health effects. Current available evidence does not allow discernment of the pollutants or pollutant combinations that are related to different health outcomes although association with tail pipe primary PM is increasingly identified.

Exhaust emissions are an important source of traffic related pollution and several epidemiological and toxicological studies have linked such emissions to adverse health effects. Road abrasion, tire wear and brake wear are non-exhaust traffic emissions which become relatively more important with progressive reductions in exhaust emissions. Toxicological research increasingly indicates that such non-exhaust pollutants could be responsible for some of the observed health effects.

Evidence on health effects of O3

The WHO AQG from 2005 found support only for short-term effects of ozone on mortality and respiratory morbidity. Since then, several cohort analyses have been published on long-term ozone exposure and mortality. There is evidence from the most powerful study, the American Cancer Society Study, for an effect of long-term exposure to ozone on respiratory and cardio-respiratory mortality, which for the latter is less conclusive (Jerrett et al., 2009; Smith et al., 2009). Also there is some evidence from other cohorts for an effect on mortality among persons with potentially predisposing conditions (chronic obstructive pulmonary disease, diabetes, congestive heart failure, and myocardial infarction). Additionally, several new follow-up long-term exposure studies have reported adverse effects on asthma incidence, asthma severity, hospital care for asthma and lung function growth. New evidence on adverse effects from short-term exposure to ozone comes from large, multicentre time-series studies in Europe, the USA and Asia. In Europe, adverse effects of short-term exposure to daily concentrations of ozone (maximum 1-hour or 8-hr mean) on all-cause, cardiovascular and respiratory mortality have been reported. Adverse effects of exposure to daily ozone concentrations on both respiratory and cardiovascular hospital admissions, after adjustment for the effects of particles (PM_{10}), have also been reported. The evidence for a threshold for short term exposure is not consistent, but where a threshold is observed, it is likely to lie below 45 ppb (90 $\mu g/m^3$) (max 1-hr).

In the AQG, toxicological data from animal and human exposure studies already provided ample support for short-term effects of ozone on a range of pulmonary and vascular health-relevant endpoints. The evidence has strengthened in the intervening period. In addition, new findings from a range of experimental animal models, including primates, provides evidence of chronic injury and long-term structural changes of the airway in animals exposed to prolonged periods to ozone, and to ozone and allergens combined. New epidemiological and experimental data, both in humans and animal models, have also arisen suggesting an effect of ozone exposure on cognitive development and reproductive health, including preterm birth.

Evidence on health effects of NO_2

New studies document associations between day-to-day variations in NO_2 and variations in mortality, hospital admissions, and respiratory symptoms. Also, more studies have now been published showing associations between long-term exposure to NO_2 and mortality and morbidity. Both short- and long-term studies have found these associations with adverse effects at concentrations that were at or below the current EU limit values, which for NO_2 are equivalent to the WHO AQG. Chamber and toxicological evidence provides some mechanistic support for a causal interpretation of the respiratory effects. Hence, the results of these new studies provide support for updating the current WHO AQG for NO_2 to give: (i) an epidemiologically based short-term guideline and (ii) an annual average guideline based on the newly accumulated evidence. In both instances, this could result in lower guidelines.

There is evidence of small effects on inflammation and increased airway hyper-responsiveness with NO_2 *per se* from chamber studies. New review reports suggest weak to moderate lung cell changes in animal studies. These occur at concentration ranges not far from those that can take place at the roadside or in traffic for multiple hours. The chamber studies examined small numbers of healthy or mild asthmatic subjects whereas the general population will include subjects who are more sensitive and may therefore experience more pronounced effects at lower concentrations.

The associations between NO_2 and short-term health effects in many studies remain after adjustment for other pollutants. The pollutants used in the adjustments include PM_{10}, $PM_{2.5,}$ and occasionally black smoke. This does not prove that these associations are completely attributable to NO_2 *per se*, as NO_2 in these studies may also represent other constituents (which have adverse health effects) not represented by currently regulated PM metrics. As there is consistent short-term epidemiological evidence and some mechanistic support for causality, particularly for respiratory outcomes, it is reasonable to infer that NO_2 has some direct effects.

It is much harder to judge the independent effects of NO_2 in the long-term studies because, in those investigations, the correlations between concentrations of NO_2 and other pollutants are often high so that NO_2 might be representing a mixture. In this case, chamber studies do not apply and toxicological evidence is limited. However, some epidemiological studies do suggest associations of long term NO_2 exposures with respiratory and cardiovascular mortality, and with children’s respiratory symptoms and lung function, that were independent of PM mass metrics. As with the short-term effects, NO_2 in these studies may represent other constituents. Despite this, the mechanistic evidence, particularly on respiratory effects, and the weight of evidence on short-term associations are suggestive of a causal relationship.

4. CONCLUSIONS

The REVIHAAP project, through answers to 24 key policy questions posed to WHO by the EC, concludes that a considerable amount of new scientific information on health effects of PM, O_3 and NO_2, has been published in the recent years. This new evidence supports the scientific conclusions of the WHO AQG, last updated in 2005, and indicates that the effects, in some cases, occur at air pollution concentrations lower than those serving to establish the 2005 Guidelines.

Significant health effects of air pollutants are observed at levels commonly present in Europe. The REVIHAAP project also provides scientific arguments for taking decisive actions to improve air quality and reduce the burden of disease associated with air pollution in Europe. It further recommends that the EC ensures that the evidence on the health effects of air pollutants and the implications for its air quality policy are regularly reviewed.

Further work has also been conducted under the follow-up WHO project HRAPIE in order to document emerging issues on health risks from air pollution related to specific source categories (e.g. transport, biomass combustion, metals industry, refineries, power production), specific gaseous pollutants or specific components of PM (e.g. size-range like nano-particles and ultra-fines, rare-earth metals, black carbon (EC/OC). As well, concentration-response functions to be included in cost–benefit analysis will be identified.

The two WHO projects described above, implemented in collaboration with the European Commission, also provide an important input to the broader work of WHO in the context of the Convention on Long Range Transboundary Air Pollution, to which the Russian Federation, and a number of other Member States from the East of European Region of WHO, are the parties. The Task Force on Health, working under the Convention, jointly with WHO will use the results of the projects to intensify support to these Member States which develop their policies independently of the European Union processes.

DISCLAIMER

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ACKNOWLEDGEMENTS

The authors gratefully acknowledge the contribution of the experts who have been involved in the project REVIHAAP. A full list of experts is provided in the REVIHAAP project report. The REVIHAAP project was carried out with funding from the European Union and World Health Organization Regional Office for Europe. The World Health Organization retains copyright and all other rights in the manuscript of this article as submitted for publication. This paper was presented at the 4th WeBIOPATR Workshop and Conference, Belgrade, 2nd-4th October, 2013.

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7.2 BLACK SMOKE AND DAILY MORTALITY OF CARDIOVASCULAR DISEASES IN NIŠ, SERBIA

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ABSTRACT

The aim of our paper was to investigate the association between ambient concentrations of black smoke and daily total non-accidental cardiovascular mortality in Niš, Serbia.. Daily cardiovascular mortality data between 2001 and 2005 were obtained in charge of coding the medical causes of death according to the International Classification of Diseases-10th Revision (I00-I99) among person 19-64-yrs-old. Daily concentrations of BS and SO_2, was monitored in the local monitoring network. The daily means of temperature, relative humidity and barometric pressure values for the same period were obtained from Republic Meteorological Department. Generalized linear model extending Poisson regression was applied. Estimated OR of unipolutant regression model for among person19-64-yrs-old was 1,001118 (95% CI: 0,97188 to 1,05208), and estimated OR of bipolutant model was 1,001107 (95% CI: 0,96991 to 1,05398) per 10µg/m^3.This mortality time series study have shown that all age cardiovascular mortality in two age groups: all age and among person 19-64-yrs-old, are not related to ambient air pollutants concentrations.

Key words:person 19-64-yrs-old,cardiovascular mortality, hospital mortality, black smoke, air pollution.

1.INTRODUCTION

Exposure to air pollution contributes to the development of cardiovascular diseases, according to epidemiological evidence (4,7). These scientific statements focus on cardiovascular hospitalisation and mortality. Air pollution is composed of many environmental factors, such as carbon sulphur dioxide, ozone, particulate matter, monoxide and others.

The potential biological mechanisms of influence air pollution on cardiovascular system have two possible interlinks-inflammatory response and abnormal autonomic control (8,11,12). Many air pollutants are in the relationship with cardiovascular damage but of special interest are particulate matters with different aerodynamic diameter. The time series data suggest that an increase in particulate pollution of 10 µg/m^3 is associated with an increase cardiovascular mortality of about 1.4% .

This paper reports the results on the effects on daily black smoke (BS) on cardiovascular mortality among person 19-64yrs in Niš, Serbia.

2.METHODOLOGY

Daily cardiovascular mortality data between 2001 and 2005 were obtained from the Republic Institute for Statistics in charge of coding the medical causes of death according to the International Classification of Diseases-10th Revision (I00-I99) among person 19-64yrs-old.

Air pollution data were provided by the Public Health Institute of Niš. Daily concentrations of black smoke (BS) and SO_2 was monitored in the local monitoring network. BS (µg/m^3) was measured by the refractometry method and SO_2 (µg/m^3) by spectrophotometer. Missing air pollution values for 6% days of the period were treated as being missing completely at random and were dropped from the analyses.

The concentrations of BS were measured for 24 hours a day during the period from 2001 to 2005. The sampling protocol was carried out by well trained personnel. The ambient level of black smoke was measured by the reflectance. The sampling was preformed by the means of a pump operating with a flow rate of 1 L/min through Whattman No1 paper filters.

The air concentration of sulphur dioxide was determined simultaneously with that of BS. A measured volume of air was bubbled through solution of potassium mercury tetrachloride. The sulphur dioxide which is presented in the air stream reacted with the solution to form a stable monochlorosulfonatomercurate. During the subsequent analysis, this complex was brought into reaction with acid-bleached pararosaniline dye and formaldehyde yielding intensely coloured pararosaniline methyl sulphuric acid. The optical density of this species was determined spectrophotometrically at 548 nm and was directly related to the collected amount of sulphur dioxide. The total volume of the air sample was determined from the flow rate and the sampling time.

The concentration of sulphur dioxide in the ambient air was computed and expressed in μg/m^3 and the lower limit of detection was 1.7 μg/m^3 .

The daily mean temperature, the mean relative humidity and the mean barometric pressure values for the same period were obtained from Republic Meteorological Department.

Generalized linear model (GLM) extending Poisson regression was applied allowing over dispersion. This model used mortality counts as the response variable, the natural cubic splines of the calendar time, temperature, relative humidity and barometric pressure, the day of week and season as indicator variables, and black smoke pollution as predictor variable. The specific model formulation for cardiovascular mortality is given below:

E[log(Yi)] = a + ns(calendar time, df=30) + indicator(season) + indicator(day of week) + ns(mean temperaturelag=0, df=4) + ns(mean temperaturelag=0-3, df=4) + ns(mean relative humiditylag=0, df=2) + ns(mean air pressurelag=0, df=3) + air pollutionlag=0

3.RESULTS AND DISCUSSION

Table 1 shows the daily number of all age cardiovascular deaths, cardiovascular deaths among person 19-64 yrs, pollutants concentrations and weather data. During the 5 years, there were 4818 all age cardiovascular mortality in the city of Niš, and 812 cardiovascular mortality among person 19-64yrs. The daily mean level for BS was 22.83±21.82 μg/m^3, minimum 1.00 μg/m^3 and maximum 225.00 μg/m^3. The daily mean number of all age cardiovascular mortality was 2.46±1.69 (0 to 10) and 0.44±0.66 (0 to 3) among person 19-64yrs.

Table 1. Summary statistics

	Mean	SD	Min	Median	Max
All age cardiovascular mortality (n)	2.64	1.69	0	2	10
Cardiovascular mortality among person 19-64 yrs (n)	0.44	0.66	0	0	4
BS (μg/m3)	22.83	21.82	1.00	17.00	225.00
SO2 (μg/m3)	14.63	12.57	1.00	11.5	107.0
Temperature (°C)	12.10	8.80	-11.60	12.80	30.50
Humidity (%)	70.33	13.08	26.00	71.00	108.00
Air pressure (mBar)	993.80	67.00	966.20	993.30	1014.80

The Pearson's correlation coefficients between air pollutants and meteorological variables are presented in Table 2.

Table 2. Correlation between air pollutants and eather variables

Parameter	Humidity	Air pressure	Temperature
BS	0,181**	0,197**	-0,305**
S02	- 0,007	0,344**	-0,3556**
Temperature	-0,512**	-0,313**	
Air pressure	0,020		

** Significant at the 0.01 level

Table 3. summarizes the results of BS influence on all age cardiovascular deaths and among person 19-64 yrs. Estimated OR of unipolutant regression model for among person 19-64 yrs was 1,001118 (95% CI: 0,97188 to 1,05208), and estimated OR of bipolutant model was 1,001107 (95% CI: 0,96991 to 1,05398)which were both not statistically significant.

The majority of the published studies have found significant associations between a 10 μg/m^3 increase in air pollutants and increase in daily number of death (5,6,9). Zmirou et al. (13) found that daily deaths of cardiovascular conditions increased 2 % with BS and 4 % with SO_2. In a study in the city of Dublin, Ireland (2), a reduction in BS concentration by 35.6 μg/m^3 was associated with a 10.3% decrease in annual cardiovascular mortality.

Table 3. Association between black smoke concentration and the number of all age cardiovascular mortality and among person 19-64 yrs

	Age	r	SGr	t	p	OR	Limit 95% CI OR	
							lower	top
Unipolutant	19 - 64 yrs	0,01112	0,02023	0,55	>0,05	1,01118	0,97188	1,05208
	≤65 yrs	0,01303	0,00879	1,48	>0,05	1,01312	0,99581	1,03072
	Total	0,01268	0,00806	1,57	>0,05	1,01276	0,99689	1,02889
Bipolutant	19 -64 yrs	0,01101	0,02121	0,52	>0,05	1,01107	0,96991	1,05398
	≤ 65 yrs	0,01007	0,00926	1,09	>0,05	1,01012	0,99195	1,02863
	Total	0,01017	0,00849	1,20	>0,05	1,01022	0,99354	1,02718

In 20 U.S. cities (10) the level of PM_{10} is associated with the rate of death from all causes and from cardiovascular and respiratory illnesses. The estimated increase in the relative rate of death from cardiovascular and respiratory causes was 0.68 percent (95 percent posterior interval, 0.20 to 1.16 percent) for each increase in the PM_{10} level of 10 μg/m^3. Levels of SO_2 were not significantly related to the mortality rate.

In two French cities no coherent results were found between SO_2 pollution and cardiovascular deaths (3). Ballester at al. (1) were found that the estimated relative risk (RR) of dying corresponding to a 10 μg/m^3 increase in mean daily BS over the whole study period was 1.009 (95% confidence interval (95% CI): 1.003, 1.015).

The results are also dependent on season and type of climates. In our country the climate is moderate continental and higher air pollutants effects are found in warmer and drier climates.

4. CONCLUSIONS

This mortality time series study have shown that all age cardiovascular mortality and among person 19-64yrs are not related to ambient black smoke concentrations. There is a risk of cardiovascular mortality with increase of 10μg/m3 black smoke, but it is not statistically significant. However, in response to air pollution exposure, different gender and age groups may respond differently.

5.ACKNOWLEDGEMENTS

This study was published thanks to the Ministry of Science and Technological Development of the Republic of Serbia (Project no. 42008 and project no. 43014).

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7.3 AIR POLLUTION AND ADVERSE BIRTH OUTCOMES

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Air pollution is associated with a range of adverse health effects, including adverse birth outcomes.

Aim is to provide an overview of the latest developments on air pollution and adverse birth outcomes

We conducted a literature of the studies on air pollution and adverse birth outcomes and reviewed some ongoing studies.

Recent meta and pooled analyses suggest associations for a range of air pollutions and adverse birth outcomes. The evidence is stronger evidence for (low) birth weight than for other outcomes such as pre-term birth, congenital anomalies and still births. Risk estimates differ, possible as a result of different methodologies used, bias and possible confounding.

Recent studies suggest that there associations between air pollution and adverse birth outcomes. Further work is needed to understand the mechanisms through which the adverse outcomes occur.

7.4 BREAST CANCER AND AIR POLLUTION: AN OVERVIEW

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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 more industrialized countries, as well in urban 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 base on the link of exposure to air pollution with breast cancer is given, drawing parallels to the related exposure to tobacco smoking and its effect on breast cancer risk.

1. INTRODUCTION

Breast cancer is the most common cancer type among women worldwide and the leading cause of death in nonsmoking women, and second to lung cancer among women who smoke (4). Accepted risk factors for breast cancer include genetic mutations, family history of breast cancer, aspects of reproductive history, and lifestyle factors, such as physical inactivity and alcohol consumption, most of which are not easy modifiable for prevention efforts (4). Only about one-third of new cases of breast cancer are attributable to known risk factors, and much of etiology remains explained (4). The relevance of environmental risk factors for breast cancer has been suggested by observed differences in breast cancer incidence between countries, and within countries, related to industrialization and urbanization. Breast cancer incidence tends to be higher in more industrialized countries than in less developed countries, and breast cancer incidence rates are higher in urban than in rural areas (25). Environmental pollutants have been linked to breast cancer mainly in laboratory experimental research, and a number of them have been found to cause mammary gland tumors in animals, to be hormonally active in mimicking estrogen, a breast cancer risk factor, or to increase susceptibility of the mammary gland to carcinogenesis (5). However, most of the knowledge on the environmental pollutants relevant to breast cancer, including air pollution, comes from toxicological studies, whereas epidemiological data are limited and mixed. In this paper, an overview of the current epidemiological evidence on the link between air pollution and breast cancer is given. In addition, a brief discussion of the biological plausibility of the link between air pollution and breast cancer is given by discussion of current knowledge about known air pollution chemicals which have been linked to mammary gland tumors, and of the link between breast cancer and tobacco smoking, an exposure related to air pollution.

2. METHODS

The PubMed database was searched for articles in English published in peer-reviewed journals through September 2013 for human studies of breast cancer and 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.

3. RESULTS AND DISCUSSION

We have identified ten epidemiological studies on air pollution and breast cancer (3,6-8,11,13,17,19,20,25) as summarized in Table 1. Of these ten studies, four were case-control studies (3,8,13,17), one cohort (19), two ecological studies of breast cancer incidence trends over time (7,25), one cross-sectional ecological study (6), one longitudinal ecological study (20), and a single study of survival after breast cancer (11). Most of the studies linked air pollution to breast cancer incidence (3,7,8,13,17,19,20,25), where single study examined breast cancer mortality (6) and another on survival after breast cancer (11). As many factors may influence survival after breast cancer diagnosis, such as access to and quality of health care, treatment, socio-economic status, etc. studies of breast cancer incidence are in this review regarded as better than those of mortality and survival, for the purpose of disentangling importance of air pollution for breast cancer etiology. Most of evidence came from USA (3,7,11,13,17,25), one study from Canada (8), Italy (20), Spain (6), and Denmark (19). An early case-control study from 1996 by Lewis-Michl et al., based in Nassau and Suffolk Counties on

Table 1. Summary of ten epidemiological studies on association between exposure to air pollution and breast cancer, before September 2013.

Author, year, place	Design, n, year	Air pollutant & OR/effect	Exposure	BC Type
Lewis-Michl, 1996 Naasau & Suffolk Counties, NY, USA	Case-control	Proximity chemical facilities: 1.61 (1.06-2.43); Traffic density: no effect	20 years prior to BC	Postmenopausal (no effect in premenopausal)
Bonner, 2005 Erie & Niagara Counties, NY, USA	Case-control 1,166/2,105 (1959-1997)	Modeled TSP: 2.42 (0.97-6.09) high: >140 µg/m^3 vs. low: <84 µg/m^3	birth, none with menarche, 1st birth, later	Postmenopausal (no effect in premenopausal)
Nie, 2007 Erie & Niagara Counties, NYS	Case-control 1,166/2,105 (1959-1997)	Modeled traffic emissions: 2.57 (1.16-5.69) high vs. low quartile	1st birth, none at birth, menarche, or later	Postmenopausal (no effect in premenopausal)
Crouse, 2010 Montreal, Canada	Case-control 383/416 (1996-1997)	Modeled NO$_2$: 1.31 (1.00-1.71) per 5 ppb	1996, none with 1985 or 2006	Postmenopausal women only in study
Ranzi, 2011 Forli, Italy	Ecological cohort 31,347 (1990-2003)	Proximity to incinerators: SIR for BC incidence: 1.15 (1.03-1.27)	13 year prior to BC	Did not differentiate pre- and post
Cambra, 2011 Basque County, Spain	Cross-sectional ecological study 1,257 (1996-2003)	Proximity (2km radius) to mineral industry BC mortality: 1.15 (1.02-1.28) None with chemical, waste, energy, metal industry	7 years prior to BC death	Did not differentiate pre- and post
Raaschou-Nielsen, 2011 Copenhagen, Arrhus, Denmark	Cohort study 1971-2010	Modeled NO$_x$ per 100 µg/m^3: 1.16 (0.89-1.51)	1971-2010	Did not differentiate pre- and post
Wei, 2011 USA	Ecological study (1986-2002)	Correlation of NO, CO, SO$_2$, and VOC with BC incidence: r = 0.89, 0.82, 0.71, 0.68, higher incidence in urban areas	-	Did not differentiate pre- and post
Chen, 2011 USA	Ecological study (19)	Motor vehicle density in 1970 correlated with BC incidence: r = 0.91	-	Did not differentiate pre- and post
Hu, 2013 California, USA	Cohort Survival study 255,128 (1999-2009)	PM$_{10}$ HR: 1.13 (1.02-1.25) per 10 µg/m^3 ; PM$_{2.5}$: 1.86 (1.12-3.10) per 5 µg/m^3	1999-2009	Did not differentiate pre- and post

OR – odds ratio; BC – breast cancer; TSP – total suspended particles; NO$_2$ – nitrogen dioxide; NO – nitrogen oxides; CO – carbon monoxide; SO$_2$ – sulfur dioxide; VOC – volatile organic compounds; PM$_{10}$ – particulate matter with diameter less than 10 µm; PM$_{2.5}$ – particulate matter with diameter less than 2.5 µm.

Long Island, NY, USA, found significantly increased risk of postmenopausal breast cancer in women living close to chemical facilities, but only slightly increased, statistically nonsignificant, risk in women living close to busy roads (13). Bonner et al. 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, reported relevance of only early (birth) but not later life exposures (menarche, first birth, 10 and 20 years prior to breast cancer) to traffic-related air pollution in terms of total suspended particles (TSP) for postmenopausal breast cancer (3).

Bonner et al. used TSP as a proxy of exposure to polycyclic aromatic hydrocarbons (PAH). Nie et al. in 2007 used the WEB case-control study adding the data on traffic emissions throughout life and found significantly increased breast cancer risk with exposures at first-birth, but none with other exposure windows: menarche, 10 or 20 years prior to breast cancer diagnosis (17). All three studies found effects for postmenopausal breast cancer only, and none in premenopausal women (13, 3, 17). In the case-control study from 2010 based in Montreal, Canada, Crouse et al. linked levels of nitrogen dioxide (NO_2), proxy of traffic-related air pollution, to postmenopausal breast cancere (13), providing most convincing evidence to date for a causative relationship. A cohort study from Denmark has linked long-term exposure of over 30 years to NO_2 to all cancer types, and reported positive but statistically nonsignificant associations with breast cancer incidence, but did not distinguish between pre- and postmenopausal breast cancer, or considered different exposure windows (19). A population based cohort study of people living close to incinerators in Forly, Italy, by Ranzi et al. linked increased risk of breast cancer in women having highest levels of exposures to heavy metals (20). Similar ecological cross-sectional study from Basque County in Spain found excess breast cancer mortality in women living close to industrial sites, specifically from mineral industry (6), but lacked data on breast cancer incidence. An ecological study from USA showed that time trends in breast cancer incidence over last 30 years correlated well with time trends in emissions of nitrogen oxides (NO_x) as well as motor vehicle density data (7). A related study looked additionally into data on geographical variations and reported higher breast cancer incidence rates in high industrial and traffic emission regions and in metropolitan areas of US than in rural areas (25). Finally, most recent study from 2013 by Hu et al. on survival after breast cancer diagnosis in 255,128 Californian 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 (11). Variety of different study designs, statistical analyses, proxies of exposure to air pollution (TSP, traffic density, proximity to busy roads, NO_2, and NO_x, PM_{10}, $PM_{2.5}$) as well as different windows of exposure were reported, making direct comparisons of effect estimates between studies difficult.

Biological Plausibility: Environmental Chemicals and Breast Cancer

Given that air pollution is causally related to lung cancer, and possibly to bladder, liver, cervical, stomach, and brain cancer (19) it is plausible that at least one of the many carcinogenic constituents in air pollution may affect breast cancer risk. Polycyclic aromatic hydrocarbons (PAHs), constituents of ambient particles, have caused mammary tumors in laboratory animals (5, 16), whereas ultrafine ambient particles which contain PAHs are able to translocate from the lung to circulatory system, adipose, mammary and other tissues (24). Brody et al. has in an extensive review of epidemiological evidence on the environmental pollutants identified in toxicological studies concluded that there is relatively small number of studies in general, and that many chemicals identified as potentially harmful in animal studies have not been yet studies in humans (5). This has been mainly explained by the lack of good exposure assessment methods, a lack of access to highly exposed and unexposed populations, and lack of clinical markers relevant for study of outcomes which may be obscured by disease latency (5). Brody concludes that evidence to date generally supports an association between breast cancer and polycyclic aromatic hydrocarbons (PAHs), which is, besides air pollution, also commonly found in tobacco smoke and cooked food, thus providing the biological plausibility for an association of air pollution and breast cancer. Brody et al. also calls one for more epidemiological studies on air pollution, diesel exhaust, traffic density, etc. and breast cancer risk (5).

Biological Plausibility: Tobacco Smoke and Breast Cancer

Tobacco smoke is the leading cause of cancer worldwide and contains over 4,000 known carcinogenic substances (12), many of which are also found in air pollution. Due to similar toxicological properties and biological mechanisms of damage to the human body of tobacco smoke and air pollution, smoking related diseases are typically also linked to air pollution later, after evidence is well established for a link with smoking, as effects of exposure to air pollution are more expensive and cumbersome to study. Finding positive associations and similar dose-response curves for both smoking and air pollution with a given disease validates and strengthens the support for causal relationship for both exposures, and thus it is convenient to study these two exposures together, as done before in relation to cardiovascular mortality (18). Brief historical review of the literature on smoking and breast cancer is given, which provides an important insight into biological plausibility of a link between air pollution and breast cancer.

No scientific consensus has been reached on whether tobacco smoke causes breast cancer, despite over 20 years of debate and over 150 epidemiological studies (21). The views on the role of tobacco smoke have fluctuated, from early suggestions that antiestrogenic effects of smoking might protect against BC (1), which was refuted later (10). Collaborative reanalysis of 53 studies showed no increased risk of BC in smokers (10), but was limited by definition of smokers as ever smokers, without data on intensity or duration. The scientific consensus groups disagreed on this issue; US Surgeon General Report (2004) concluded that there was suggestive but insufficient evidence of a link between active smoking and BC (23), whereas the International Agency for Research on Cancer in (2009) concluded that evidence is inconclusive and limited (22). However, most recent large prospective cohorts studies (2,9,14,26) and meta-analyses (9) published since 2011, with high quality data on smoking duration, intensity, well defined windows of exposure (before and after first birth), all show consistently increased risk of breast cancer in active smokers. Furthermore enhanced risk of breast cancer was related to younger initiation of smoking (26), longer duration and higher intensity (2,9,14), with especially high risk of breast cancer related to smoking before first childbirth (2,9). These four studies provide powerful evidence base for association between smoking and breast cancer, contributing with over 23,000 breast cancer cases in total, from a cohort of 79,900 women from American Women's Health Initiative Study from over 40 clinical centers in USA (14), 200,150 women from the Nurses' Health Study (26), 302,865 Norwegian women (2), and 73,388 women from American Cancer Society's Cancer prevention Study II (CPS-II) Nutrition Cohort (9). This increasing evidence of an association between tobacco smoke and breast cancer strengthens the plausibility of a link between air pollution and breast cancer.

4. CONCLUSIONS

Epidemiological evidence on the link of air pollution with breast cancer is limited, but suggestive of possible positive association. Recently increasing evidence of an association between tobacco smoke and breast cancer (2,9,14,26) strengthens the plausibility of a link between air pollution and BC, and makes the studies of air pollution and breast cancer more pending. 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. Only single cohort study on the topic was considering all cancer types with respect to air pollution, which precluded presentation of breast cancer incidence data in more detail, in terms of pre- and postmenopausal type, or different windows of exposure (19). Some consistency in current literature is noted. Studies which present data separately for pre- and postmenopausal breast cancer (3,13,17) are consistent in finding relevance of air pollution for postmenopausal breast cancer only. This is in agreement with study by Crouse et al. (8) who present data for postmenopausal women only, and may possibly explain lack of statistical association for positive association between air pollution and breast cancer reported by Raaschou-Nielsen et al. (19). Relevance of traffic related air pollution for breast cancer suggested from case-control (3,8,13,17) and cohort studies (19) is consistent with ecological studies (7,25). Only single study has reported that association with air pollutions were limited to life-time nonsmokers (17). 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. Current weak evidence base suggestive of air pollution relevance for breast cancer, calls for large prospective cohort studies with good quality air pollution data, able to separate windows of exposure, particularly before first birth, as well with good data on breast cancer type, and smoking exposures, in order to disentangle whether there is a causal association between air pollution and breast cancer risk.

5. ACKNOWLEDGEMENTS

This paper was presented at the 4th WeBIOPATR Workshop and Conference, Belgrade, 2th - 4th October, 2013"

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7.5 HEALTH RISK ASSESSMENT OF TRACE METALS ASSOCIATED WITH PM_{10} IN BELGRADE DISTRICT

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ABSTRACT

Twenty-four hour mass concentrations and trace metal content (As, Cd, Cr, Mn, Ni, Pb) of PM_{10} collected at three automatic monitoring stations (Slavija, Lazarevac and Grabovac) in Belgrade district during the 2012 were analyzed. Average annual PM_{10} mass concentrations were higher than the air quality standard of 40 µg m^{-3} at Slavija and Lazarevac. Arsenic exceeded the target value of 5 ng/m^3 at Lazarevac by the factor of four. Health risk assessment associated with exposure to PM_{10}-bound trace metals through inhalation was carried out as well. Cumulative cancer risks were higher than the acceptable limit of 10^{-4} at two out of three locations. The major contributor to obtained cancer risks was Cr - about 90%, 60% and 80% at Slavija, Lazarevac and Grabovac, respectively. Hazard index was lower than 1 at all three stations, indicating no adverse non-carcinogenic health effects.

1. INTRODUCTION

Polluted air is one of the dominant factors influencing quality of the environment in urban and industrial areas. One of the major concerns appears to be the influence of ambient particulate matter (PM) because of its adverse effects on human health. Numbers of epidemiological studies have demonstrated the relation between acute and chronic health effects and exposure to inhalable PM_{10} (aerodynamic diameter less than 10 µm) [Ackermann-Liebrich et al., 1997; Laden et al., 2000; Pope et al., 1995]. Their ability to pass through the nose and throat and get deep into the lungs can increase the risk of developing cardiovascular and respiratory diseases and lung cancer. This is partially connected with the presence of toxic trace metals. Some of them such as Cr, Ni, Cd, As and Pb are carcinogenic while most of other metals are toxic [IARC, 1980; IARC, 1990; IARC, 1993].

Belgrade district is the commercial center of the Republic of Serbia and, as important intersection of roads and industry, requires special attention. Recently developed air quality monitoring network allows determination and control of pollution levels, which are needed for concrete action in order to identify the sources and reduce emission of pollutants. In this study, we focus on the analysis of mass concentrations and trace metal content of PM_{10} measured at three monitoring stations in Belgrade district, as well as on conducting the health risk assessment (both carcinogenic and non-carcinogenic) associated with exposure to PM_{10}-bound trace metals through inhalation.

2. METHODOLOGY

Data were obtained by the Institute of Public Health of Belgrade. Twenty-four hour mass concentrations and trace metal content (As, Cd, Cr, Mn, Ni, Pb) of PM_{10} were analyzed according to EN 12341:1998 and EN 14902:2005 ambient air quality standards, respectively. Samples were collected during the 2012 at three automatic monitoring stations (Slavija, Lazarevac and Grabovac) in Belgrade district. Slavija represents a typical urban traffic station, located at the very center of Belgrade city. Lazarevac is placed in the namesake city near the Kolubara coal basin, while location of Grabovac is about 10 km from the two biggest thermal power plants in Serbia.

In order to estimate the risk associated with exposure to analyzed PM_{10}-bound trace metals, we used the US EPA health risk assessment model [USEPA, 1989; USEPA 1991]. The assessment of health risk requires evaluation of their toxicity and estimate of the exposure to them. Chronic daily intake (*CDI*) describes the exposure and is calculated as follows:

$$CDI = \frac{C \cdot IR \cdot EF \cdot ED}{BW \cdot AT}.$$

Here *C* represents the concentration of the chemical in the air, *IR* is inhalation rate, *EF* is exposure frequency, *ED* is exposure duration, *BW* is body weight and *AT* is period over which the exposure is averaged. Values of these parameters are given in Table 2.1.

Table 2.1 Values of parameters used for calculation of CDI

Parameter	Value
C	Chemical specific (ng m^{-3})
IR	20 $m^3 day^{-1}$
EF	350 days $year^{-1}$
ED	30 years
BW	70 kg
AT	70 x 365 days = 25 550 days for carcinogenic effects 30 x 365 days = 10 950 days for non-carcinogenic effects

In conducting health risk assessment, the carcinogenic and non-carcinogenic effects are considered separately. The capacities of chemical to cause adverse health effects, toxicity parameters, are given as slope factor (*SF*) for carcinogenic effects and reference dose (*RfD*) for non-carcinogenic effects. Toxicity parameters used in this study were calculated from Unit Risk and Reference Concentration values, obtained from Risk Assessment Information System (*RAIS*) chemical toxicity database [RAIS], and are given in the Table 3.1. together with health risk assessment results.

Carcinogenic health risk due to exposure to PM_{10}-bound trace metals was assessed by calculating the incremental lifetime cancer risk (*ILCR*) value:

$$ILCR = CDI \cdot SF \cdot 10^{-6}.$$

This value represents an incremental probability of an individual developing cancer over lifetime as a result of exposure to these metals through inhalation. Non-carcinogenic health risk assessment due to exposure to analyzed elements was conducted by calculation of hazard quotient (*HQ*):

$$HQ = CDI \cdot 10^{-6}/RfD.$$

All calculations were done with assumption that the bioavailability of trace metals is 100%.

3. RESULTS AND DISCUSSION

Basic statistics for the 24-h mass concentrations and trace metal content of PM_{10} for three monitoring stations is presented in Table 3.1. Average annual PM_{10} mass concentrations at Slavija, Lazarevac and Grabovac were 52, 48 and 32 µg m^{-3}, respectively. This indicates that the air quality in studied area was very affected by particulate pollutants. Comparison of the measured values to annual average air quality standard of 40 µg m^{-3} (EU Directive 2008/EC/50), shows that it was exceeded at Slavija and Lazarevac, indicating that these locations were subjected to large inputs of anthropogenic contaminants, possibly produced by both stationary sources and mobile sources (related to traffic). Furthermore, the 24-h PM_{10} mass concentrations, at Lazarevac and Grabovac, were higher than 50 µg m^{-3} for 96 and 60 days during the measurement period, respectively. Frequency limit according to EU Directive 2008/EC/50 is 35 times per calendar year. Although the measured annual average values were lower than at Slavija, this frequency transgressions at Lazarevac and Grabovac should be of special concern during the winter time, given the proximity to the coal mine and the thermal power plants. Moreover, this indicates that the risks associated with accidental releases of pollutants, resulting in acute exposure to high concentrations with potential impacts on human health, should be also considered. However, that was not the subject of this study.

Considering the average annual concentrations of Pb, Mn, Cr and Ni, one can see that they were higher at Slavija than at Lazarevac. Concentrations of these metals at Grabovac were very low comparing to the other two stations. We attribute this to the influence of road traffic and industrial activity at Slavija and Lazarevac since emissions of Pb, Mn, Cr and Ni are connected with vehicle exhaust and production and processing of metals [Sternbeck et al., 2002]. Annual mean of As exceeded the target value of 5 ng/m^3 at Lazarevac by the factor of four (EU Directive 2008/EC/50) and was very high at Slavija and Grabovac. Arsenic is characteristic for coal combustion [Pacyna, 1987] and its high concentrations at Lazarevac were probably due to the proximity of coal mine and the thermal power plants.

Table 3.1. Statistical parameters for twenty-four hour mass concentrations and trace metal content of PM_{10} in Belgrade district

		Mean (ng m^{-3})	Min (ng m^{-3})	Max (ng m^{-3})	10th Percentile (ng m^{-3})	95th Percentile (ng m^{-3})	Range (ng m^{-3})	Std.Dev. (ng m^{-3})
Slavija	PM_{10}	53510	7430	213590	27540	115760	206160	29850
	As	5.00	0.25	26.73	1.09	13.44	26.48	4.80
	Cd	0.23	0.00	2.39	0.00	0.93	2.39	0.38
	Cr	19.24	9.73	45.54	13.12	30.82	35.81	6.12
	Mn	21.58	1.19	64.24	10.10	41.69	63.05	11.11
	Ni	11.10	1.81	50.61	4.09	22.51	48.80	7.97
	Pb	18.67	4.41	69.03	7.22	48.36	64.61	12.89
Lazarevac	PM_{10}	47480	9420	228990	17750	123550	219570	38050
	As	22.87	0.15	203.27	1.68	85.48	203.13	35.61
	Cd	0.25	0.00	2.22	0.00	0.96	2.22	0.37
	Cr	16.70	0.10	38.57	11.70	24.06	38.46	5.36
	Mn	10.62	0.81	42.40	4.35	21.43	41.59	6.83
	Ni	5.25	0.13	23.80	2.07	14.56	23.67	4.04
	Pb	14.46	0.00	78.19	4.01	35.54	78.18	12.70
Grabovac	PM_{10}	33460	5800	209240	12500	80250	203440	25410
	As	4.06	0.25	45.55	0.67	13.91	45.30	6.24
	Cd	0.10	0.00	2.15	0.00	0.34	2.14	0.24
	Cr	7.46	3.88	23.01	5.14	11.82	19.13	2.72
	Mn	2.88	0.88	10.70	1.63	5.11	9.82	1.62
	Ni	1.98	0.31	12.91	0.62	4.11	12.60	1.84
	Pb	5.38	1.32	16.66	2.17	14.10	15.34	3.77

Table 3.2. Values of slope factor (*SF*), reference dose (*RfD*), and calculated incremental lifetime cancer risk (*ILCR*) and hazard quotient (*HQ*) for analyzed PM_{10}-bound trace metals in Belgrade district

	Metal	SF (mg kg^{-1} day^{-1})$^{-1}$	RfD (mg kg^{-1} day^{-1})	$CDI_{canc.}$ (ng kg^{-1} day^{-1})	$CDI_{noncanc.}$ (ng kg^{-1} day^{-1})	ILCR	HQ
Grabovac	Pb	$4.20 \cdot 10^{-2}$	-	0.63	1.47	$2.65 \cdot 10^{-8}$	-
	Cd	$6.30 \cdot 10^{0}$	$2.86 \cdot 10^{-6}$	0.01	0.03	$7.71 \cdot 10^{-8}$	$9.99 \cdot 10^{-3}$
	Ni	$1.68 \cdot 10^{0}$	$1.43 \cdot 10^{-5}$	0.23	0.54	$3.90 \cdot 10^{-7}$	$3.79 \cdot 10^{-2}$
	Cr	$4.20 \cdot 10^{1}$	$2.86 \cdot 10^{-5}$	0.88	2.04	$3.68 \cdot 10^{-5}$	$7.15 \cdot 10^{-2}$
	Mn	-	$1.43 \cdot 10^{-5}$	0.34	0.79	-	$5.51 \cdot 10^{-2}$
	As	$15.05 \cdot 10^{0}$	$1.50 \cdot 10^{-5}$	0.48	1.11	$7.18 \cdot 10^{-6}$	$7.42 \cdot 10^{-2}$
	Sum					**$4.45 \cdot 10^{-5}$**	**$2.49 \cdot 10^{-1}$**
Lazarevac	Pb	$4.20 \cdot 10^{-2}$	-	1.70	3.96	$7.13 \cdot 10^{-8}$	-
	Cd	$6.30 \cdot 10^{0}$	$2.86 \cdot 10^{-6}$	0.03	0.07	$1.85 \cdot 10^{-7}$	$2.39 \cdot 10^{-2}$
	Ni	$1.68 \cdot 10^{0}$	$1.43 \cdot 10^{-5}$	0.62	1.44	$1.04 \cdot 10^{-6}$	$1.01 \cdot 10^{-1}$
	Cr	$4.20 \cdot 10^{1}$	$2.86 \cdot 10^{-5}$	1.96	4.57	$8.23 \cdot 10^{-5}$	$1.60 \cdot 10^{-1}$
	Mn	-	$1.43 \cdot 10^{-5}$	1.25	2.91	-	$2.04 \cdot 10^{-1}$
	As	$15.05 \cdot 10^{0}$	$1.50 \cdot 10^{-5}$	2.69	6.26	$4.04 \cdot 10^{-5}$	$4.18 \cdot 10^{-1}$
	Sum					**$1.24 \cdot 10^{-4}$**	**$9.06 \cdot 10^{-1}$**
Slavija	Pb	$4.20 \cdot 10^{-2}$	-	2.19	5.12	$9.21 \cdot 10^{-8}$	-
	Cd	$6.30 \cdot 10^{0}$	$2.86 \cdot 10^{-6}$	0.03	0.06	$1.73 \cdot 10^{-7}$	$2.25 \cdot 10^{-2}$
	Ni	$1.68 \cdot 10^{0}$	$1.43 \cdot 10^{-5}$	1.303	3.04	$2.19 \cdot 10^{-6}$	$2.13 \cdot 10^{-1}$
	Cr	$4.20 \cdot 10^{1}$	$2.86 \cdot 10^{-5}$	2.26	5.27	$9.49 \cdot 10^{-5}$	$1.84 \cdot 10^{-1}$
	Mn	-	$1.43 \cdot 10^{-5}$	2.53	5.91	-	$4.14 \cdot 10^{-1}$
	As	$15.05 \cdot 10^{0}$	$1.50 \cdot 10^{-5}$	0.59	1.37	$8.84 \cdot 10^{-6}$	$9.14 \cdot 10^{-1}$
	Sum					**$1.06 \cdot 10^{-4}$**	**$9.24 \cdot 10^{-1}$**

The human health risk assessment was carried out as already described. The calculated incremental lifetime cancer risks and hazard quotients for analyzed PM_{10}-bound trace metals in Belgrade district are given in Table 3.2. Cumulative cancer risks, determined as a sum of individual ILCR, were $1.06 \cdot 10^{-4}$, $1.24 \cdot 10^{-4}$ and $4.45 \cdot 10^{-5}$ at Slavija, Lazarevac and Grabovac, respectively. These *ILCR* values suggest that risk reduction measures are required at Slavija and Lazarevac area, because the value of 10^{-4} is considered as an acceptable limit. Value of 10^{-6} which represents the usual goal and corresponds to the exposure to unpolluted air [USEPA, 2005] was exceeded at all three locations.

Individual values of ILCR exceeded the value of 10^{-6} for Ni, Cr and As at Slavija and Lazarevac, and for Cr and As at Grabovac. The major contributor to the obtained cancer risks was Cr - about 90%, 60% and 80% at Slavija, Lazarevac and Grabovac, respectively. Knowing that its sources are mainly anthropogenic (industrial processes, fuel combustion, etc.), this points to the need for reduction in emissions of this metal. It should be also noted that the contribution of As to the estimated cancer risk at Lazarevac was very high (32%) comparing to Grabovac (about 15%) and Slavija (0.8%) which suggests major contribution of coal mine and thermal power plant emissions to the obtained health hazard.

Non-cancer risk was estimated as well. Hazard index, obtained as the sum of HQ values of individual elements, was lower than 1 at all three stations, indicating no adverse non-carcinogenic health effects.

4. CONCLUSIONS

Measured mass and PM_{10}-bound trace metal concentrations in Belgrade district, in comparison with European air quality standards, do not give very satisfactory results. Both annual and daily limit values of PM_{10} mass concentrations were exceeded at two out of three stations. Together with the obtained health risk estimations, these results indicate the need for significant decrease of PM_{10} emission in order to meet the current air quality standards and reduce harmful effects of it constituents to human health and environment.

5. ACKNOWLEDGEMENTS

This paper was realized as a part of the project No III43007 financed by the Ministry of Education and Science of the Republic of Serbia within the framework of integrated and interdisciplinary research for the period 2011-2014. The authors would also like to thank to the Institute of Public Health of Belgrade for their permission to utilize air quality data for this study.

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7.6 HEALTH EFFECTS OF AMBIENT PARTICULATE MATTER ON PRESCHOOL CHILDREN IN THE CITY CENTER OF NIŠ, SERBIA

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ABSTRACT

This paper is a study of causality between ambient air pollution with $PM_{2.5}$ particulates and health risk in the subpopulation of children up to the age of 6. Based on the statistical analysis of the measured concentration of pollutants in the City of Niš from 1995 to 2011, it can be concluded that there is a need to establish the relationship between the exposure to pollutants emitted from motor vehicles and the occurrence of health effects in the exposed population. Since detailed analysis of the impact of $PM_{2.5}$ particulates on the health of the exposed population was not performed in the vicinity of roads in the City of Niš, an automatic measuring station was placed in the area of a kindergarten located on a busy crossroads. The measurements of $PM_{2.5}$ particulate concentrations showed exceeding limit values, ranging from 43.11% to 107.4%. $PM_{2.5}$ particulates represent a significant health risk for preschool children, presented in this paper through calculation of individual health risk and a review of respiratory diseases in the exposed children.

Keywords: exposure, health risk, potential dose, $PM_{2.5}$ particulates

INTRODUCTION

Numerous toxicological and epidemiological studies have confirmed that certain properties of air pollutants cause acute or chronic diseases in the exposed human population, either individually or in a group. The effects of air pollutants on human health occur through chemical, physical, and physicochemical processes. These processes occur over time and/or after the recipients have been exposed to a certain pollutant concentration.

Exposure implies contact of individuals (recipients) with pollutants (toxicants) and it is a function of pollutant concentration and their effect time. If an individual is exposed to the air (exposure medium) of a given location, the concentration of pollutants in that location determines the level of exposure. If an individual spends time in more than one location, the sum effect of individual exposure for a specific period of time is determined as the mean value of concentrations of atmospheric air substances for every location. Adopted criteria of atmospheric air quality are used as a temporal property of the effect of air pollutants on human health. The adopted criteria of air quality based on the potential health effects of pollutants begin with exposure duration. High pollution concentrations do not cause unwanted human health effects if they are outside the zone of impact on humans; however, if pollutants are within the impact zones (with constant human presence), they can be hazardous to human health even in low concentrations. Accordingly, the most important factor for air pollution health risk assessment is the establishment of health risk zones.

The effects of air pollutants on human health are varied and dependent on the factors such as: type of pollution, duration and level of exposure, individual organism sensitivity, and characteristic pollutant toxicity. The most common air pollutant effects on human health are: reduced pulmonary function, asthma attacks, respiratory diseases, cardiovascular diseases, reduced activity, lowered immune function, and carcinogenic diseases.

Any assessment of air pollutant effects on human health requires data on pollutant effects on individuals, data on the manner of individual exposure to pollutants (inhalation, ingestion, or dermal absorption), data on pollutant air concentrations, and data on pollutant concentrations (doses) that affect the health of representative individuals divided into specific groups (children, adults, the elderly, and the sick).

Deposition of aerosols, particulate toxic substances from the ambient air, in the epithelium of respiratory organs depends on particulate size, shape, and mass. Particulates are deposited in the epithelium through various mechanisms: inertial impaction, sedimentation, diffusion, and turbulence. With any change of air stream direction depending on its velocity, both solid and liquid particulates of a sufficient mass maintain their direction and collide with the wet epithelium surface, where they are deposited by the force of the impact.

Particulates larger than 5μm in diameter are usually retained by the hairs in the nasopharyngeal area (nose and throat) and deposited due to air turbulence. They are removed by sneezing or nose blow. Soluble large-diameter particulates are dissolved in the mucus and are either transported to the throat or absorbed in the blood through the epithelium.

Particulates ranging from 2 to 5 μm in diameter reach the tracheobronchial area (trachea and bronchi) where they are transported via mucous cells to the gastrointestinal tract, as coughing and sneezing move the particulates in the mucus rapidly towards the mouth.

Particulates smaller than 1 μm in diameter penetrate all the way through to the alveoli, from where they are removed by means of different processes: phagocytosis (macrophages), intercellular space migration, or dissolution and transfer to the blood or the lymph. Particulate removal from the alveoli is slow and depends on particulate solubility.

The absorption of solid and liquid particulates in the respiratory tract based on their diameter is shown in Figure 1.

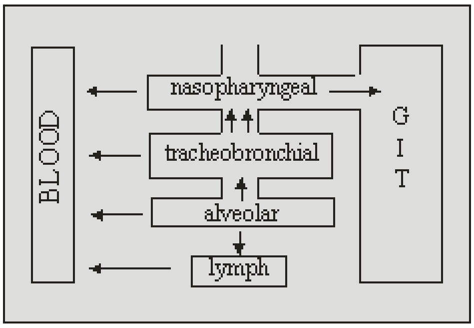


Figure 1. – Absorption of inhaled particulates

METHODOLOGY

During chemical interaction between a toxic substance and the biological system (macromolecules, cell parts, cell, tissue, organism), there is a transitional state, i.e. the toxicant–living organism complex. If the toxic reaction is irreversible, there is a toxic effect, i.e. there is no detoxification (the toxicant–living organism complex does not dissociate into initial components).

There is no toxic effect if the toxic reaction is reversible because the toxicant–living organism complex dissociates into initial components. Interaction between a toxic substance and the organism proceeds on different levels: a single organ, tissue, cell, or molecule. The interaction causes a toxic effect in the form of physiological, biochemical, functional, or structural changes in the organism. There is rarely only one type of change since the toxic effect is usually a sum of several types of change. The toxic effect is produced by toxicokinetic (absorption, distribution, biotransformation, and excretion) and toxicodynamic (affecting enzymes and other biochemical parameters, cell organelles, and DNA and RNA) changes. Toxic effect development equally depends on the exposure duration and the toxin concentration. This dependency is quantitatively generalized with the equation that explains the uptake of toxic substances through respiratory organs (Haber’s law):

$$D = c \cdot t \,. \tag{1}$$

The toxic effect, or the dose (D) that causes the toxic effect, is directly proportional to concentration (c) in atmospheric air and exposure duration (t). In theory, this relationship could be constant, i.e. longer exposure duration with lower toxin concentration could produce the same effect for shorter exposure duration with higher toxin concentration.

The dose-effect relationship expresses one of the fundamental laws, whereby every toxic effect is proportional to the amount of given dose. Toxic effects are noticeable after exposure to a single and sufficiently large dose of a certain substance. The quantitative relationship between the dose and the intensity of instigated response by the organism, i.e. the toxic effect, can be determined only by studying toxic effects from different doses. Increased limit dose increases the corresponding toxic effect intensity until the effect becomes lethal. Consequently, when the dose is minimal, a small number of receptors are involved in the response, and when the dose is maximal, all receptors become occupied by toxin molecules.

Based on the aforementioned, we conclude that air pollution health risk assessment is a function of toxicity of a pollutant in ambient air. Successful risk assessment must contain the following stages: hazard identification, exposure assessment, dose-response assessment, and risk characterization. Hazard identification implies characterization of the toxic agent effect and the occurrence of health problems due to pollution. Since it is difficult to determine with complete certainty the relationship between exposure, received dose, and the response it causes (internal dose) due to the existence of absorption barriers situated inside the exposed individual's organism, exposure is often equated with potential dose during risk assessment.

The general potential dose equation is:

$$D_{pot} = \int_{t_1}^{t_2} C(t) \cdot IR(t)\, dt \ , \qquad (2)$$

where: D_{pot} – potential dose [mg/kg/day], IR – respiratory rate per unit time [m^3/day], $C\ (t)$ – exposure agent concentration per unit time [m^3/kg/h], and t_1 – exposure duration [h].

Equation (2) can be explicitly expressed as the sum effect of chemical agent *i*, which results in known or expected reactions:

$$D_{pot} = \sum_i C_i \cdot IR_i \cdot ED_i \ . \qquad (3)$$

If the exposure duration is short, concentration C_i and the respiratory rate per unit time IR_i can be taken as approximately constant values, in which case the following equation is used:

$$D_{pot} = \bar{C} \cdot \bar{IR} \cdot ED \, , \qquad (4)$$

where: ED – exposure sum duration for a specific response to the chemical agent effect, $\bar{C}$ and $\bar{IR}$ – arithmetic value of the C_i and IR_i. Equation (4) is not considered as valid in case of large oscillatory values of the C and IR parameters. In that case, the values of the aforementioned parameters in Eq. (3) are taken as approximate constants. If it is not possible to apply the equations (3) and (4), the potential dose is calculated with the basic form of Eq. (2).

Average Daily Dose (ADD) can be calculated starting with Eq. (2) and taking the average potential dose (average exposure time per individual body weight). Specifically, by using Eq. (4) derived from Eq. (2) and considering the dynamic balance of C and IR parameters, we can obtain the Average Daily Potential Dose (ADD_{pot}).

$$ADD_{pot} = \frac{\left[\bar{C} \cdot \bar{IR} \cdot ED\right]}{\left[BW \cdot AT\right]} \, , \qquad (5)$$

where ADD_{pot} – average daily potential dose [mg/kg/day], BW – body weight of the individual [kg], AT – time expressed by days over the averaged exposure duration.

Exposure assessment is performed by means of a qualitative-quantitative evaluation of the exposure magnitude and a determination of the exposure duration frequency and exposure effects manifestations. The magnitude of exposure is a function of the chemical agent exposure concentration and the time interval of its effect, and it is expressed with the following equation:

$$E = \int_{t_1}^{t_2} C(t)\,dt\,, \tag{6}$$

where: E – magnitude of exposure [mg/m^3/duration]; $C(t)$ – concentration of agent as a function of time [mg/m^3]; and t_2 - $t1$ – exposure duration [ED]. ED is a continuous period of exposure (e.g. a day, a week, a year, etc.).

Exposure quantification includes determination of the size, frequency, and duration of each identified exposure pathway. Exposure quantification is conducted by assessment of concentrations and calculation of toxic agent uptake.

Assessment of concentrations involves determination of concentrations of the identified chemical agents in an environmental medium, to which an individual of a given subgroup is exposed during a certain period of time. Concentration of chemical agents in a given environmental medium is established by use of standardized measuring methods; if measuring is not possible, the adequate mathematical models for concentration prediction can be used.

Uptake calculation involves calculation of the quantity of chemical agent coming into contact with the exposed person's body per unit body weight per unit time (expressed as mg/kg/day), according to the defined uptake pathway:

$$Uptake\,dose = C_{i,x}\left(\frac{IR_y}{BW_y}\right)\left(\frac{ED_i \cdot ET_i \cdot EF_i}{AT_x}\right)\left[mg/kg/day\right], \tag{7}$$

where: Ci,x – concentration of pollutant x in environment i [mg/m^3]; IRy – individual respiratory rate at rest per unit time for a representative individual in subgroup y in environment i [m^3/day]; ETi – exposure time of the representative individual in environment i [days/years]; BWy – body weight of the representative individual in the observed subgroup, represented as y [kg]; EDi – exposure duration for the representative individual in environment i [year]; ATx – average time of effect duration of pollutant x [days]; and EF_i – exposure frequency [day/year].

Exposure is calculated with the following physical equation when the uptake dose is known:

$$E_{\mathrm{i,x,y}} = 0{,}001 \cdot \mathrm{C}_{\mathrm{i,x}}\left(\frac{IR_y}{BW_y}\right)\left(\frac{ED_i \cdot ET_i \cdot EF_i}{AT_x}\right), \tag{8}$$

where: Ei,x,y – exposure, or the average uptake of pollutant x as a function of time, for the representative individual y in the observed subgroup in environment i [mg/kg per day].

Risk characterization is conducted based on known dose and exposure, and it represents the final stage in health risk assessment. Individual health risk is defined as

$$\mathrm{R_i} = \mathrm{Dose} \cdot \mathrm{Toxicity}. \tag{9}$$

Individual health risk is expressed as one in a million (.000001) or as percentage (0001%) of the probability of occurrence of health risk from e.g. asthma or lung cancer. Individual health risk $\mathrm{R_i}$ can be calculated through the potential dose and the SFI (Inhalation Slope Factor).

$$\mathrm{SFI} = \text{unit risk } (\mu g/m^3)^{-1} \cdot \mathrm{BW\ (kg)} \cdot \mathrm{IR\ (m^3/day)^{-1}}. \tag{10}$$

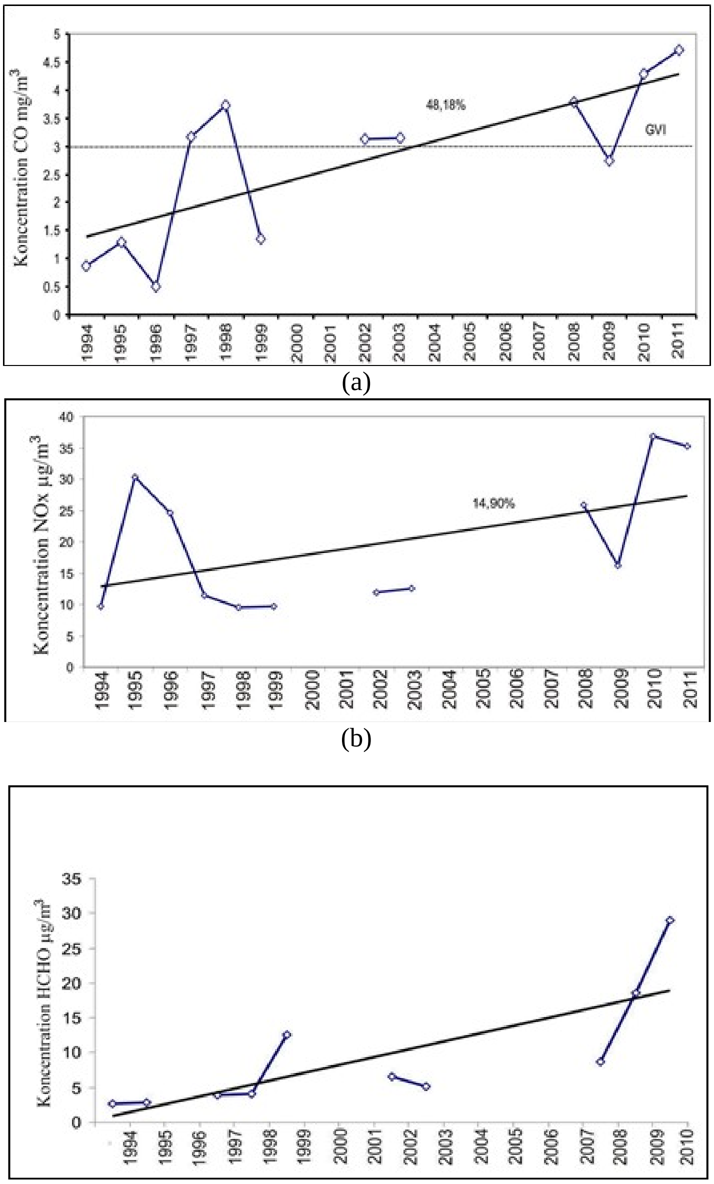
For the assessment of carcinogenic effects due to long-term exposure to pollutants, the potentially higher risk of carcinogenic diseases can be determined as the product of exposure and carcinogenic coefficient, established for every carcinogenic pollutant. The potentially higher risk of an individual in subgroup y developing cancer due to exposure to pollutant x is:

$$ICR_{i,x,y} = E_{i,x,y} \cdot SF_x\,, \tag{11}$$

where: *ICRi,x,y* – probability of individual cancer risk for individual *y* exposed to pollutant *x* in environment *i, SFx* – carcinogenic coefficient of pollutant *x* [mg/kg/day].

RESULTS AND DISCUSSION

Analysis of concentrations of standard pollutants in the City of Niš between 1994 and 2011 indicates that it is necessary to determine the relationship between exposure to pollutants emitted from motor vehicle exhausts and the occurrence of health effects in the exposed population. The diagram (Figure 2 a, b, and c) shows the concentration trends of the following pollutants: carbon monoxide (CO), nitrogen oxides (NO_x), and formaldehydes (HCHO).



(a)

(b)

(c)

Figure 2. – Average annual concentrations of CO, NO_x, and HCHO in ambient air in the City of Niš with a trend line for the analyzed monitoring period

For the monitoring period of average annual CO, NO_x, and HCHO concentrations, the trend line shows an increase in concentrations – CO for 48.18%, NO_x for 14.90 %, and HCHO for 14%. From 2003 onward, CO concentrations in the City of Niš exceeded the threshold value (Figure 2a).

For the aforementioned reasons, the 2012 study consisted of ambient air concentration measurements of particulates 2.5 µm in diameter ($PM_{2.5}$) with the help of automatic measuring station at the “Bambi” kindergarten, subsidiary of the Preschool Institution “Pčelica”, located at Bulevar Nemanjića bb, Niš

(Figure 3). We conducted the measuring from April 23 to May 25, 2012 and monitored subchronic exposure of children. “Bambi” kindergarten is located in a densely populated part of the city with prominently heavy road traffic due to the vicinity of the crossroads of Bulevar Nemanjića and Vojvode Mišića Street (Figure 3).

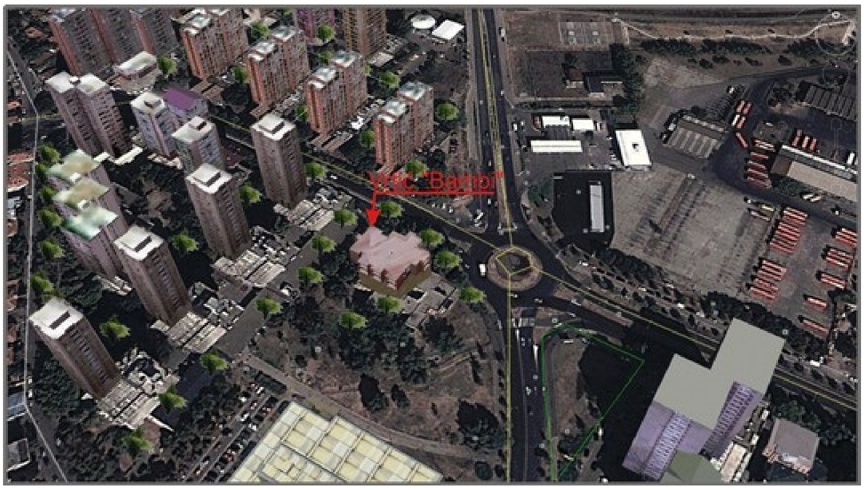


Figure 3. – Micro-location of the “Bambi” kindergarten in Niš

The results of eight-hour measurements by monitored weeks are given in Table 1. The eight-hour period concentrations were specially selected to be monitored during the time children were attending the kindergarten – from 8am to 4pm. We selected this particular monitoring interval because exposure duration and pollutant concentration are equally important for the development of toxic effect.

Concentration trends from 8am to 4pm within the monitored 24-hour concentrations did not change significantly during the monitoring period (Apr. 23–May 25), as shown by the example of daily concentrations obtained on May 10, 2012 (Figure 4).

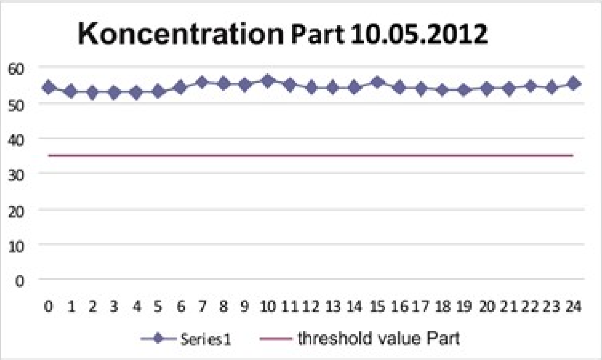


Figure 4. – Pollutant concentrations monitored at the “Bambi” kindergarten in Niš

The results given in Table 1 indicate that $PM_{2.5}$ concentrations during subchronic exposure caused the occurrence of harmful health effects in preschool children. During the entire monitored period, in April and May, $PM_{2.5}$ concentrations considerably exceeded the allowed immission concentrations by 43.11 % to 107.4 %.

Table 1. – Eight-hour concentrations of $PM_{2.5}$ from April 23 to May 21, 2012

Concentrations of $PM_{2.5}$ [µg/m^3] by monitored weeks									
1st monitored week		2nd monitored week		3rd monitored week		4th monitored week		5th monitored week	
Date	Concen.	Date	Concen.	Date	Concen.	Date	Concen.	Date	Concen.
23.04.2012	56.2188	30.04.2012	64.1044	07.05.2012	55.94	14.05.2012	50.7222	21.05.2012	53.7977
24.04.2012	54.6666	01.05.2012	64.17	08.05.2012	54.8788	15.05.2012	50.6277	22.05.2012	56.2711
25.04.2012	57.3666	02.05.2012	62.7122	09.05.2012	54.7644	16.05.2012	51.0344	23.05.2012	53.9166
26.04.2012	56.6533	03.05.2012	64.43	10.05.2012	54.8755	17.05.2012	51.0966	24.05.2012	60.4877
27.04.2012	64.3755	04.05.2012	63.6977	11.05.2012	55.1211	18.05.2012	50.0911	25.05.2012	72.5944
28.04.2012	61.9466	05.05.2012	57.59	12.05.2012	53.1511	19.05.2012	50.6744		
29.04.2012	61.8033	06.05.2012	55.9533	13.05.2012	50.8533	20.05.2012	51.4111		

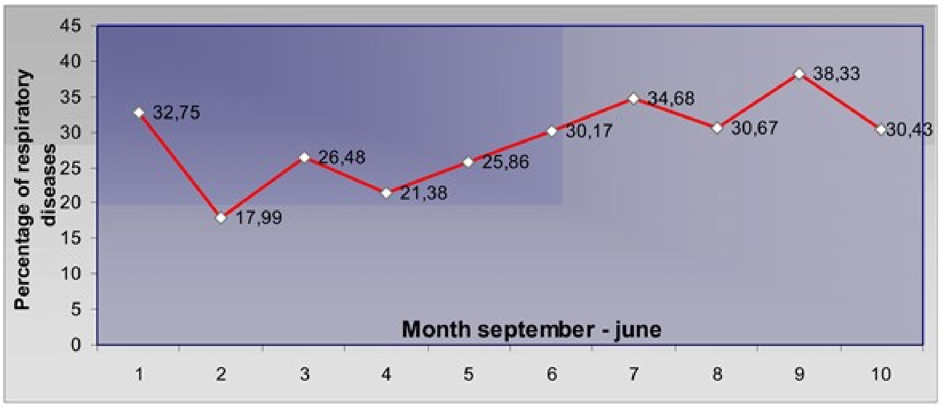


Figure 5. – Percentage of respiratory diseases in the exposed preschool children between September 2011 and June 2012

Out of the total number of exposed preschool children, 30.67 % suffered from a respiratory disease in April and 38.33 % in May (Figure 5).

Table 2 shows the individual risk Ri calculated by equations (9) and (10). The probability of individual cancer risk was calculated by equations (7), (8), and (11). The individual risk and the probability of cancer were calculated only for two-hour exposure to $PM_{2.5}$ concentrations ranging from 50.09 to 72.59 µg/m^3 for 33 days of exposure.

Table 2. – Individual risk and probability of cancer in children exposed to
$PM_{2.5}$ particulates at the "Bambi" kindergarten

Children's age	Individual risk Ri	Probability of individual cancer risk ICR
Under 1	1.624 %	2.13·10-6
1 to 3	8.84 %	1.19·10-5
3 to 6	21.84 %	6.39·10-5

CONCLUSION

Based on the obtained study results, we can conclude the following:

- Measured $PM_{2.5}$ concentrations from April 23 to May 25, 2012 at the "Bambi" kindergarten exceeded the threshold values by 43.11% to 107.4%.
- Individual risk (Ri) from respiratory diseases in preschool children upon subchronic exposure ranged from 1.624 % to 21.84 %.
- The probability of individual cancer risk (ICR) ranged from $2.13 \cdot 10^{-6}$ to $6.39 \cdot 10^{-5}$, which means that this exposure level can affect two in a million exposed children up to six in 100,000 exposed children.

- The analysis of respiratory disease incidence in the observed subpopulation (preschool children) in 2012 showed the highest percentage of affected children for the month of May – 38.33 %.
- This study suggests a possibility of a direct causal relationship between increased $PM_{2.5}$ concentrations in ambient air and the incidence of respiratory diseases in preschool children. Consequently, there is a need for continuous monitoring of ambient air concentrations and the incidence of respiratory diseases. There is a justifiable probability that the trend line of respiratory disease sufferers is correlated with the trend line of concentration change, which would confirm the causal relationship between air pollution from $PM_{2.5}$ particulates and health risk.

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7.7 RESPIRATORY AND INFLAMMATORY RESPONSES IN LOW AND HIGH LEVELS OF TRAFFIC-RELATED AIR POLLUTION WITH AND WITHOUT PHYSICAL ACTIVITY

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Short term exposure to traffic related air pollution has been associated with adverse respiratory outcomes. Moderate physical activity in polluted air may increase pollutant uptake and increase health effects.

The objective was to assess respiratory and systemic subclinical responses in a healthy population in Barcelona following short term exposure to traffic related air pollution with and without moderate physicalactivity.

Well controlled crossover study design comparing lung function, airway inflammation [Fraction of exhaled Nitric Oxide (FeNO)], and systemic inflammation markers in blood at baseline and up to 6 hours after exposure to traffic related air pollution, with or without physical activity. Healthy non-smoking subjects were exposed for 2 hours to contrasting pollution levels while either cycling or resting (n=28). Each volunteer participated in all four conditions (high vs. low exposure; moderate physical activity vs. resting). On-site exposure monitoring included particulate matters (UFP, PM10, PM2.5), nitrogen oxides (NOx), and elemental carbon (EC). Data were analyzed using mixed effect models for repeated measures.

Physical Activity, but not air pollution, increased statistically significantly FEV1, (Coef. 0.034, $p<0.001$), FeNO (Coef. 0.880, $p=0.047$), neutrophil counts (Coef. 18.66%, $p<0.001$), and serum interleukin-6 (Coef. 52.67%, $p=0.034$) levels. Physical activity (Coef.9.699, $p<0.001$) and PM10 and PM2.5 exposure statistically significantly increased leukocytes counts. High vs low air pollution exposure and Interquartile increases in UFP (Coef.-0.004, $p=0.001$), EC (Coef.-0.004, $p=0.003$), NOx (Coef.-0.004, $p=0.002$), PM2.5 (Coef.-0.005, $p=0.001$), and PM10 (Coef. -0.003, $p=0.002$) decreased significantly the ratio FEV1/FVC. There was no interaction between air pollution and physical activity for any of the outcomes of interest.

This study suggests that generally short term physical activity, but not short term air pollution, is an important predictor in acute systemic and local (or local) inflammation and assessed respiratory markers except for the ratio of FEV1/FVC for which air pollution showed small effects .

7.8 EFFECTS OF OUTDOOR AIR POLLUTION ON RESPIRATORY HEALTH OF SCHOOL AGE CHILDREN IN NIš, SERBIA

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ABSTRACT

Previous studies of the impact of long-term exposure to outdoor air pollution on the respiratory health of children have yielded different results. The aim of this study was to investigate effects of outdoor air pollution exposure on respiratory symptoms and illnesses among schoolchildren. Epidemiological study included 354 participants (49.15 % male) aged 11-14 years from the city of Niš, Serbia. We used the questionnaire of the American Thoracic Society's Division of Lung Diseases (ATS-DLD-78-C). According to the official data, the 10-year average concentrations of outdoor air pollutants, monitored at the relevant background monitory stations , were statistically higher in vicinity of school of exposed group of children. We found the significant association between outdoor air pollution exposure and increased prevalence of upper respiratory symptoms and bronchitis and asthma. It is necessary to inform parents on the risks of environmental outdoor air pollution exposure during childhood.

1. INTRODUCTION

Outdoor air pollution is one of the major public health concerns of today.Numerous studies have reported associations between airborne particles and a range of respiratory outcomes from symptoms to mortality (Ilić, M. et al, 2005; Li, S., et al, 2012; Altuğ, H. et al, 2013.). Children living in the urban areas are particularly vulnerable(Samet, Maynard, 2005; Nordling, E. et al, 2008;). Studies of the impact of long-term exposure to outdoor air pollution on the prevalence of respiratory symptoms and lung function in children have yielded mixed results(Saravia, J., et al, 2012; Stankovic, A., et al, 2007; Sram, R.J., et al, 2013.), partly related to differences in study design, exposure assessment, confounder selection and data analysis. Several research projects in Serbia provided important contributions to knowledge regarding associations between air pollution exposure and health of populations living in Serbia (Jovašević-Stojanović, Bartonova, 2010.), but there are relatively few number of studies about air pollution and respiratory health of schoolchildren from Serbia (Nikolić, M. 2000). The aim of the present study was to investigate effects of exposure to outdoor air pollutants on respiratory symptoms and illnesses among school children.

2. METHODOLOGY

The effects of air pollutants (PM, SO_2, NO_2) were assessed in 354 children (49.15 % males), aged 11-14 from two primary schools (classes 5-8) in the City of Niš (Serbia). Exposed group of children (n=215) were attending the school located in a city area of Niš with a high level of air pollution, while the children (n=139), in the other comparison group, designed as non-exposed group, were attending the school in the area of Niš with a lower level of air pollution. The examinations took place at the schools after the parents were informed about the aims and performance of the study and had given written consent. The procedure was approved by the Regional School Authorities of Niš (Serbian Ministry of Education). The children were surveyed by the questionnaire of the American Thoracic Society's Division of Lung Diseases (ATS-DLD-78-C) (Ferris., B.G., 1978.), filled by their parents in personal interviews.Data about the prevalence of respiratory symptoms (cough, phlegm, blocked-runny nose, wheezing and dyspnea) in the last 12-month period of life and lifetime prevalence of respiratory illnesses (asthma, pneumonia and bronchitis) were obtained. The questions about respiratory symptoms were the following: Did you have coughs for > 3 weeks in the last 12 months? Did you have phlegm in your nose or throat in the last 12 months when you did not have a flu? Did you have wheezing in your chest in the last 12 months when you did not have a flu? Have you ever had attacks of shortness of breath in the last 12 months? In the past 12 months, have you had a problem with a runny or a blocked nose when you did not have a flu? Asthma was considered if an affirmative answer was given to the following questions: “has any doctor diagnosed your child with asthma?” and “has your son/daughter ever had asthma?”. The same situation was with other respiratory illnesses.

In order to limit exposure misclassification, the analysis were restricted to children who were at the same address from birth. According to the official data, the 10-year average concentrations of outdoor air pollutants monitored at the relevant background monitory stations were statistically higher in vicinity of school of exposed group of children.

A statistical package SPSS 10.0 was used for data analysis.Descriptive statistics was computed for all variables. Mantel-Haenszel chi-square test was used to compare frequencies of categorical variables between two groups. Student's t test was used to compare respiratory symptoms and disease frequencies between the groups. Statistical significance was set at an a level of 0.05.

3. RESULTS AND DISCUSSION

There were 354 complete answers from the parents (response rate 92.9%). Of the final study sample, 215 children (60.73%) were outdoor air pollution exposed and 139 (39.27%) were non-exposed. Baseline characteristics of study population are reported in Table 1. There were no statistically significant differences in age between the two group.

Table 1. Distribution of the children by gender and age

Characteristics of children	Total (n=354)	Exposed (n=215)	Non-exposed (n=139)
Male/Female , n	174/180	101/114	73/66
Age,yrs (mean ±SD)	12.96±1.54	12.78±1.56	12.95±1.52
11 yr, n	109	60	98
12 yr, n	107	54	53
13 yr, n	79	55	24
14 yr, n	59	46	13

Table 2 shows the basic characteristics of examined children. The children exposed to air pollution had better educated parents and statisticaly lower density of habitation than non-exposed children. There were no statistically significant differences in ambient exposure during pregnancy, type of heating, dampness/mold damage, keeping pets and parental history of allergic disease between examined groups (Table 2).

Table 2. Characteristics of examined schoolchildren

Characteristics	Exposed (n=215)	Non-exposed (n=139)	P*
Parental education level			
Elementary	15.12%	30.93%	p<0.05
Above elementary	84.88%	69.06 %	
ETS exposure during pregnancy	21.62%	22.66%	p>0.05
Density of habitation (person/room) (mean±SD)	0.82±0.32	0.88±0.29	p<0.01
Wood or coal heating	20.0%	25.53%	p>0.05
Dampness/mold damage	9.76%	8.99%	p>0.05
Pets	24.88 %	25.18 %	p>0.05
Parental history of allergic disease	19.53 %	17.98 %	p>0.05

* Mantel-Haenszel chi-square test

We found the significantly association between outdoor air pollution exposure and increased prevalence of upper respiratory symptoms and bronchitis and asthma in the sample of examined children. (Table 3).

Based on the result of the present study, outdoor air pollution exposure is an important determinant of childhood respiratory health. We found that outdoor air pollution was significantly associated with increased prevalence of respiratory symptoms (dyspnea, wheezing) and bronchitis and asthma in the children aged 11-14 years in Niš.

We found the significantly association between outdoor air pollution exposure and increased prevalence of upper respiratory symptoms and bronchitis and asthma in the sample of examined children. In exposed children, the prevalence of asthma increased significantly [odds ratios (95% confidence interval) - 1.38 (1.21–1.93), respectively]. Also, the difference of bronchitis prevalence were statistically significant among different group of children. The prevalence of upper respiratory symptoms were statistically higher ($p < 0,01$) among exposed children.

Table 3. Exposure to air pollution and children's respiratory health

Symptoms and diseases	Exposed		Non-exposed		X^2	OR	CI
	Yes	No	Yes	No			
Upper respiratory symptoms	58	372	23	255	4.53*	1.63	1.03-2.58
bronchitis	60	370	18	260	4.62*	2.34	1.3-3.57
asthma	34	396	11	267	4.42*	1.38	1.21-1.93
pneumonia	58	372	31	247	0.84	1.21	0.8-1.82

*$p<0.05$

This 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., 2013.). For example, the almost perfect correlation was found between atopy in asthmatics and atopy in the nonasthmatic part of the childhood population shows that the prevalence of atopy in asthma depends on environmental factors that simultaneously induce atopy in asthmatic and nonasthmatic subjects.

Air pollutants may impact anatomy and/or physiological functioning of the lung and interrelated systems. Programming effects may result from pollutant-induced shifts in a number of molecular, cellular, and physiological states and their interacting systems. Specific key regulatory systems susceptible to programming may influence lung development and vulnerability to respiratory diseases, including both central and peripheral components of neuroendocrine pathways and autonomic nervous system (ANS) functioning which, in turn, influence the immune system. Starting in utero, environmental factors, including air pollutants, may permanently organize these systems toward trajectories of enhanced pediatric (e.g., asthma, allergy) as well as adult disease risk (e.g., chronic obstructive pulmonary disease). Evidence supports a central role of oxidative stress in the toxic effects of air pollution. Additional research suggests xenobiotic metabolism and subcellular components, such as mitochondria are targets of ambient air pollution and play a role in asthma and allergy programming. Mechanisms operating at the level of the placenta are being elucidated. Epigenetic mechanisms may be at the roots of adaptive developmental programming.

Some methodological limitations need to be kept in mind when interpreting these study results. Respiratory illnesses status was assigned on the basis of parental report of physician diagnosis of asthma, pneumonia and bronchitis and symptoms based on parental recall. Exposure to outdoor air pollution was assessed retrospectively, using questionnaire responses and was not validated by objective measurements. We were unable to investigate any dose-response relationship because we don't have information on the intensity and the duration of exposure. We used the presence of a person who smoked as a surrogate for passive smoking among children, which might have led to underestimation of the strength of the association between environmental tobacco smoke and respiratory health.

Our findings have clinical and public health sinificance. 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) (Crozier-Kegler, M., Miner, K. 2004.) could be set.

Finally, the study provides 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). Many parents mispercieve the risks to their children of air pollution. Health care workers and other who care of children must try to limit as much as possible, the exposure of children to this environmental factor. One of the most important challenges for the future is the development of effective preventive measures that are suitable to different cultures and socio-economic groups in Serbia. Pregnant women and parents of young children must be top targets for intervention (Crozier-Kegler, M., Miner, K. 2004.).

4. CONCLUSIONS

To conclude, the present data support experimental and epidemiological findings according to which outdoor air pollution could have negative effects on respiratory health in children. It is necessary to inform parents of the risks of environmental outdoor air pollution exposure during childhood.

Education about the health consequences of ambient air pollution exposure among children is urgently needed in Serbia, a country with high emission of air pollutants.

5. ACKNOWLEDGEMENTS

This study was published thanks to the Ministry of Science and Technological Development of the Republic of Serbia (Project no. 42008 and Project no. 43014).

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7.9 APPROACHES TO CARCINOGENIC RISK ASSESSMENT FOR PAHS

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ABSTRACT

The main problem that complicates the carcinogenic risk assessment of the complex mixtures of PAHs is the lack of knowledge to what extent the PAH fraction contributes to carcinogenicity. Component-based approaches involve dose addition of various PAHs with estimated TEFs (compiled from studies measuring carcinogenic potency and surrogate biomarkers). For the index chemical is chosen BaP, classified in IARC Group 1, because there are robust cancer dose-response data on chronic exposures available for that substance and large database of studies in which BaP is compared with the potency of other PAHs. The list of PAHs with estimated TEFs was extended by many authors over the last two decades. For the improvement of cancer risk assessment, TEFs for a large number of PAHs should be derived and new methods may be applied, including genotoxic effect measured *in vitro* and analyzed with mathematical models, or predictions based on molecular structure -activity relationships.

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a large group of organic compounds with two or more fused aromatic rings made up of carbon and hydrogen atoms. PAHs do not occur in the environment as isolated entities, but primarily occur in complex mixtures generated from the incomplete combustion of organic materials such as the processing of coal, crude oil, combustion of natural gas, refuse, vehicle emissions, heating, cooking and tobacco smoking, as well as natural processes including carbonisation. Low-molecular-weight PAHs (two and three rings) were mainly distributed in the vapor phase in the atmosphere, while multi-ringed PAHs were usually present as particles. The number of chemicals that comprise the PAHs class is unknown; however, there are thought to be hundreds of individual PAHs present as components of complex mixtures (WHO, 1998). The scientific, regulatory, and public interest in PAHs is primarily based on the potential role of these substances as cancer-causing agents.

Ingestion is quantitatively the main route for PAH human exposure (ATSDR, 1995). However, inhalation is also a significant route because of the ubiquitous presence of these compounds in the atmosphere and human data on carcinogenicity are mainly based on inhalation exposure to mixtures of PAHs. Exposure to PAHs from coke ovens, roofing tar pots and diesel engines emissions may be connected with cancer development. The most widely acknowledged epidemiological evidence of PAHs carcinogenic effect represents the development of lung, pharynx, larynx and oesophagus cancer in tobacco smokers (Polesel, 2008). Exposure to PAHs has been reported in several industries, including those of the aluminum production, coal gasification, coke production, iron and steel foundries, coal tar and related products, carbon black and carbon electrodes production. Occupational exposure to PAHs by inhalation is associated with a increased risk of respiratory and urinary cancer (Armstrong, 2004, Bosetti, 2007). There is substantial body of evidence that some PAHs (and complex mixtures of PAHs) are tumorigenic and genotoxic in animal bioassays and genotoxicity tests.

2. APPROACHES FOR CARCINOGENIC RISK ASSESSMENT OF PAHS

The three approaches that have been advocated for carcinogenic risk assessment of PAHs (EPA, 2000) are assessment from long-term human exposure to a particular PAH mixture, toxicity data on a “sufficiently similar” mixture, or component-based approach using toxicity equivalency factors (TEFs) for various PAHs in the mixture. The term PEF (potency equivalency factor) instead of TEF was suggested by Collins et al. (1998) and is deemed more appropriate for carcinogenic risk assessment of PAHs, as it does not infer an evaluation of other toxicological effects of PAHs. In recent years IRIS EPA (2010) uses the term RPF (relative potency factor).

EPA Guidelines suggest that the selection of a chemical mixture risk assessment method depends on type of available data. It starts with with an assessment of data quality and then leads the risk assessor to selection of a method through evaluation of the available data. The major concerns for the user are whether the available data are on components, or whole mixtures, whether the data are composed of either similar components or similar mixtures that can be thought of as acting by similar toxicological processes, and whether the data may be grouped by emissions source, chemical structure, or biologic activity. Human health risk assessments done by US EPA generally follow the paradigm established by the National Academy of Sciences (1983). This paradigm describes a group of interconnected processes for performing a risk assessment that include hazard identification, dose-response assessment, exposure assessment, and risk characterization.

Risk assessment for cancer from chronic exposure to the PAHs mixture of concern

In accordance with EPA guidance for health risk assessment of chemical mixtures, assessment of the cancer risk from long-term human exposure to a particular PAH mixture would best be conducted with quantitative information on the dose-response relationship for cancer from chronic exposure to the mixture of concern. If risk assessment for PAHs treats a mixture as a single entity (especially in epidemiological studies), results are based on actual mixture effects. Such approaches inherently address the toxicity of all, including unidentified, components in mixtures and specific interactions among them. Thus, they do not require assumptions regarding the toxicity of individual components (e.g., dose or response additivity). While whole mixture assessment is preferred, there are challenges and disadvantages associated with using this approach. There are very few toxicity data available for whole PAH mixtures and, in most cases, chemical analyses of the composition of mixtures are limited. In addition, PAH- containing mixtures tend to be very complex and the composition of these mixtures appears to vary because of differences in source types or weather and other conditions, so toxicity data from one mixture may not adequately represent others. However, the main problem that complicate the carcinogenic risk assessment of the complex mixtures of PAHs to which human exposure occurs is lack of knowledge to what extent the PAH fraction, as opposed to other chemicals and particulate matter, contributed to carcinogenicity. For these reasons, a whole mixtures approach may not always be practicable for risk assessment purposes.

Risk assessment for cancer from chronic exposure to a "sufficiently similar" PAHs mixture.

When data for the mixture of concern are not available, EPA guidance recommends using toxicity data on a "sufficiently similar" mixture. However, quantitative cancer dose-response information exists only for a few complex mixtures generated from the combustion or pyrolysis of organic matter. EPA's IRIS database currently includes assessments very limited number of PAH-containing mixture like coke oven emissions, creosote, or diesel emissions (EPA, Albert, 1983, Bostrom, 2002). This comparative potency approach is used to estimate the potency of mixtures without having to identify or quantify the individual components. The carcinogenic risk due to exposure to the PAHs present in a reference mixture is estimated and expressed per unit amount of BaP.

Oral carcinogenicity bioassays for risk assessment of mixtures like manufactured gas plant residue (Weyand, 1995) and coal tar preparations (Culp, 1998, Gaylor, 1998) are developed expanding the PAH mixture cancer database. For instance, Culp et al. reported results for several types of tumors induced by benzo[a]pyrene (BaP) and two coal tar mixtures and these dose–response data are used to determine a guideline value.

Assessment of *sufficiently similar" PAHs mixture* raises questions as to whether BaP is the best indicator of the carcinogenicity of all PAHs present in the mixture because it is not clear whether the PAH profile (concentration of individual PAHs relative to BaP) of different sources has changed. Several assumptions are made when using this approach. The first is that the risk attributable to PAHs in any given mixture is proportional to that of BaP in the mixture. The second is that the concentrations of individual PAHs relative to BaP are relatively stable from mixture to mixture. If the mixture has a considerably different PAH profile, particularly in respect of high potency PAHs, than the reference mixture, the estimate of risk may not be acceptable. There is some evidence to suggest that PAH-rich complex environmental mixtures are approximately the same in both their PAH composition and their carcinogenic potencies when expressed in terms of BaP levels, regardless of the source of the mixture (WHO, 1998). However, it is noted that some source mixtures can vary considerably in composition. For example, Nesnow et al. (1982) showed that BaP concentrations in four diesel emissions varied by over a 600- fold range.

Component-based risk approach

Component-based approaches involving dose addition are possible in case of PAHs, if we assume that all PAHs in the mixture act in a toxicologically similar manner. Molecular mechanism of PAHs induced carcinogenicity is that most PAHs are metabolised to diol epoxides, which bind to DNA and induce mutations in specific, cancer-related genes, ultimately leading to tumourigenesis. It has to be clear dose-response effect for every component which should be compared to the index chemical. The other assumption is that interactions among PAH mixture components do not occur at low levels of exposure typically encountered in the environment.

In 1993, EPA published the Provisional Guidance for Quantitative Risk Assessment of PAHs (EPA, 1993). It recommended estimated orders of potential potency (termed EOPP) for individual PAHs that could be used in a component-based approach and most common PAHs were categorized as Group B2 (probable human carcinogens). For the index chemical is chosen benzo[a]pyrene (BaP), one of the most carcinogenic PAHs, classified in IARC Group 1, because there are robust cancer dose-response data on chronic exposures available for that substance and large database of studies in which the potency of benzo[a]pyrene is compared with the potency of other PAHs. Key limitations to the RPF approach, relative to whole mixture approaches, are that RPFs have been derived for a limited number of PAHs and that cancer risks from non-PAH components, unidentified PAHs, heterocyclic and substituted PAHs in PAH mixtures are not estimated. The first disadvantage of component based approach may be reduced by the derivation of RPFs for numerous PAHs. The second may be addressed by comparing the cancer risk of a PAH mixture measured experimentally with the cancer risk that was predicted using the RPF method. However, there is a small number of compounds for which RPFs and analytical data were available (Clement Associates 1990).

The list of PAHs with estimated equivalency factors (recently named RPFs by EPA), compiled from studies measuring carcinogenic potency and surrogate biomarkers, was extended by many authors over the last two decades. However, IRIS EPA in 2010 recommended RPF approach for limited number of PAHs based on their experimentally observed RPFs and changed some previously estimated factors to higher or lower values. The criteria to include studies on PAHs for RPF estimation were:

- BaP was tested simultaneously with another PAH;
- A statistically increased incidence of tumors was observed with BaP administration, compared with control incidence;
- BaP produced a statistically significant change in a cancer-related endpoint finding;
- Quantitative results were presented;
- The carcinogenic response observed in either the BaP or other PAH-treated animals at the lowest dose level was not saturated (i.e., tumor incidence at the lowest dose was <90%), with the exception of tumor multiplicity findings; and
- There were no study quality concerns or potential confounding factors that precluded use (e.g., no concurrent control, different vehicles, strains, etc. were used for the tested PAH and BaP; use of cocarcinogenic vehicle; PAHs of questionable purity; unexplained mortality in treated or control animals).

Studies with positive findings were used for calculation of RPFs. Studies with nonpositive findings were used in a weight of evidence evaluation to select PAHs for inclusion in the RPF approach.

The advantages of a RPF approach for carcinogen risk assessment of PAHs are that it considers individual PAHs and is adaptable to potential variations in concentrations of PAHs between mixtures. This approach could also be adapted to take into account new data on DB[a,l]P and other highly potent PAHs.

Recommendations by EPA are based on widely accepted animal studies and genotoxicity tests. However, for the improvement of cancer risk assessment, TEFs for a large number of PAHs should be derived and new methods may be applied. It may include genotoxic effect measured in vitro and analyzed with mathematical models, or predictions based on molecular structure -activity relationships in the absence of detailed laboratory toxicity and long-term studies in rodents.

3. CONCLUSION

Every approaches used for inhalation carcinogenic risk assessment for mixtures containing PAHs has its advantages and disadvantages. Assessment of whole mixture is simple and requires inexpensive monitoring, but is not adaptable to changes in PAH mixtures and needs selection of appropriate markers for comparison with other mixtures. The advantages of a RPF approach for carcinogenic risk assessment of PAHs are that it considers individual PAHs and is adaptable to potential variations in concentrations of PAHs between mixtures. This approach could also be adapted to take into account new data on DB[a,l]P and other highly potent PAHs.

Recommendations by EPA are based on widely accepted animal studies and genotoxicity tests. However, for the improvement of cancer risk assessment, RPF s for a large number of PAHs should be derived and new methods may be applied. It may include genotoxic effect measured in vitro and analyzed with mathematical models, or predictions based on molecular structure -activity relationships in the absence of detailed laboratory toxicity and long-term studies in rodents.

ACNOWLEDGEMENTS

This paper was supported under projects : III41028 (2011-2014), INGEMAS, Ministry of Education, Science and Technological Development of Serbia and III42008 (2011-2014), Evaluation of Energy Performances and Indoor Environment Quality of Educational Buildings in Serbia with Impact to Health, Ministry of Education, Science and Technological Development of Serbia.

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7.10 POSSIBILITY OF MICROBIAL CONTAMINATION IN INDOOR AIR AND ITS IMPACT ON HUMAN HEALTH

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ABSTRACT

Indoor air pollution is present in literally each and every indoor space, and the exposure is particularly significant for vulnerable populations such as children, pregnant women, elderly, ill and disabled, considering the amount of time spent indoors. According to WHO report, indoor air pollution is responsible for 2.7% of the global burden of diseases. There is wide range of biological contaminants in indoor air, such as house dust mites, fungi, bacteria, protozoa, and viruses. These microorganisms produce allergens, toxins, and other volatile organic chemical compounds which may affect human health. Common prerequisite condition for their growth, development, and multiplication is dampness. Considering the variety of microbes, possible synergistic effects, the characteristics of endangered population, as well as problems in detecting techniques, further investigations in this field are needed.

Key words: indoor air pollution, microorganisms, health impact

1. INDOOR AIR POLLUTION

Indoor air quality has become an important field of research in the last decades. However, it is a very old problem. Human beings have always been subjected to the indoor pollution, otherwise, interest in indoor air quality emerged in USA in the 1970, when „Sick Building Syndrome" was first described (1). Many office workers reported headache, mucous membrane irritation, and difficulty concentrating during working hours. All symptoms disappeared at home. Understanding of risk factors underlying this epidemic led to improvement of legislation regarding ventilation rates and maintenance, so the number of complaints decreased in the 1990s. Moreover, in urbanized societies people spend more than 90% of their time indoors or in vehicles. According to The World Health Organization report 2002, indoor air pollution is responsible for 2.7% of the global burden of diseases.

So, indoor air quality is one of the most significant factors affecting the health and well-being of people who inhale 10m^3 of the air every day, and spend between 80-95% of tme indoors (2,3).

Indoor air pollution is present in literally each and every indoor space, with the exception of strictly controlled and sterile spaces in pharmaceutical, medical and research facilities. Humans are inevitably exposed to such pollutants, considering the amount of time spent indoors, as it was mentioned before, but the influence of the pollution on human health may vary, depending on age, health condition, and individual predisposition.

The interest in indoor air monitoring is growing worldwide every year, considering the indoor pollution ranged among the first five leading causes of illness in the world (4). World Health Organization (WHO) Regional Office for Europe, in 2009 prepared Guidelines for indoor air quality (5), according to previously formulated postulate *The right to healthy indoor air*. In these Guidelines, WHO presents public health risks due to dampness, associated microbial growth and contamination of indoor air.

2. BUILDING DAMPNESS AND ITS IMPACTS ON INDOOR AIR QUALITY AND HUMAN HEALTH

Abundant previous work conducted on building dampness includes the causes of excess building dampness, the influence of dampness on indoor biological and organic chemical contaminants, and the effects of dampness and of dampness-related indoor contaminants on people's health. There is also extensive literature on how to prevent building dampness (6).

Estimations of dampness and mold presence vary from 20% buildings in Scandinavia (7) to 50% buildings in United States (8). Fewer studies were conducted in low-income countries; nevertheless, they suggest that the problem of indoor dampness is even greater (9). The dampness and mold are traditionally related to overcrowded accommodations without adequate heating, ventilation and insulation, hence, the lower income is – these problems are more evident. Climatic changes such as global warming with more frequent occurrence of storms and heavy rains lead to gradual increase in sea level. Together with more frequent floods, it results in increase in percentage of buildings affected by dampness and mould, particularly in areas near the rivers. Increased indoor dampness provides optimal conditions for increased growth of dust mites, fungi and bacteria (10,11).

The dampness and mold growth may occur on visible interior surfaces in the building, including within basements or crawl spaces, or be hidden inside walls and air conditioning systems. Based on surveys, approximately half of U.S. homes and many schools and office buildings have visible evidence of a dampness problem or mold contamination. When building materials or furnishings are damp for a sufficient time period, mold and bacteria will often colonize the materials producing microscopic airborne particles, some containing allergens or chemicals with the potential to induce inflammation in the respiratory system. Molds and bacteria are also sources of odorous volatile organic compounds in the indoor air. High indoor relative humidity in damp buildings can also increase the number of house dust mites present indoors and these mites are an important source of indoor allergens. Many building materials also emit chemicals into indoor air and increased dampness in these building materials may also lead to increases in emission rates of gaseous non-microbial chemicals, for example formaldehyde (12,13).

Finally, excess moisture in indoor spaces creates optimal conditions for insects and rodents. These animals release their own allergens into the indoor environment, but can also represent the reservoir of contagious diseases agents.

In 2009, the World Health Organization (WHO) completed a review of the available scientific literature pertaining to the health consequences of building dampness and mold (5). Based on the review, dampness and mold in homes is associated with increases in several adverse health effects including upper respiratory symptoms, cough, wheeze, difficulty breathing, asthma exacerbation, development of new asthma, bronchitis, allergic rhinitis (allergy-caused inflammation of the nasal passages with runny nose or congestion), and eczema (14).

The specific agents, e.g., molds, bacteria, or organic chemicals, causing these health effects were uncertain and insufficient scientific data were available to draw conclusions about the association of dampness and mold with several other health effects. Nevertheless, the reviews concluded that building dampness and mold represented a public health problem and that steps should be taken to reduce building dampness and mold, including various education efforts, reviews of buildings codes and contracts, and an exploration of financial incentives for reduced dampness. Building dampness and mold were determined to be associated with 30% to 50% increases in a variety of respiratory and asthma-related health outcomes (15). Relative to research on the health risks of dampness and mold in houses, far less research has been performed on the health risks of dampness and mold in workplaces and schools. However, the available evidence suggests that the health risks of dampness in these buildings may be substantial. Based on review of nine studies, the evidence supporting an association of dampness or mold in offices and institutional buildings with respiratory or other health effects of occupants, or respiratory-health related sick leave, is reasonably robust. In the several of the studies, the risk for at least one health effect more than doubled.

Research has clearly demonstrated that **dust mite allergen** increases the risk of various health effects. Where concentrations of mite allergen in house dust are greater than approximately 2 micrograms allergen per gram of dust, susceptible people have a much higher risk of becoming sensitized to (i.e., have an allergic response to) dust mite allergen. Those who are sensitized to dust mite allergen have a several-fold increased risk of asthma. Mite allergens exacerbate allergic rhinitis (inflammation of the nasal tissues due to allergen exposures causing sneezing, runny nose, postnasal drip, and congestion) and atopic dermatitis (allergen-caused inflammation of the skin resulting in rash and itching). Unfortunately, control of indoor dust mites has proven difficult (16,17). Some molds can produce highly toxic chemicals called **mycotoxins** under some growth conditions. Some bacteria can also produce toxic chemicals. Studies with exposures of living cells and animals to mycotoxins indicate that some mycotoxins are very potent, i.e., only very small amounts of some mycotoxins can produce substantial effects in cells or animals. However, it is not known whether the indoor air concentrations of mycotoxins caused by microbial growth in damp buildings can become high enough to cause health effects (18). The health risk of the increases in **microbial and non-microbial indoor gas-phase chemical chemicals** in indoor air from building dampness are not well understood.

Many studies have found that health risks are increased by exposure to microorganisms, but there is growing evidence that exposure in early life to endotoxins and/or fungal agents protects against atopy and allergic disease. A prospective birth cohort study suggested an inverse relation between the levels of these pollutants and wheezing problems in 4 years old children (19). These results are in agreement with findings obtained from several studies of reduced incidence of hay fever, eczema and asthma in children who grew up on farms compared to urban children, and thus supported the „hygiene hypothesis“ which suggests the protective role of microbial exposure.

3. BIOLOGICAL AND MICROBIOLOGICAL POLLUTANTS IN INDOOR AIR

Biological pollutants may originate from human activity, building materials and carpets; they may also penetrate from outdoor environments by forced ventilation, diffusion or infiltration. The air inhaled by people is abundantly populated with microorganisms which form so-called bioaerosol. Bioaresol is a colloidal suspension, formed by liquid droplets and particles of solid matter in the air, whose components contain or have attached to them viruses, fungal spores and conidia, bacterial endospores, plant pollen and fragments of plant tissues (20). Possible sources of biological contamination of indoor air include: people, organic dust, various materials stored in the buildings, and the air inflowing from the ventilation and air conditioning systems.

There is a wide range of possible biological contaminants in indoor air, with different origin and patterns of spreading. For example, pollen and spores of plants are predominantly emitted from outside the building, transferring through doors and windows, or by personal contacts. Various species of bacteria, fungi, algae, and protozoa can originate both from outside space and from materials inside the buildings. According to conclusions of WHO working group (5), there are no specific microorganisms that can be specifically associated with indoor air pollution; rather they represent common allergens and other pathogens. However, some agents such as house dust mites and pet hairs are predominantly present in indoor air. Considering the variety of microorganisms and their characteristics, it is virtually impossible to quantify their concentrations in a form of tolerable levels of exposure.

The findings of epidemiological research indicate that exposure to high concentrations of microbes in the air frequently leads to allergies, asthma, hay fever, pneumonia, and many other health side-effects, including infections. Biological factors such as fungal spores and mites are involved in sick building syndrome, a complex situation in which occupants experience a variety of symptoms and become generally unwell, recovering only when they cease to frequent the building (20,6).

Indoor air contains numerous microorganisms of very different types. For example, **house dust mites** are small arachnids. Among numerous various species, few are of major importance for indoor air contamination, and their growth is directly related to relative humidity (45-50%) (21,22). The common foods for house dust mites are skin scales, but they are adapted to use other food sources as well. House dust mite allergens are commonly produced by *Dermatophagoides pteronyssinus* (proteolytic allergens Der p I and Der p II), and *Dermatophagoides farina* (Der f I). The faecal particles containing these allergens are predominantly found in house dust, mattresses and pillows (23).

Other common indoor air pollutants are **fungi.** Their presence in indoor air is result of transportation from outside environment via building materials, carpets, furniture, wallpapers, etc. Ventilation and air-conditioning systems are another common ways of penetrating of fungi into the buildings. The rate of further growth, spreading and multiplication depends exclusively on moisture content in indoor air, regardless the type of surface (24). The natural food source for fungi vary from plant, animal and human particles in house dust, to fragments of construction materials such as floor and wall textile coverings, furniture, residua of cooking traces, food storage, paper materials. Since these materials are in ample in every building, and considering that optimal temperature for fungi growth ranges from 10-35 ºC, the only limiting factor for development of fungi and mold contamination is dampness. Fungi may be extremely harmful for human health, but may also destruct the building itself, particularly the wooden parts, such as roofs, timbers, and other materials. Some fungi species produce strong allergens, which initiate IgE mediated immune reaction type I. For example, the indoor contamination with *Alternaria*, *Penicillium*, *Aspergillus* and *Cladosporium* spp., is related to asthma and other allergic respiratory diseases. Some of these species, such as *Penicillium* and *Aspergillus* can also induce type III allergy (IgG mediated), while at high concentrations, may also initiate combined type III and IV reaction manifested as hypersensitivity pneumonitis. Major fungal allergens are isolated and identified (such as Cla h I from *Cladosporum herbarum*, Alt a I and Alt a II from *Alternaria alternata* and Asp f I and Asp f III from *Aspergillus fumigatus*)(25). Nevertheless, even dead particles carry substantial health risk, because they may contain possibly harmful (1→3)-β-D-glucans with the potential to impair respiratory functioning (26), and mycotoxins. The harmful effect of mycotoxins is manifested by interference with RNA synthesis leading to DNA damage. Sometimes this toxicity is beneficial – e.g. penicillin, a strong bactericidic antibiotic, is a mycotoxin produced by fungi *Penicillium*. But, in general, fungi mycotoxins have strong genotoxic, cancerogenic, and immunotoxic potential. The cancerogenic effects of aflatoxin (mycotoxin produced by *Aspergillus flavus* and *Aspergillus parasiticus*) are well known. The most important mycotoxins related to indoor air contamination are trichotechens, generated by fungi *Stachybotrys chartarum* (macrocyclic trichotechens, trichodermin, sterigmatocystin and satratoxin G) (27). Several fungi also produce volatile organic compounds as the result of their metabolic processes, but their effects on human health are yet to be investigated. The assessment of fungi contamination in indoor air is very difficult. In study conducted by Pietarinen et al., culture methods identify only few of species that were recognized and quantify by quantitative PCR (28). *Penicillium*, *Aspergillus* and *Streptomyces* were predominantly identified by both methods. But, culture method successfully identified *Aspergillus fumigates* only in samples containing the amount of total viable fungi more than 10^6 cfu/g. Likewise, culture method was able to detect *Stachybotrys chartarum* only in samples with very high level of fungi contamination, contrary to qPCR method. These results are in agreement with another Finnish study which confirmed the highest prevalence of *Penicillium/Aspergillus* species in house dust, with more precise results obtained by qPCR method (29). Same authors indicated that concentrations of fungi differ significantly between seasons with the highest concentrations of *Aspergillus* detected in winter (more that 10000 cells/mg of dust).

Numerous species of **bacteria** are also common contaminants of indoor air. Contrary to relatively harmless saprophytic species originated from people, the species that actively grow in the indoor substrates may be potentially harmful. Although the health aspects of molds and fungi in indoor air are extensively studied, similar investigations of bacteria influence have been of little interest so far. The common features for both types of microorganisms are requirements for water and temperature ranges for optimal growth and development. Hence, we can fairly assume that bacteria grow in the same sites as fungi, preferably on damp substrates. This suggestion is confirmed by evidences that species such as *Streptomycetes*, which are not normally present in indoor environments, easily grow on wet surfaces, so their presence is used in screening for moisture problems in buildings (30). Very few studies were conducted so far regarding this problem, apart from several investigation conducted by Finnish authors who identified *Sreptomyces* and *Mycobacteria* in indoor surfaces (28,31,32,33). The latter bacteria have particularly strong immunogenic potential originated from cell wall components. The majority of culturable bacteria in indoor dust and air are Gram-positive *Micrococcus*, *Staphylococcus* and *Bacillus* strains. Similarly to fungi, there is a certain doubt regarding the method for determination of bacterial load in house dust. Culture method is relatively simple, but only 1% of airborne bacteria in indoor air are culturable. Culturable bacterial concentrations range from $7{,}3 \times 10^4$ to $1{,}85 \times 10^7$ cfu/g (public buildings) and $1{,}1 \times 10^4$ to $2{,}1 \times 10^7$ cfu/g in samples of house dust (27). Chemical markers analysis, i.e. detection of chemical compounds that build the bacterial cell wall (3-hydroxy fatty acids for Gram-negative bacteria and muramic acid for Gram-positive bacteria), has limited value, since these compounds are non-specific, and gas chromatography-mass spectrometry method requires complex sample preparation. (33). Another study conducted in Finland also indicated that culture method failed to detect *Aspergillus fumigates*, while qPCR in same samples detected the average of $2{,}21 \times 10^3$ cells/g. The average concentrations of *Penicillium spp.* and *Aspergillus spp.* were significantly lower when detected by culture method than qPCR ($9{,}01 \times 10^3$ cfu/g vs. $1{,}96 \times 10^5$ cells/g and $1{,}35 \times 10^4$ cfu/g vs. $5{,}44 \times 10^6$ cells/g, respectively) (31).

Finally, **protozoa** may also be present in indoor air in damp buildings. Yli-Pirila with co-workers detected amoebae in 22% of 124 samples of various materials collected from buildings with evident moisture damage; among them there were 11 samples (collected from the most severely damaged surfaces) contained ciliates and flagellates (34). Field studies of presence and concentrations of protozoa in indoor air, as well as health aspects of these microorganisms in given conditions are still lacking, with the exception of one *in vitro* study conducted by the same authors, who suggested that amoebae act synergistically with certain bacteria, enhancing their cytotoxic and pro-inflammatory potential (25).

4. CONCLUSION

Nowadays indoor air problems can even surpass those caused by outdoor pollution. For instance mold contamination in buildings has recently been one of the main issues regarding the environmental problems.

Epidemiological, clinical and toxicological evidence suggest that microbiological contamination of indoor air may be related to numerous diseases and health conditions. Damp and humid environment are obligatory factors for growth, development and multiplication of microbes, hence, the main public health goal should be targeting these problems. Considering the variety of microorganisms, possible synergistic effects, the fact that the most endangered populations are children, women, elderly (who spent relatively substantial time indoors), disadvantages of determination techniques and lack of evidence-based risk assessment, it should be concluded that further investigations are needed.

The most effective way to manage microbial contaminants, such as mold, that are the result of damp indoor environments is to eliminate or limit the conditions that foster its establishment and growth by respecting some building recommendations. When microbial contamination is found, it should be eliminated by means that not only limit the possibility of recurrence but also limit exposure of occupants and persons conducting the remediation.

Therefore the good indoor air quality is important in order to avoid adverse health outcomes.

5. ACNOWLEDGEMENTS

This work was funded by the Grant of the Ministry of Education, Science and Technological Development of Republic of Serbia, as a part of Projects III42008: “Evaluation of Energy Performances and Indoor Environment Quality of Educational Buildings in Serbia with Impact to Health”

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7.11 ASSOCIATION BETWEEN FINE PARTICULATE MATTER AND EXACERBATIONS OF ADULT ASTHMA AND COPD IN PATIENTS LIVING IN SMEDEREVO, SERBIA

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ABSTRACT

Smederevo is one of the most polluted towns in Serbia because of a steel factory, fossil fuel or coal combusting heating system and traffic pollution. The aim of study was to investigate the association between air pollution (PM_{10} and $PM_{2.5}$) and exacerbation episodes among adult COPD and asthma patients.

Number of days with high levels of $PM_{2.5}$ was statistically significantly associated with number of both moderate and severe exacerbation episodes among asthma and COPD female patients. There was statistically significant association between $PM_{2.5}$ and number of exacerbations in next subgroups with moderate asthmatic exacerbations: all nonsmokers, no smoking obese patients, all females, obese females, and no smoking females. A significant association between the number of days with excess of PM_{10} and the number of moderate exacerbation episodes patient of asthma is shown only in subgroup consisted of obese, nonsmoking patients.

1. INTRODUCTION

Recent studies have shown that in general, particulate matter is responsible for adverse health effects, but it is still unclear which fraction has the highest risk on public health.[9] Urban pollution is also associated with increase of emergency visits and hospital admissions due to respiratory diseases like asthma and chronic obstructive pulmonary disease (COPD). Impact of smoking and air pollution on COPD seems to overlap in the group of adult patients.[10] The importance of these factors, beside smoking status, should also be considered in terms of age, gender, and nutritional status of exposed population.[8] Smederevo is one of the most polluted towns in Serbia because of the steel factory functioning in this town, majority of individual households with fossil fuel or coal combusting heating system and traffic pollution by aged vehicles. High levels of PM_{10} and $PM_{2.5}$ have been measured there over the past six years.

The aim of this study was to investigate whether average monthly levels of air pollutants including number of days per month with high levels of PM_{10} and $PM_{2.5}$ and certain meteorological conditions during 2011 were associated with increased number of exacerbation episodes per month among adult COPD and asthma patients.

2. METHODOLOGY

The study was conducted in secondary care general hospital in Smederevo covering approximately 81 000 inhabitants living in the area of 7 km around automatic station for air quality monitoring. Data of meteorological conditions (average daily values of air pressure, temperature and wind speed) and air pollutants (average daily values of PM_{10} and $PM_{2.5}$) were obtained from Serbian Environmental Protection Agency. This verified data were collected from the automatic station for air quality monitoring (Grimm analyser, all analyses on 2 m height) located in Radinac near the steel factory in Smederevo. Number of days with air pollutants limit level excess was identified. Data on patients with COPD and asthma were obtained from medical records. The source of study population consisted of patients registered and followed up as asthma suffering (n=955) and COPD patients (n=625). The patients younger than 18 years were excluded from the study, as well as patients from villages around Smederevo located more than 7km from automatic station for air quality monitoring. Descriptive statistical parameters of air characteristics are given in Table 1.

Study was designed to identify adult patients with moderate and severe exacerbations of COPD and asthma during 2011 which required additional therapy in Pulmology Emergency room (oral or parenteral corticosteroid preparation 2-12 days) or admittance to hospital, and to investigate correlation between number of these exacerbations per month and average monthly levels of air pollutants and meteorological conditions, or number of days per month with excess of air pollutants limit level.

The total number of patients with obstructive respiratory disease exacerbations was 420 (318 with moderate, and 102 with severe exacerbations), with mean patients age of 60,2 years, and subgroups of COPD n=201 (123 with moderate and 78 with severe exacerbations) with mean patients age of 66,0 years, and Asthma n=219 (195 with moderate and 24 with severe exacerbations), with mean patients age of 54,8 years.

The total number of exacerbations were n=570, COPD n=300, and Asthma n=270. Number of exacerbations during 2011 per patients were 1-6 (moderate), and 1-4 (severe) (Table 2).

Table 1. Descriptive statistical parameters of air characteristics

	STATISTICAL PARAMETERS							
VARIABLES	**Min**	**max**	**Mean**	**sd**	**cv %**	**SE_{χ}**	**med**	**IR**
Meteorological conditions (mean/month)								
Δ Temperature [˚C]	0.09	23.57	12.05	9.29	77.10	2.68	12.17	19.31
Δ Air pressure[mbar]	999.07	1014.80	1006.42	4.32	0.43	1.25	1005.61	6.24
Δ Wind speed [m/s]	1.20	2.21	1.62	0.27	16.67	0.08	1.57	0.37
Air pollutants (mean/month)								
Δ PM_{10} [µg/m3]	46.55	170.13	85.21	35.10	41.19	10.13	78.72	51.48
Δ $PM_{2.5}$µg/m3]	21.07	130.77	56.33	36.13	64.14	10.43	45.70	62.58
Number of days with exceedance of daily level (per month)								
$PREKPM_{10}$ [days/month]	9.00	31.00	21.25	6.47	30.45	1.87	22.00	9.25
$PREKPM_{2.5}$[days/month]	1.00	31.00	15.75	11.78	74.79	3.40	15.00	23.25

Legend: Δ Temperature- average monthly air temperature, **Δ Air pressure**- average monthly air pressure, **Δ Wind speed** – average monthly wind speed, **Δ SO_2** - average monthly SO_2, **Δ NO_2**- average monthly NO_2, **Δ PM_{10}**- average monthly PM_{10}, **Δ $PM_{2.5}$**- average monthly PM $_{2.5}$, **$PREKPM_{10}$**- number of days per month with excess of PM $_{10}$ 24h-limit value(50µg/l*), **$PREKPM_{2.5}$**- number of days per month with excess of PM $_{2.5}$ 24h-limit value (35 µg /l*).

* According to Serbian Law of air protection **, Serbia only has goal annual limit level of $PM_{2.5}$ until 2020., so in this study U.S. 24 hrs limit value for $PM_{2.5}$ in 2011. is taken – available at www.epa.gov/air/criteria.html

Table 2. Descriptive statistical parameters of patients characteristics

Groups of patients with exacerbation episodes (per month)	STATISTICAL PARAMETERS							
	n	**min**	**max**	**mean**	**sd**	**cv %**	**SE_{χ}**	**Med**	**IR**
A	570	19.00	63.00	47.17	12.28	26.03	3.54	51.50	14.50
Aa	300	8.00	36.00	24.67	7.71	31.25	2.23	26.00	9.25
Ab	270	11.00	33.00	22.50	5.71	25.38	1.65	22.00	6.75
B	442	9.00	55.00	36.50	12.41	34.00	3.58	38.10	14.00
Ba	267	4.00	35.00	21.92	8.21	37.45	2.37	24.00	7.25
Bb	175	5.00	21.00	14.58	5.30	36.35	1.53	14.50	10.00
C	128	4.00	16.00	10.67	3.58	33.55	1.03	10.00	5.25
Ca	33	1.00	5.00	2.75	1.48	53.82	0.43	2.50	2.75
Cb	95	3.00	12.00	7.92	2.75	34.72	0.79	7.00	5.00

Legend: A– asthma and COPD patients with moderate and severe exacerbations, **Aa**– asthma patients with moderate and severe exacerbations, **Ab**– COPD patients with moderate and severe exacerbations, **B** - asthma and COPD patients with moderate exacerbations, **Ba**- asthma patients with moderate exacerbations, **Bb**- COPD patients with moderate exacerbations, **C**- asthma and COPD patients with severe exacerbations, **Ca**- asthma patients with severe exacerbations, **Cb** – COPD patients with severe exacerbations.

For moderate exacerbations, correlation with air pollutants and meteorological factors was separately investigated for next subgroups and their combinations: by diagnosis, by gender, by smoking status and by body-mass index status. Patients which were analysed by diagnoses and gender were also observed through other two categories in different combinations (for example, obese male smokers suffering of COPD). Diagnosis of Asthma or COPD were confirmed by pulmologist according to ICD-10, for asthma as defined by Global Initiative for Asthma[3], and for COPD as defined by Global Initiative for Chronic Obstructive Lung Disease (GOLD)[4] based on clinical symptoms and standard spirometric examination (adequate spirometric post bronchodilators answer). Patients with asthma who developed COPD according previous criteria before beginning of year 2011, were considered as COPD patients. Literature data considering smoking status indicated that ex-smokers were not significantly different from non-smokers respecting most of asthma outcomes.[2] According to this, correlation of air pollution and meteorological conditions with number of moderate exacerbations was considered with two subgroups of asthma patients regarding smoking status: one consists of smokers and one consists of taken together never-smokers and ex-smokers. On the other side smoking cessation in adult COPD patients results in improving in lung function, and it is even shown that quitting for ten years or more prior to engagement in study reverses the excess risk of COPD mortality to a level similar to that observed among never-smokers in men.[11] According to this, correlation of air pollutants and meteorological conditions with number of moderate exacerbations was considered with three subgroups of COPD patients regarding smoking status: one consists of active smokers, the other consists of taken together active smokers and ex-smokers who quit smoking for less than 10 years and the last group consists of taken together never-smokers and ex-smokers who quit smoking for more than 10 years. Different studies have shown increasing evidence relating body-mass index to the prevalence and incidence of asthma in both children and adults.[12] By the body-mass index status, two subgroups of patients were analyzed: patients with BMI up to 24,9, and obese patients with BMI above 25,0. For patients with severe exacerbation who were admitted to hospital, the correlation between air pollution or meteorological factors and number of severe exacerbations was separately investigated for next subgroups: by diagnosis and by gender. Mixed groups of patients with both moderate or severe exacerbations of COPD or/and asthma have been analysed only for diagnosis and gender based subgroups.

Statistical method

Distributions of patients age in male and female group were tested with Kolmogorov-Smirnoff Zed test in order to check its normality. Independent samples Student- T test was used then to test the significance of difference between age of male and female patients groups in this study. Chi square test with Yates correction was used to test the significance of difference between frequencies of exacerbations by gender, as well as between frequencies of exacerbations by diagnosis. Same test was used to examine the difference between frequencies of moderate and severe exacerbation episodes. All variables were then tested with Kolmogorov-Smirnoff Zed test in order to check the normality of distribution. The correlation between average monthly values of meteorological factors, or PM levels, or number of days per month with excess of daily limit value for PM, and monthly number of exacerbations of asthma and COPD in groups and subgroups of patients was tested with parametric and non-parametric Pearsons bivariate correlation test in program SPSS (Statistical Package for the Social Sciences) software (version 10, SPSS Inc. Chicago, IL) with the complex sample module. A significance level of $p<0.05$ was considered statistically significant based on two-tailed tests.

3. **RESULTS AND DISCUSSION**

Total number of patients with moderate and severe exacerbations of COPD and asthma in Smederevo during 2011 was 420 out of 1580 observed previously diagnosed patients, which live in observed area around automatic air quality station. In group of male patients: n= 209, average age was 61,2 and in group of female patients n= 211, average age was 59,1. According to KSZ test, distribution of years within gender groups of patients was normal (for males: p=0,292; p>0,05, for females: p=0,163; p>0,05). There was no significant difference between age of male and female group: t=1,443; df=418; p=0,161; p>0,05. Comparing frequencies of patients with exacerbations by gender, no significant difference was found between groups: f_{male}=209; f_{female}=211; χ^2_Y =0,010; df=1; p=0,922; p>0,05. There was no significant difference in frequencies of exacerbation between diagnosis:f_{asthma}=300; f_{COPD}=270; χ^2_Y=1,579; df=1; p=0,209; p>0,05. Concerning severity of exacerbations among all exacerbations, the number of moderate exacerbations was significantly higher than severe exacerbations: $f_{moderate}$=442; f_{severe}=128; χ^2_Y =172,975; df=1; p=0,000; p<0,01. Concerning frequencies of exacerbations at the same time in two categories (severity: moderate/severe, and diagnosis: asthma/COPD), we have found statisticly significant difference: $f_{moderate\ asthma}$=267; $f_{moderate\ COPD}$=175; $f_{severe\ asthma}$=33; $f_{severe\ COPD}$= 95; χ^2_Y=46,355; df=1; p=0,000; p<0,01. In both groups of patients, with asthma and with COPD, there were more moderate than severe episodes of exacerbations. Also, the number of moderate exacerbations was higher in group of patients with asthma than in group COPD patients. On the other side, the number of severe exacerbations was higher in the group of COPD patients comparing to the group with asthma patients. Analyzing frequencies of both types of exacerbation in males and females, and by the diagnosis, we have found a significant difference: $f_{asthma\ male}$=97; $f_{asthma\ female}$=203; $f_{COPD\ male}$ =181; $f_{COPD\ female}$= 89; χ^2_Y=67,117; df=1; p=0,000; p<0,01. The number of asthma exacerbations was higherr in the group of female patients, and the number of COPD exacerbations was higher in the group of male patients. Considering all patients, with moderate and severe episodes of both COPD and Asthma, the significant association (p=0,048) is shown only between monthly number of days with excess of PM $_{2.5}$ limit level and number of exacerbations in female patients. In subgroups made by the diagnosis, border significant association (p=0,05) is shown between monthly number of days with excess of $PM_{2.5}$ limit level and monthly number of moderate and severe exacerbation episodes of all patients with asthma. Further subgroup analysis shows that this association become stronger in the following subgroups of patients with moderate episodes of asthma exacerbations: among all female patients: p=0,020, among non-smokers: p=0,029 (female non-smokers: p=0,028), among obese female: p=0,011, and the most significant among obese, non-smokers: p=0,010. Among all obese asthmatic patients with moderate exacerbations, association with monthly number of days with excess of $PM_{2.5}$ limit level is tested with non parametric test. It is close but doesn't reach statistical significance p=0,055.The significant association between monthly number of days with excess of PM_{10} limit level and monthly number of moderate exacerbation episodes patients with asthma is shown only in the subgroup consisted of obese, non smoking patients p=0,044. Association between high levels of PM_{10} and monthly number of exacerbations was also close but with no statistical significance among all patients with both types of asthma exacerbations: p=0,053, and among females asthmatic with moderate exacerbations: p=0,054. The results are shown in Table 3.

Table 3. Single correlation between number of diseases exacerbations per month and air characteristics

Variables	Patients with exacerbations	Statistical parameters			
		r	p	ρ	p
$PREKPM_{2.5}$	Af	0.581	**0.048**	0.474	0.120
	Aa	0.576	0.050	0.482	0.112
	Aaf	0.657	**0.020**	0.672	0.017
	J45f	0.631	**0.028**	0.656	0.021
	J45n	0.628	**0.029**	0.519	0.083
	J45nf	0.630	**0.028**	0.531	0.076
	J45o	0.677	0.015	0.566	0.055
	J45on	0.708	**0.010**	0.639	0.025
	J45of	0.700	**0.011**	0.662	0.019
$PREKPM_{10}$	Aa	0.570	0.053	0.641	0.025
	Aaf	0.568	0.054	0.718	0.009
	J45on	0.589	**0.044**	0.661	0.019
Δ Temperature	Aaf	-0.577	0.050	-0.676	0.016
	J45f	-0.576	0.050	-0.628	0.029
	J45on	-0.601	**0.039**	-0.541	0.069
	J45of	-0.645	**0.024**	-0.636	0.026
Δ Air pressure	J44sf	0.580	**0.048**	0.407	0.189

Legend: $PREKPM_{10}$- number of days with excess of PM_{10} 24h-limit value (50µg/l), **$PREKPM_{2.5}$**- number of days with excess of $PM_{2.5}$ 24h-limit value (35µg/l), **Δ Temperature** - average monthly air temperature, **Δ Air pressure**- average monthly air pressure, **Af**- asthma and COPD female patients with moderate and severe exacerbations, **Aa**– asthma patients with moderate and severe exacerbations, **Aaf**- asthma female patients with moderate and severe exacerbations, **J45f**- asthma female patients with moderate exacerbations, **J45n**- asthma ex-smokers and never-smokers with moderate exacerbations, **J45nf**- asthma ex-smokers and never smokers female patients with moderate exacerbations, **J45o**- asthma obese patients with moderate exacerbations, **J45on**- asthma obese ex- and never-smokers patients with moderate exacerbations, **J45of**- asthma obese female patients with moderate exacerbations, **J44sf**- COPD smokers and for less than 10y ex-smokers female patients with moderate exacerbations

Considering group of meteorological conditions, average temperature is in negative significant association with number of moderate exacerbation in next subgroups of asthma patients: females (border association: p=0,050), obese females (p=0,024), obese, non smoking patients (p=0,039). There is also border significant negative association between total number of moderate and severe exacerbations of asthma in female patients and average monthly temperature (p= 0,050) (Figure 1).

For patients with asthma, exacerbations and poor control can be the result of exposure to environmental triggers, such as allergens and air particulates.[14] Approximately 25% of COPD exacerbations are likely due to non-infectious causes, so air pollution could be one of the main non-infectious triggers of COPD exacerbations[7]. Air pollution particles cause oxidative stress and inflamatory response in respiratory tract even in healthy individuals[5], so it could be the mechanism of exacerbation in obstructive respiratory disease patients. Because PM_{10} and $PM_{2.5}$ are generaly a heterogenous mixtures of particle types, both types of particulate matter are with significant association with asthma exacerbation, but also important determinant of their adverse health risk is their composition, which is various in different parts of the world.

In this study, female asthmatic patients were more prone to air pollution than males, potentially because of smaller lungs related to body size. The mechanisms underlying the relationship between obesity and asthma have not been fully established, but adipose tissue-derived hormones have certain role in pathogenesis and control of asthma[13]. Other studies[1] have shown that BMI is a strong predictor of incident asthma among adult women, and in our study reported that obese subgroup was more sensitive to air pollution of high $PM_{2.5}$ levels than other subgroups.

Association with high levels of $PM_{2.5}$ is proven also in the subgroup of elderly non-smoking asthma patients. It seems that non-smokers are more prone to particulate air pollution, which is opposite to most of done studies. In Smederevo, the number of days with exceedance of PM_{10} limit level is associated with number of exacerbation episodes only in the group of obese, non-smokers asthmatics. Like in other studies[15], ambient temperature is negatively associated with number of asthma exacerbation.

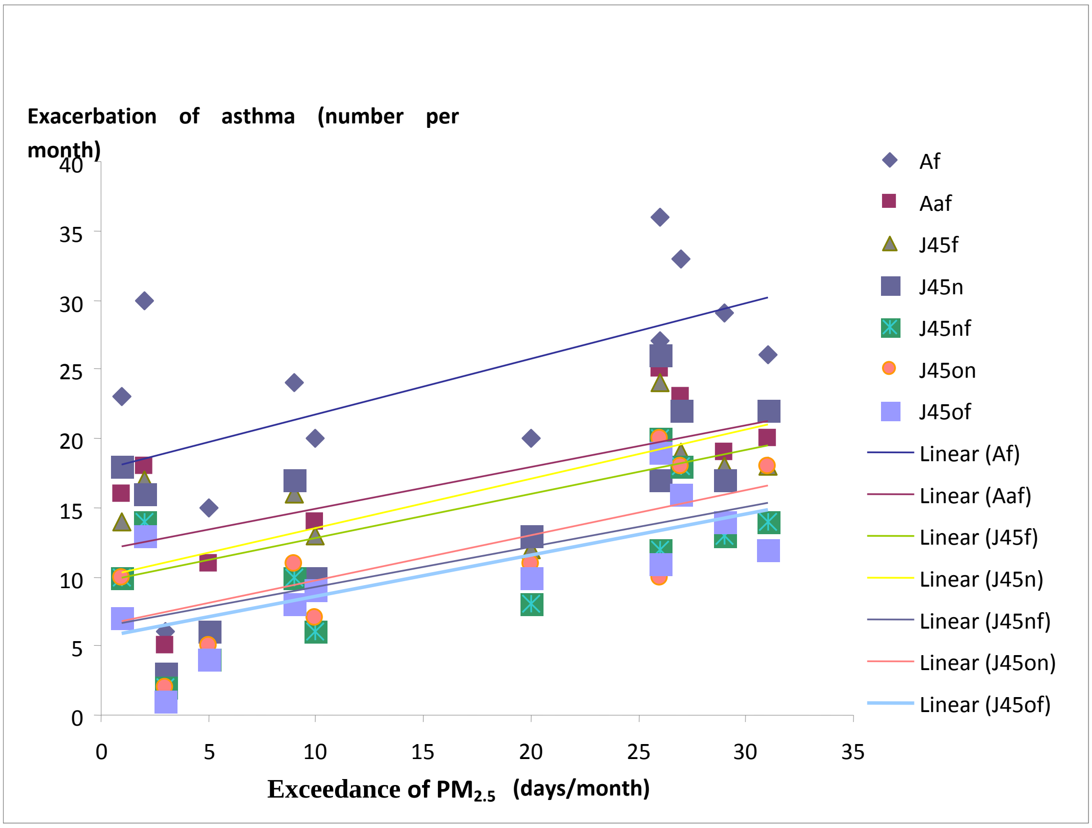

Figure 1. Correlation between number of days with PM 2.5 exceedance and number of sthma exacerbations per month

Legend: **Af**- asthma and COPD female patients with moderate and severe exacerbations, **Aaf**- asthma female patients with moderate and severe exacerbations, **J45f**- asthma female patients with moderate exacerbations, **J45n**- asthma ex-smokers and never-smokers with moderate exacerbations, **J45nf**- asthma ex-smokers and never smokers female patients with moderate exacerbations, **J45on**- asthma obese ex-smokers and never-smokers patients with moderate exacerbations, **J45of**- asthma obese female patients with moderate exacerbations.

Number of COPD exacerbations is associated with average air pressure which is hypothesis generating, and is not proven in other settings. Potential confounders which could also be a cause of exacerbation, but were not considered in this study are influence of infections and use of antibiotics, quantity of smoking, patients drug compliance and family history of asthma or/and COPD. Relatively small number of exacerbations, especially in single subgroups directed us to design the study of comparing monthly numbers of exacerbations, and monthly levels of air pollutants as well as meteorological conditions. Revealed association leads us to further “fine tuning” in study design, in order to assess range of the objective latency and exact quantity of particulate matter excess which cause exacerbations of asthma within certain subgroups of patients. Also, the fact that the non-smokers asthmatics in this study are more prone to high levels of air pollutants than smokers, requests further elaboration. The composition of particulate matters PM_{10} and $PM_{2.5}$ should also be explored in order to explain dominant influence of $PM_{2.5}$ on asthma exacerbations in Smederevo.

4. CONCLUSION

Our results indicate that in Smederevo, particle exposure, mainly $PM_{2.5}$, and low temperature may trigger asthma exacerbations requiring emergency care. Reducing exposures, especially among certain groups of asthmatic patients, may secure certain health benefits.

5. AKNOWLEDGEMENTS

This paper was produced under projects III41028 - INGEMAS funded by Ministry of Education, Science and Technological Development of Serbia (January 2011-December 2014).

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APPENDIX A

AUTHOR INDEX

Author name	Institution	Paper (s)	Page(s)
Andersen Z.J.	*The Faculty of Health Sciences, University of Copenhagen,* ***Denmark***	7.4	200
Aničić Urošević M.	*Institute of Physics, University of Belgrade,* ***Serbia***	6.4; 6.7	171; 185
Antanasijević D.	*Faculty of Technology and Metallurgy, University of Belgrade,* ***Serbia***	6.7	185
Apostolovski -Trujić T.	*Mining and Metallurgy Institute, Bor,* ***Serbia***	4.9	121
Arandjelović M.	*School of medicine University of Niš, Serbia*	7.8	218
Arbutina D.	*Nuclear Facilities of Serbia,* ***Serbia***	3.5	69
Bartonova A.	*NILU – Norwegian Institute for Air Research,* ***Norway***	5.1; 2.3; 5.3; 5.4	122; 33; 132; 137
Belegante L.	*National Institute of Research and Development for Optoelectronics,* ***Romania***	3.2	52
Bengalli R.	*Research Centre Polaris, University of Milano, Italy*	6.6	180
Binkova B.	*Institute of Experimental Medicine,* ***Czech Republic***	6.1	151
Bottle S.	*Queensland University of Technology, Brisbane,* ***Australia***	2.1; 2.2; 5.5	23; 29; 141
Bouso L.	*CREAL-Center for Research in Environmental Epidemiology,* ***Spain***	7.7	217
Brown R.	*Queensland University of Technology, Brisbane,* ***Australia***	2.1; 2.2	23; 29
Camatini M.	*Research Centre Polaris, University of Milano, Italy*	6.2; 6.6	159; 180
Capasso L.	*Research Centre Polaris, University of Milano,* ***Italy***	6.2	159
Carrasco G.	*CREAL-Center for Research in Environmental Epidemiology,* ***Spain***	7.7	217
Castell N.	*NILU – Norwegian Institute for Air Research,* ***Norway***	3.1;5.1	45;122
Chen Y.X.	*East China University of Science and Technology, Shanghai,* ***China***	4.4	97
Cirach M.	*CREAL-Center for Research in Environmental Epidemiology,* ***Spain***	5.4	137
Cole-Hunter T.	*CREAL-Center for Research in Environmental Epidemiology,* ***Spain***	5.4; 2.5	137; 44
Cvetković A.	*Public Health Institute of Belgrade,* ***Serbia***	2.3; 4.1; 4.3	33; 78; 91
D'Anna A.	*Dept of Chemical Engeneering, University Federico II,* ***Italy***	6.2	159
De Nazelle A.	*CREAL-Center for Research in Environmental*	7.7	217

	Epidemiology, ***Spain***		
Deljanin I.	*Faculty of Technology and Metallurgy, University of Belgrade,* ***Serbia***	6.7	185
Denby B.R.	*NILU – Norwegian Institute for Air Research,* ***Norway***	3.1	45
Dimović S.	*Vinca Institute of Nuclear Sciences, University of Belgrade,* ***Serbia***	3.5	69
Djonović N.	*Institute of Public Health of Kragujevac,* ***Serbia***	4.2	82
Djurić Z.	*Institute of Chemistry, Technology and Metallurgy, University of Belgrade,* ***Serbia***	5.6	147
Djurković S.	*Institute for Plant Protection and Environment, Serbia*	6.5	176
Djordević A.	*Faculty of Occupational Safety Niš, University of Niš,* ***Serbia***	4.7; 7.6	113; 209
Dragicević V.	*Maize Research Institute,* ***Serbia***	6.5	176
Drajić D.	*DunavNET DOO, Serbia*	5.3	132
Dramlić D.	*Institute of Physics, University of Belgrade,* ***Serbia***	3.5	69
Dramlić S.	*Institute of Physics, University of Belgrade*	3.5	69
Drinić G.	*Maize Research Institute,* ***Serbia***	6.5	176
Fernandez A.	*Sensing & Control,* ***Spain***	5.4	137
Frantlovic M.	*Institute of Chemistry, Technology and Metallurgy, University of Belgrade,* ***Serbia***	5.6	147
González Ortiz A.	*EEA-European Environment Agency,* ***Denmark***	3.1	45
Gršić Z.	*Nuclear Facilities of Serbia, Serbia*	3.5	69
Gržetić I.	*Faculty of Chemistry, University of Belgrade,* ***Serbia***	4.3	91
Gualtieri M.	*Research Centre Polaris, University of Milano,* ***Italy***	6.2; 6.6	159; 180
Guerra S.	*CREAL-Center for Research in Environmental Epidemiology,* ***Spain***	7.7	217
Guerreiro C.	*NILU – Norwegian Institute for Air Research,* ***Norway***	3.1	45
Hedayat F.	*Queensland University of Technology, Brisbane,* ***Australia***	5.5	141
Heroux M.-E.	*WHO, European Centre for Environment and Health,* ***Germany***	7.1	189
Jerrett M.	*University of California, Berkeley, USA*	5.2	127
Jevtić M.	*Institute of Public Health of AP Vojvodina,* ***Serbia***	4.2	82

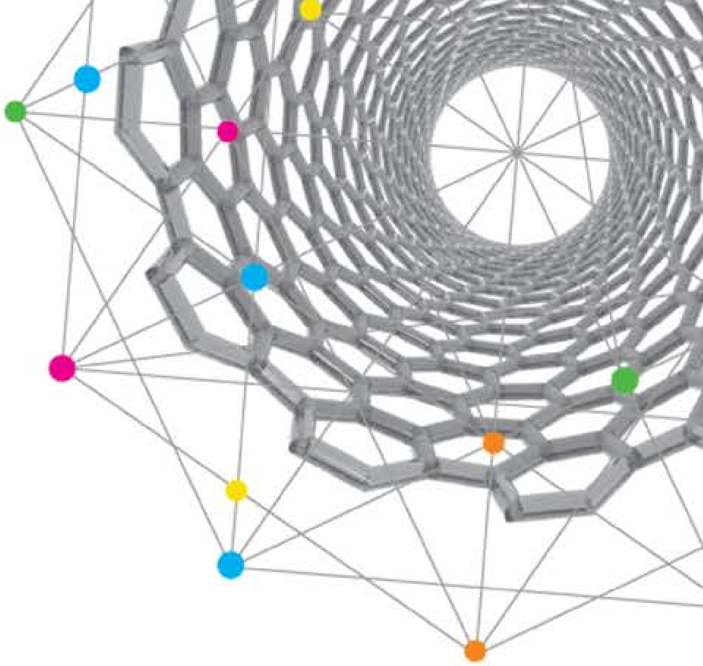
Jokić I.	*Institute of Chemistry, Technology and Metallurgy, University of Belgrade,* ***Serbia***	5.6	147
Jovašević-Stojanović M.	*Vinca Institute of Nuclear Sciences, University of Belgrade,* ***Serbia***	2.3; 2.5; 4.1; 4.3; 4.6; 4.7; 5.3; 7.9; 7.10; 7.11	33; 44; 78; 91; 109; 113; 222; 132; 226; 232
Jović B.	*Serbian Environmental Protection Agency, Belgrade,* ***Serbia***	1.3	19
Jović-Stošić J.	*National Poison Control Centre, Military Medical Academy,* ***Serbia***	7.9; 7.11	222; 232
Kaljević J.	*Vinca Institute of Nuclear Sciences, University of Belgrade,* ***Serbia***	3.5	69
Kovačević R.	*Mining and Metallurgy Institute, Bor,* ***Serbia***	2.5; 4.7; 4.8; 4.9	44; 113; 117; 121
Kubesch A.	*CREAL-Center for Research in Environmental Epidemiology,* ***Spain***	7.7	217
Kuzmanoski M.	*Institute of Physics, University of Belgrade,* ***Serbia***	3.2; 6.4; 7.5	52; 171; 205
Lahoz W.A.	*NILU – Norwegian Institute for Air Research,* ***Norway***	5.1; 3.3	122; 60
Lazović I.	*Vinca Institute of Nuclear Sciences, University of Belgrade,* ***Serbia***	4.3; 4.6	91; 109
Liu H.-Y.	*NILU – Norwegian Institute for Air Research,* ***Norway***	5.1	122
Longhin E.	*Research Centre Polaris, University of Milano,* ***Italy***	6.2; 6.6	159; 180
Maluckov B.	*Mining and Metallurgy Institute, Bor,* ***Serbia***	4.8	117
Manojlović D.	*Faculty of Chemistry, University of Belgrade,* ***Serbia***	2.5	44
Mantecca P.	*Research Centre Polaris, University of Milano,* ***Italy***	6.2	159
Marjanović M.	*University of Defence, Belgrade,* ***Serbia***	7.10	226
Marković D.A.	*Faculty for Applied Ecology "Futura",* ***Serbia***	2.3	33
Martinez D.	*CREAL-Center for Research in Environmental Epidemiology,* ***Spain***	7.7	217
Masri A.	*Queensland University of Technology, Brisbane,* ***Australia***	2.2	29
Matić B.	*Institute of Public Health of Serbia,* ***Serbia***	4.2	82
Matić-Besarabić S.	*Public Health Institute of Belgrade,* ***Serbia***	2.3; 4.1	33; 78
Mihajlović E.	*Faculty of Occupational Safety Niš, University of Niš,* ***Serbia***	7.6	209
Mijailović I.	*Faculty of Occupational Safety Niš, University of Niš,* ***Serbia***	7.6	209

Mijić Z.	*Institute of Physics, University of Belgrade,* ***Serbia***	2.4; 3.1; 3.4	39; 52; 64
Milcova A.	*Institute of Experimental Medicine,* ***Czech Republic***	6.1	151
Milinčić M.	*Faculty of Geography, University of Belgrade,* ***Serbia***	3.5	69
Milivojević D.	*Institute for the Application of Nuclear Energy,* ***Serbia***	6.5	176
Miljevic B.	*Queensland University of Technology, Brisbane,* ***Australia***	2.1; 5.5	23; 141
Milošević L.	*Faculty of Occupational Safety Niš, University of Niš,* ***Serbia***	7.6	209
Nicolau D.	*National Institute of Research and Development for Optoelectronics,* ***Romania***	3.2	52
Nieuwenhuijsen M.	*CREAL-Center for Research in Environmental Epidemiology, Spain*	5.4; 7.3; 7.7	137; 199; 217
Nikezić D.	*Vinca Institute of Nuclear Sciences, University of Belgrade,* ***Serbia***	3.5	69
Nikolić B.	*Institute for Plant Protection and Environment,* ***Serbia***	6.5	176
Nikolić M.	*(1)School of medicine University of Niš, (2) Public Health Institute Niš,* ***Serbia***	7.2; 7.8	195; 218
Paunović E.	*WHO, European Centre for Environment and Health,* ***Germany***	7.1	189
Pavlović S.	*Nuclear Facilities of Serbia,* ***Serbia***	3.5	69
Pergal M.	*Faculty of Chemistry,University of Belgrade,* ***Serbia***	6.4	171
Perić-Grujić A.	*Faculty of Technology and Metallurgy, University of Belgrade,* ***Serbia***	6.7	185
Perišić M.	*Institute of Physics, University of Belgrade,* ***Serbia***	2.4; 3.4; 7.5	39; 64; 205
Pham P.	*Queensland University of Technology, Brisbane,* ***Australia***	2.2	29
Pokrić B.	*DunavNET DOO, Serbia*	5.3	132
Popović A.	*Faculty of Chemistry, University of Belgrade,* ***Serbia***	6.4	171
Popović T.	*Serbian Environmental Protection Agency, Belgrade,* ***Serbia***	1.3	19
Pourkhesalian A.	*Queensland University of Technology, Brisbane,* ***Australia***	2.2	29
Radaković S.	*University of Defence, Belgrade,* ***Serbia***	7.10	226
Radulović K.	*Institute of Technical*	5.6	147

	Sciences SASA, SANU, ***Serbia***		
Rahman M.	*Queensland University of Technology, Brisbane,* ***Australia***	2.2	29
Rajšić S.	*Institute of Physics, University of Belgrade,* ***Serbia***	2.4; 3.4	39; 64
Rakić U.	*Institute of Public Health of Serbia,* ***Serbia***	4.2	82
Reicherd T.	*EFCA and Fraunhofer ICT,, Pfinztal, Germany*	1.2	14
Reid C.	*University of California, Berkeley,* ***USA***	5.2	127
Ristanović E.	*University of Defence, Belgrade,* ***Serbia***	7.10	226
Ristić M.	*Faculty of Technology and Metallurgy, University of Belgrade,* ***Serbia***	6.7	185
Ristovski Z.D.	*Queensland University of Technology, Brisbane,* ***Australia***	2.1; 2.2; 5.3; 5.5	23; 29; 132; 141
Rossner P.	*Institute of Experimental Medicine,* ***Czech Republic***	6.1	151
Rossnerova A.	*Institute of Experimental Medicine,* ***Czech Republic***	6.1	151
Schmuczerova J.	*Institute of Experimental Medicine,* ***Czech Republic***	6.1	151
Sekulić Z.	*Public Health Institute of Belgrade,* ***Serbia***	6.7	185
Sivertsen B.	*NILU – Norwegian Institute for Air Research,* ***Norway***	1.1	7
Solansky I.	*Institute of Experimental Medicine, Czech Republic*	6.1; 6.3	151; 165
Sram R.J.	*Institute of Experimental Medicine,* ***Czech Republic***	6.1; 6.3	151; 165
Stanković A.	*(1)School of medicine University of Niš, (2) Public Health Institute Niš,* ***Serbia***	7.2; 7.8	195; 218
Stevanović I.	*General Hospital Smederevo,* ***Serbia***	7.9; 7.11	222; 232
Stevanovic S.	*Queensland University of Technology, Brisbane,* ***Australia***	2.1; 2.2; 5.5	23; 29; 141
Stevanović M.Ž.	*Vinca Institute of Nuclear Sciences, University of Belgrade,* ***Serbia***	4.3	91
Stevanović Ž .Ž.	*Vinca Institute of Nuclear Sciences, University of Belgrade,* ***Serbia***	3.4; 4.6	64; 109
Stojić A.	*Institute of Physics, University of Belgrade,* ***Serbia***	2.4	39
Surawski N.	*CSIRO Ecosystem Sciences, Acton ACT,* ***Australia***	2.1	23
Svecova V.	*Institute of Experimental Medicine, Czech Republic*	6.1; 6.3	151; 165
Šoštarić A.	*Public Health Institute of Belgrade,* ***Serbia***	2.4; 7.5	39; 205
Tasić M.	*Institute of Physics, University of Belgrade,* ***Serbia***	2.4	39
Tasić V.	*Mining and Metallurgy*	2.5; 4.3; 4.6; 4.7; 4.8;	44; 91; 109; 113; 117;

	*Institute Bor, **Serbia***	4.9	121
Todorović M.	*Institute of Physics, University of Belgrade, **Serbia***	7.5	205
Tomašević M.	*Institute of Physics, University of **Belgrade***	6.4; 6.7	171; 185
Topalović D.	*Vinca Institute of Nuclear Sciences, University of Belgrade, **Serbia***	5.3	132
Topinka J.	*Institute of Experimental Medicine, **Czech Republic***	6.1; 6.3	151; 165
Tošović S.	*Public Health Institute of Belgrade, **Serbia***	4.1	78
Turco E.	*Sensing & Control, **Spain***	5.4	137
van Ham, J.	*EFCA, Burg., Delfgauw, **The Netherlands***	1.2	14
Vuković G.	*Institute of Physics, University of Belgrade, **Serbia***	6.4	171
Vuković Mirković B.	*Medical Faculty of Niš, **Serbia***	7.2	195
Waisi H.	*Institute for hydrology “Jaroslav Černi, **Serbia***	6.5	176
Wang H.	*School of Aerospace, Mechanical and Mechatronic Engineering, The University of Sydney, **Australia***	2.2	29
Wang L.	*East China University of Science and Technology, Shanghai, **China***	4.4	97
Westerdahl D.	*CREAL-Center for Research in Environmental Epidemiology, **Spain***	7.7	217
Williams M.	*CRIC, Catalonian Research and Innovation Centre, **Spain***	5.4	137
Xiu G.	*East China University of Science and Technology, Shanghai, **China***	4.4; 4.5	97; 102
Xu F.	*State Administration for Cultural Heritage, Shanghai Museum,**China***	4.4	97
Wu L.	*East China University of Science and Technology, Shanghai, China*	4.4	97
Zhan T.	*East China University of Science and Technology, Shanghai, **China***	4.4; 4.5	97; 102
Zhang D.	*East China University of Science and Technology, Shanghai, **China***	4.4; 4.5	97; 102
Zhang P.	*East China University of Science and Technology, Shanghai, **China***	4.4	97
Zhu M.	*East China University of Science and Technology, Shanghai, **China***	4.5	102
Zou J.	*East China University of Science and Technology, Shanghai, **China***	4.5	102

Živković M.	*Vinca Institute of Nuclear Sciences, University of Belgrade,* ***Serbia***	4.3; 4.6; 4.7	91; 109; 113
Živković N.	*Faculty of Occupational Safety Niš, University of Niš,* ***Serbia***	4.7; 7.6	113; 209



CIP - Каталогизација у публикацији
Народна библиотека Србије, Београд

502.3:502.175(082)
613.15(082)
66.071.9(082)

INTERNATIONAL WeBIOPATR Workshop Particulate
Matter: Research and Management (4 ; 2013 ;
Beograd)
Proceedings from the 4th WeBIOPATR
Workshop & Conference Particulate Matter:
Research and Management, WeBIOPATR2013,
Belgrade, Serbia, 2.-4.10.2013. / Milena
Jovašević-Stojanović and Alena Bartoňová,
eds. - Belgrade : Public Health Institute,
2013 (Beograd : Gradski zavod za javno
zdravlje). - 247 str. : ilustr. ; 30 cm

Tiraž 200. - Str. 2: Preface / Milena
Jovašević-Stojanović and Alena Bartoňová. -
Bibliografija uz svaki rad. - Registar.

ISBN 978-86-83069-40-8
1. Jovašević-Stojanović, Milena [уредник]
[аутор додатног текста] 2. Conference
Particulate Matter: Research and Management
(2013 ; Beograd)
a) Ваздух - Контрола квалитета - Зборници
b) Здравље - Заштита - Зборници c)
Отпадни гасови - Штетно дејство - Зборници
COBISS.SR-ID 204064780

ISBN 868306940-0
9 788683 069408 >

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