OR 37/2009

Particulate Matter: Research and Management

Proceedings from the 2nd WeBIOPATR Workshop, Mokra Gora, Serbia 31.8.-2.9.2009

Alena Bartonova and Milena Jovašević-Stojanović, eds.

Norsk institutt for luftforskning
Norwegian Institute for Air Research
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Preface

The WeBIOPATR project aims to provide evidence and assess characteristic of particulate matter (PM) at local and regional level, and in different urban environments. This information is important for air quality management aiming to reduce risks to human health. Public outreach and scientific dissemination are important activities.

Two scientific workshops with international participation were organized during the project. The first workshop was held in Belgrade, May 20-22, 2007, supported by the project grant, from the Ministry of Science and Technological Development of the Republic of Serbia and other organisations. Book of Extended Abstracts (M.Jovašević-Stojanović and A.Bartonova, ISBN 978-86-7306-086-6) is available from the organizers or from the web site http://www.vinca.rs/webiopatr/index.php.

This report compiles workshop materials from the 2nd workshop, organized in Mecavnik, Serbia, 31.8.-2.9.2009, with support from the project grant and from the Ministry of Science and Technological Development.

The workshop sessions covered research and management issues including:

- Framework for integrated environmental health impact assessment and air quality management
- Fundamentals of particulate matter composition, formation and atmospheric transport
- Evidence of health effects and methods for their assessment
- Evidence of levels of ambient air pollutants
- Methods for indirect PM assessment, including atmospheric transport modelling and modelling of source contributions using source apportionment
- Principles of monitoring for compliance and prospective and retrospective assessment.

The workshop audience included experts from 8 countries. In addition, representatives of the Ministry of Health, Ministry of Science and Technological Development, and a guest from the WHO ECEH Serbia were present.

The main conclusions of the workshop confirmed, that in Serbia, the expertise necessary for research and management of particulate matter is available in Institutes of Public Health, the Hydrometeorological Institute and other research institutes. The knowledge basis is increased since the first workshop. For regulatory purposes, both environmental and health monitoring needs to take increasingly into account the needs of modern air quality management. Integrative research projects, combining environmental and health expertise, are able to provide such support, and should be supported, if possible, in collaboration between the different authorities and granting agencies across sectors. In order to

further strengthen the knowledge base, national, as well as international collaboration should be promoted.

The WeBIOPATR project, “Outdoor concentration, size distribution and composition of respirable particles in WB urban areas” (2006- 2009) was executed in collaboration between the Vinča Institute of Nuclear Sciences, Belgrade Serbia, the Institute of Public Health of Belgrade, Serbia and NILU - Norwegian Institute for Air Research. It was funded by the Research Council of Norway through Norwegian Cooperation Programme on Research and Higher Education with countries in the Western Balkans, http://siu.no/en/programoversikt/vest_balkan_2006_2009.

Contents

1 Introduction

1.1 Outdoor concentration, size distribution and composition of respirable particles in WB urban area - the WeBIOPATR project

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Background

Research projects that investigate heath effects of particulate matter (PM) from anthropogenic and natural sources are performed in European countries but are not common in West Balkan countries. Differences in climate, long range transport, type of domestic heating, quality of petrol and other factors related to human activities influence the formation and physical and chemical properties of PM in outdoor and indoor environment. The WeBIOPATR project aims to provide evidence and assess characteristic of PM at local and regional level, and in different urban environments. This information is important for air quality management aiming to reduce risks to human health.

Objectives

1. To provide the Serbian partners with monitoring capabilities for physical and chemical characterisation of fractionated particulate matter using European reference sampler with varying inlets as a sampling device
2. To generate data about particle mass in different size fractions, about chemical composition of particulate matter (selected heavy metals, Benzo-a-Pyrene, organic and elemental carbon content, up to two selected source tracers such as levoglucosan for wood burning), and to attempt source apportionment based on these data
3. To support training of a PhD student in Serbia, and to disseminate relevant information both to scientific community in Serbia and to the authorities through two workshops.

Activities

The project aims were translated to the following activities:

- To establish monitoring methods in one site, to establish procedures for 3gravimetric measurements of PM in three size fractions, for PM_{10}, $PM_{2.5}$ according to relevant international standards (EN, EPA), and for PM_1 (no standard available)
- To organize field campaigns for collection of PM_{10}, $PM_{2.5}$, PM_1 and meteorological data at one site participating in the municipal monitoring network in Beograd
- To perform physical and chemical characterisation of the collected particulate matter, and to identify and quantify sources contributing to the particulate matter concentrations
- To support training of MSc and PhD students and Doctoral theses in Serbia, and to organize two international workshops for the scientific community and

to the authorities in Serbia, with the aim of promoting dialogue and dissemination of up-to-date information about PM research and management.

Experimental results

After consultations and field visit, an urban residential background site in New Belgrade, Omladinskih Brigada Street, was chosen as the field site for the project. This site is located about 50 meters from the nearest throughway, about 300 m from the river, in flat terrain, without any major point source in the immediate vicinity (the heating plant "New Belgrade", 0,5 km, is the nearest point source). The field site was located on the roof of the building, while the routine monitoring site of Belgrade network is situated at the ground level.

Gravimetric analyses of the collected particulate matter were done in the newly established facility at the GZZZ, a clean weighing laboratory complying with European standards. This is the first facility established in Serbia of its kind. Chemical analyses were partly done at the GZZZ, with field visits of the Norwegian experts, and partly at NILU (tracer analyses for biomass burning).

Quality assurance and quality control procedures were very important part of work in all activities of the project, from field work to chemical analyses to database establishment and data analyses.

In the first phase of the project, the aerosol samples were collected in four seasonal campaigns conducted in autumn: Nov 13-Dec 03, 2007, winter: Feb 07-28, 2008, spring: May 06-28, 2008 and summer: July 17- August 15, 2008. The results show that PM_{10} values in Belgrade were high in autumn and winter (heating season), with a number of samples exceeding the limit value of 50 $\mu g/m^3$. During spring campaign number of exceeded values was three out of 22 and all values during summer campaign were below 50 $\mu g/m^3$.

PM_{10} values at all sites of the municipal network followed the same trend. The highest concentrations at all monitoring sites were during periods: Nov 20-Nov 25, 2007 and Feb 19-Feb 23, 2008.

A very first source apportionment analysis of data obtained from the Belgrade urban area was performed on the data set resulting from the first phase of the project. A total of 42 samples collected during autumn and winter were sampled to reflect the heating season, whereas 49 samples collected in spring and summer were sampled to reflect the non-heating season. The monitoring program was optimized according to current knowledge about possible sources of aerosols.

The multivariate receptor model Unmix was used to analyze PM_{10} ambient aerosol data set. The number of analyzed species were 31/32 during winter/summer period. The analysis generated source profiles for five source categories, i.e. biomass burning, soil/crustal, secondary aerosols, gasoline and diesel. The project provided the first demonstration of an Unmix analysis for the Belgrade urban area, showing seasonal variation in source contributions. Biomass burning was found to be the dominant source (52%) in winter, whereas soil/crustal (28%) and secondary aerosols (27%) dominated in summer. Further,

the relative diesel and gasoline contribution was higher during summer (25%) compared to winter (10%). This work was the basis of one Doctoral thesis, that has been successfully defended.

In the second phase of the project, a second PhD candidate joined, and was able to expand the spectrum of chemical analyses for 16 polycyclic aromatic hydrocarbons (PAHs) that are: Naphtalen, Acenapthylen, Acenaften, Fluoren, Fenantren, Antracen, Fluoranten, Pyren. Benzo(a)antracen, Kryzen, Benzo(b)fluoranten, Benzo(k)fluoranten, Benzo(a)pyren**,** Indeno(1,2,3-cd) pyren, Dibenzo(ah)antracen, Benzo(ghi)perilen. PAH are analysed from PM_{10} and PM_1 fraction. In order to verify the findings, and especially to further investigate the contribution of biomass burning that is expected to be low outside the heating season, four additional measurement campaigns were performed and the list of species to quantify was expanded. It is expected that results of complete analyses of campaing V-VIII will give further inforamation of and bring more clarity to the source composition and contribution. The campaigns V to VIII were performed between February 2009 and December 2009.

PAHs are formed during incomplete combustion or pyrolysis of organic material and in connection with the use of oil, gas, coal and wood in energy production, vehicle exhaust, industrial generations, aluminium production, cement manufacture, production coal tar, coke and asphalt, and petroleum catalytic cracking. PAHs are a mixture, rather than a single compound, and benzo(a)pyrene (BaP) may be adopted as a marker for the overall PAH mixture. BaP is the PAH most widely studied, abundance of information on toxicity and occurrence of PAHs is related to this compound. As the BaP is the most toxic, the risk from cancer for humans related to PAHs is expressed as BaP equivalent. Preliminary calculations show that in much higher in heating than in non heating season. BaP in PM_{10} in heating season about 4 times higher in PM_{10} and 2.5 times higher in PM_1 in heating season than in non heating season. Air samples for analysis of BaP in PM_{10} were collected at 13 monitoring sites within municipal air quality monitoring network in 2008, and 16 sites in the period 2004-2007. In the period of 2004-2008, annual averages were over the limit value of 1.0 ng/m^3 . Data analysis shows the same annual patterns as seen elsewhere, with higher concentrations at almost all measuring sites during the heating season.

Results from these campaigns are being analyzed. The data set is unique both due to the geographic location (the area of Western Balkan lacks this kind of data), due to its extent (number of chemical species and completeness of the data, including meteorological information and data from routine monitoring), but also due to the fact that the quality control and quality assurance routines were extensively implemented, and documented. Each result is accompanied with an estimate of its uncertainty, which enables the use of advanced state-of-the-art statistical methods, but also provides increased means of interpretability.

Dissemination

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

issues. In Serbia, the research community is scattered, and the management activities are only starting. To support the Serbian actors, the project has performed two international workshops.

The 1st WeBIOPATR workshop "Particulate matter: Research and Management" was held in Beograd, 20.-22. May 2007. The workshop was attended by more than 70 participants, has attracted 35 contributions, and received also media attention (newspaper article and TV coverage on national "Radiotelevision of Serbia", July 2007). It was noted, that in addition to providing information about latest research in Serbia and internationally, the workshop has contributed to the communication within the research community in Serbia, and between the research community and the responsible authorities (Ministry of Health, Ministry of Environment, Serbian Environmental Agency).

The 2nd WeBIOPATR workshop "Particulate matter: Research and Management" was held in Mecavnik, Serbia, 28.August -1.September 2009. It has attracted over 40 participants, notably also participants from the neighbouring countries. The participants presented research results and discussed air quality issues, research needs and management tools and strategies. 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.

Scientific dissemination from the project consists of one published article in a Journal of Serbian Chemical Society (impact factor 0,611 in 2008), over 20 contributions to the workshops, two books of abstracts from the workshops, special number of CI&CEQ with about 10 papers present at the 2nd workshop and three major articles planned for international peer-review journals. These articles will be finalized in the course of 2010.

Conclusions

The project aims were fully met. The scope of the project was extended, having taken the opportunity to recruit an additional PhD student partly supported nationally, and being able to increase the number of monitoring campaigns due to additional funds from the RCN. GZZZ performed much more analyses then is was planned at the beginning of project. The project has generated important new data, has led to an upgrade of monitoring capabilities of the urban monitoring network in Belgrade, and has contributed to scientific education and dissemination to research and expert public. Nationally, the project is followed up by research activities within the PhD thesis of the 2nd candidate, and through ongoing project (TR21009, 2008-2010, project leaded M. Jovasevic-Stojanovic) funded by Ministry of Science and Technological Development. Further, the research team is in dialogue with the authorities about transfer of knowledge from the team to support national monitoring capabilities, stakeholder interactions and compliance with European legislation that has been adopted into Serbian legislation.

The project has provided new evidence and has strengthened the ability of the Serbian actors to participate in International research activities.

1.2 The Importance of PM monitoring for Estimating Related Health Impacts in the Republic of Serbia as a support to evidence based decision making

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Introduction

The accuracy of air quality data and their representativeness in space and time are important for the quality of the assessments produced from the data. For health impact assessment, this is of the utmost importance. Monitoring networks design should be done in a way to inform decision-makers and the public in a sufficient way. For PM usually, mass concentration, shown as $\mu g/m^3$, is reported and regulated with standards. We should be, at a policy maker level, aware of the fact that the toxicity of particles is related not only to their size but also to their physical and chemical properties, including their number, shape, composition and reactivity.

Characterization of inhaled particles, their deposition and clearance in the respiratory tract and the ammount reached the upper and lower airway and the alveoli, toxicity studies and last but not the least, epidemiological studies.are needed. As the evidence grew, in some countries standards shifted to regulate smaller particles, because they cause greater negative impacts on human health and now the scientific debate is whether PM_1 should be measured as well.

More than two thirds of $PM_{2.5}$ mass is contributed to anthropogenic sources and major source categories include the combustion of fossil fuels, biomass burning (residential wood burning, wildfires and other biomass burning and ammonia emissions from agricultural operations.

Rationale

Average monthly fuel consumption in Serbia is about 80 litres per vehicle. Some 59% of respondents in the Belgrade area travel more than 5,000 kilometres a year, with 32% of respondents travelling more than 10,000 a year. On average, people living in urban regions drive 33% more a year than in rural areas.

Up to 70% of marketed fuel does not meet the requirements prescribed by national standards (which are harmonized with EU standards). Neither the standard for lead and benzene content of unleaded gasoline nor the standard for sulphur and aromatic compounds for diesel fuel is being met. Phasing out lead from gasoline would reduce lead emissions in the air to less than $0.2\mu g/m^3$.

Almost all children (97.4%) from 13 to 15 years of age are exposed to second hand tobacco smoke in their homes.
Exposure to heavy metals in some industrially polluted areas (Pb, Hg, Cd, As etc.) is present. More than half of all households and 75% among the poor use fossil fuel and biomass heating/ cooking devices.

Electric Power Industry of Serbia production is based on lignite. Their emissions of PM are during past several years significantly cut due to technological improvements. Total estimated costs for Serbia's emissions of 60 000t of PM_{10} per year, are between 70.4 and 127.5 millions EUR.

In Serbia, typical attitude of the population (but also of the policy makers, polluters, NGOs) is that compliance with air quality standards implies that little or no risk is being posed to health. This, for sure is not the case for some pollutants, and significant risks have been demonstrated even below standard levels.

Conclusion

There is an urgent need for improvement of databases for health impact assessment of PM, focused on children as the most vulnerable group. On the same level, there is a need of monitoring data improvement.

1.3 Application of Full Chain Approach to Outdoor Air Pollution: the HEIMTSA project

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The Health and Environment Integrated Methodology and Toolbox for Scenario Assessment (HEIMTSA[1]) project is developing tools and methods for evaluating the environmental health effect of policies at the EU level. The "Outdoor Case Study" looks at perhaps the most studied and assessed group of pollutants, with the most strongly established methodologies. The aim is to implement recent methods developments. The common methodology applied in HEIMTSA is based on a "full chain approach". In the "Outdoor case study", the impact pathway is relatively simple, and a substantial body of evidence has been established during the last 20 years.

There are important political and methodological reasons for revisiting the issues. Politically, the requirements for future revisions of the legislation recognize the large health impacts on the one hand and the potentially large expenses for pollution abatement on the other. New evidence has been accepted regarding effects of long term exposures. Methodologically, the multi-sector nature of measures affecting air quality is increasingly recognized, as well as issues related to population and sub-population exposures to air pollutants, and the issues of multi-stressors exposures. Advances have been achieved in several other areas including atmospheric dispersion modeling, life-tables based analysis of epidemiological evidence, and methods for monetary valuation. The idea of "uncertainty analysis" has progressed from intentions to application stage.

HEIMTSA starts with an assessment for particulate matter (considering the different origins of PM where possible), ozone, nitrogen oxides, sulphur dioxide and carbon monoxide. First, we will improve the conventional approach with risk estimates linking ambient concentrations to various health endpoints in several ways. The environmental models to be incorporated will strive to combine the results of a finer resolution models with regional concentration fields. To assess mortality impacts, we are using the life-table approach for predictions, and combining the predictions with monetary valuation estimates based on own data collection. Throughout the "full chain", we are implementing methods for uncertainty analysis and assessment, which will lead to methods for an uncertainty assessment globally, for the "full chain" as a whole.

We will assess both concentrations and exposures to the pollutants in different geographic areas and population groups. For exposure assessment, we are developing a grid-specific Exposure Scaling Factor that takes into account exposures for age-, gender- ad employment status-specific subpopulations. An "exposure" is a result of a combination of environmental, behavioral and individual factors, and we draw on large European surveys of population time activity data, and on the advances in environmental modeling. For the first time ever, we will describe some of the direct effects policies may have on exposure-related behavior. We are considering whether and how these developments can be carried through to assessment of health impacts, based on exposure-response rather than on concentration-response function.

[1] supported by the 7th FRP for Research and Development of the EU, contract GOCE-CT-2006-036913-2.

2 Sources and source apportionment of particulate matter

2.1 An investigation of high summertime ozone levels in Istanbul using MM5/CMAQ Modeling System

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Ozone and its precursor are being measured at different monitoring stations located at urban, semi-urban and rural points in Istanbul since July 2007 under the COST-728 project. High ozone levels were observed during the summer of 2008, particularly in June and July at these locations. Istanbul is a megacity with a population well over 13 million. Local industry, traffic and transport from the Izmit Bay may all be leading to those ozone episodes. As previous research showed, Istanbul can also be affected by long-range transport of air pollutants from Europe.

An air quality modeling framework was set up in order to better understand the meteorological and chemical conditions leading to those high ozone days. The models consist of the non-hydrostatic meteorological model MM5 version 3.7.0 and the Community Multiscale Air Quality (CMAQ) model version 4.6. The modeling domain covers Europe with 50 km x 50 km grids in the horizontal and 23 levels in the vertical. The physical options used in the MM5 simulations are the mix phase moisture scheme, Kain-Fritsch 2 cumulus scheme, MRF scheme for PBL parameterization, and RRTM scheme for radiation. Emissions for the modeling domain were obtained from EMEP. Codes were written in Matlab to process the emissions and create hourly, speciated and vertically distributed emissions for input to CMAQ. Biogenic emissions were estimated using a methodology, which employs the land cover data from USGS and Photochemically Active Radiation (PAR) values that are calculated from the outputs of the MM5 simulation. A finer grid domain was also placed over Istanbul and its surroundings with a horizontal grid resolution of 2 km. A local emissions inventory was developed for this domain including residential heating, industrial combustion, shipping and biogenic emissions. Traffic and point source emissions were obtained from other sources. The new inventory provides more detailed information on local emissions and reduces the uncertainties in the EMEP inventory. Also, the temporal profiles and chemical speciations used represent the actual conditions in İstanbul much better.

This paper will present the modeling results for both the coarse and finer grid domains and will include comparisons to monitoring data and an evaluation of model performance. The intercomparisons of the results from the two modeling grids provide important information on the reasons for elevated ozone levels in İstanbul. The sensitivity of the pollutant levels to different emission sources are also tested by applying reductions to emissions.

2.2 Source apportionment of the carbonaceous aerosol –Quantitative estimates based on ^{14}C- and organic tracer analysis

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The World Health Organization (WHO) points towards combustion derived primary particles when ascribing the negative health effects that ambient particles have on human health. These particles consist mainly of carbonaceous material. Large uncertainties are associated with the contribution from natural sources to the ambient carbonaceous aerosol concentration.

Until recently, there has been no way of separating carbonaceous combustion particles from particles from other sources in the ambient air. By combined effort of thermal optical, ^{14}C-, and organic tracer analysis this is now possible. Statistical analysis using Latin Hypercube Sampling (LHS) allows to apportion the ambient aerosol carbonaceous material to a total of seven different sources, i.e., elemental carbon from combustion of biomass (EC_{bb}) and fossil fuel (EC_{ff}), organic carbon from combustion of biomass (OC_{bb}) and fossil fuel (OC_{ff}), primary biogenics (OC_{pb}), secondary organic aerosols from anthropogenic (ASOA) and biogenic (BSOA) precursors. The approach makes it possible to separate not only primary versus secondary aerosols, but also to separate between natural and anthropogenic sources. This information is necessary for abatement strategies for reducing man-made emissions of combustion derived primary particles.

The carbonaceous aerosol originating from the above mentioned seven sources has been examined with respect to size fraction (PM_{10} and PM_1), time of the day and season for one rural background site (Hurdal) and one urban background site (Oslo) in Norway. The results show that combustion derived primary particles (EC_{bb}, EC_{ff}, OC_{bb}, OC_{ff}) accounted for 45% of the carbonaceous material in PM_{10} in Oslo in summer, 46% of the carbonaceous material came from natural sources (OC_{pb}, BSOA). For PM_1, combustion derived primary particles accounted for 47% of the carbonaceous material, whereas 36% originated from natural sources. The major source of combustion derived primary particles in Oslo in summer was combustion of fossil fuel, constituting approximately 25-30% of the total carbonaceous content followed by combustion of biomass (16-21%). In winter, combustion derived primary particles constituted 81% of the carbonaceous material in the ambient aerosol in Oslo, of which 48% could be attributed to biomass burning and 33% to combustion of fossil fuel. Natural sources was the major contributor to the total carbonaceous material in PM_{10} (72%) and PM_1 (66%) at the rural site in summer, whereas it was negligible in winter (< 8%).

One of the important conclusions from this study is that the population in Oslo could be subject to severe exposure with respect to combustion derived primary particles in winter. The finding that approximately 50% of the ambient aerosol carbonaceous material in Oslo in summer originates from natural sources is crucial knowledge when attempting to sort out abatement strategies for the urban PM level.

2.3 Source Apportionment of Belgrade PM_{10} Aerosols with the Unmix Receptor Model

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ABSTRACT
The multivariate receptor model Unmix has been used to analyse a PM_{10} ambient aerosol data set collected at an urban residential background site in New Belgrade in Omladinskih Brigada Street. The aerosol samples were collected within four seasonal campaigns. Samples from autumn and winter campaigns (heating periods) are analysed as a winter period and samples from spring and summer campaigns as a summer period (non-heating periods). The preliminary analysis generated source profiles for five sources categories: biomass burning, soil/crustal, secondary aerosols, gasoline and diesel. This paper provides the first demonstrations of the Unmix analysis for the Belgrade urban area showing seasonal variations in source composition. Biomass burning is indicated as the dominant source (52%) during the winter period and soil/crustal is dominant source (28%) together with secondary aerosols (27%) during the summer. Moreover, diesel and gasoline contribution was higher during the summer (25%) than during the winter period (10%).

1. INTRODUCTION
Receptor modelling is the application of multivariate statistical methods to address the identification and quantitative apportionment of air pollutants to their sources.[4] Several years ago different models including principal component analysis and absolute principal component scores[2], edge analysis,[1,8] chemical mass balance[5] and positive matrix factorization[3] have been applied to identify and to establish the sources' contributions. Multivariate receptor models are based on the analysis of the correlation between measured concentrations of chemical species assuming that highly correlated compounds come from the same source[9]. The objective of this paper is to perform a very first, preliminary source apportionment analysis of database obtained from the Belgrade urban area during four seasonal campaigns. PM_{10} ambient aerosol data set collected at urban residential background site in New Belgrade in Omladinskih Brigada Street. The aerosol samples were collected within four seasonal campaigns. A total of 42 samples from autumn and winter campaigns (heating periods) are analysed as a winter period and a total of 49 samples from spring and summer campaigns as a summer period (non-heating periods). Recently, the comprehensive study on PM_{10}, $PM_{2.5}$ and PM_1 in aerosols of urban Belgrade area have started in the frame of the WeBIOPATR project.[6]. The results obtained should define sources the for PM_{10} aerosol fraction during winter/summer season.

2. METHODOLOGY
The study was performed in the Omladinskih Brigada Street, the fast-developing New Belgrade area of the Serbian capital city (44°49'7" N, 20°28'5" E, 116 A) during four periods Nov 13-Dec 03, 2007, winter: Feb 07-28, 2008, spring: May 06-28, 2008 and summer: July 17- August 15, 2008 by using a European

reference low-volume sampler (Sven/Leckel LVS3) provided with inlets to collect particulate matter onto 47 mm Whatman QM-A double-sided quartz fibre filters. Samples were collected on a daily basis (24 hours, beginning at 7.a.m.).[5]

The concentrations of 9 elements: Al, Ba, Ca, Fe, K, Mg, Na, Ti, Zn were determined by ICP-OES while the concentrations of 12 elements As, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se and V were determined by ICP-MS.[11] Quality control and verification of applied procedures for microwave digestion and multi-elemental trace analysis by ICP MS was done using 2783 NIST (National Institute of Standard and Technology, MD, USA) standard reference material containing $PM_{2.5}$ fraction of urban dust from the mixed industrial urban area of Vienna, collected on the polycarbonate membrane filter. The following ions were analysed by standard ion chromatography: NO_3^-, SO_4^{2-}, NH_4^+, K^+, Ca^{2+} and Na^+.[5]

Thermal optical analysis (TOT) was used to quantify the sample content of elemental (EC) and organic carbon (OC). After that OC is divided into OC_1, OC_2, OC_3, OC_4 and OP in order to ensure better Unmix source apportionment analysis. Levoglucosan[12] were quantified using high performance liquid chromatography/high-resolution mass spectrometry (HPLC/HRMS).
Unmix version 6.0 used for source apportionment analysis in this study is available at EPA site (http://www.epa.gov/heasd/products/unmix/unmix.htm). A value equal to one half the analytical detection limit was used in source apportionment modelling for species with concentrations below the detection limit. Data base for Unmix analysis consists of following species: PM_{10} gravimetric mass, levoglucosan, mannosan, galactosan, EC, OC, TC, OC_1, OC_2, OC_3, OC_4, OP, NO_3^-, SO_4^{2-}, NH_4^+, Na^+, K^+, Ca^{2+}, Al, Ba, Ca, Fe, K, Mg, Na, Ti, Zn, As, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se and V. A total of 42 samples from autumn and winter campaigns (heating periods) are analysed as a winter period and a total of 49 samples from spring and summer campaigns as a summer period (non-heating periods). The number of analysed species were 31/32 during winter/summer period. Outlier test and species exclusion were not possible because of the small number of samples. More than 50% of the values for Mo, Mg and Co were below the detection limit and those species were excluded from analysis. The model was set to consider PM_{10} as the total mass.

3. RESULTS AND DISCUSSION

Winter period

After analysing the winter period (42 samples), the most satisfactory result of applying Unmix to the present data base was a five-source solution, using 31 species (PM_{10}, levoglucosan, mannosan, galactosan, EC, OC_1, OC_2, OC_3, OC_4, OP, NO_3^-, SO_4^{2-}, NH_4^+, Na^+, K^+, Ca^{2+}, Al, Ba, Fe, Ti, Zn, As, Cd, Cr, Cu, Mn, Ni, Pb, Sb, Se and V). The following species: K, Na and Ca were discarded because they are already present as ionic species and they cannot be included twice. OC also makes sum of OC_1, OC_2, OC_3, OC_4 and OP and TC sum of EC and TC. Species such as Mo, Mg and Co were below the detection limit and were discarded by the model. Numerical values for the solution's diagnostic indicators were according to the requirements of this model ($r^2 > 0.80$ and signal/noise >

2.0). The minimum correlation coefficient (r^2) was 0.87 with a minimum signal to noise ratio of 2.13.

Source 3 was identified as a crustal/soil (36%). Crustal/soil was the most easily identified source because it is characterized by the typical crustal elements such as Al, Ba, Ti, K, Ca, Mn and Fe. Crustal elements Al and Ti and also Mn and Fe that have maximal abundances in this source are very well correlated. More than a half of the ambient concentration of Ca, Ba and Zn are attributed to the crustal/soil source.[7]

Source 1 that shows high EC, OC_1- OC_4 and strong Zn and Mn represents gasoline source (5%).[8] In this source OC dominates EC. Pb has maximal abundance in this source as expected. Fe is also significant species in the gasoline profile.[10] Figure 2 shows the difference between diesel and gasoline carbon thermal fractions during winter sampling period.

Source 4 (5%) with significant EC emissions which is comparable with OC in contrast to the previous source in which OC dominated is identified as a diesel source. OP in this source is significantly higher than in gasoline source. The diesel profile shows lower Fe and Mn abundance than the gasoline profile. The presence of Ca, a soil related element, in diesel profile could be mainly due to the mixture of soil during transportation.

The profile of secondary aerosols (2%) is represents by Source 2. with highest abundances SO_4^{2-} (65%) and significant ion species NH_4^+, NO_3^- and crustal species Na and Ca that are also quite well determined.

Source 5 (52%) is also well and easy defined profile with strong cellulose burning tracers levoglucosan, mannosan, galactosan and EC, OC_1-OC_4, OP, NO_3^-, SO_4^{2-}, NH_4^+ and K^+ species. The evidence which identified this source with wood and cellulose burning is 61% of water soluble potassium (K_w) and the fact that emissions of OC dominate emission of EC.[7,10] This source could also be named as a coal combustion with secondary aerosol source because of presence of Se (concentrations are higher than during the summer period) and SO_4^{2-}.[10]

Summer period

After analysing the summer period (49 samples), the most satisfactory result of applying Unmix to the present data base was a five-source solution, using 31 species (PM_{10}, levoglucosan, mannosan, galactosan, EC, OC_1, OC_2, OC_3, OC_4, OP, NO_3^-, SO_4^{2-}, NH_4^+, Na^+, K^+, Ca^{2+}, Al, Ba, Fe, Ti, Zn, As, Cd, Cr, Cu, Mn, Ni, Pb, Sb, Se and V). The following species: K, Na and Ca were discarded because they are already present as an ions species ad they cannot be included twice. OC also makes sum of OC_1, OC_2, OC_3, OC_4 and OP and TC sum of EC and TC. Species such as Mo, Mg and Co were below detection limit and were discarded by the model according to suggest exclusion. Numerical values for the solution's diagnostic indicators were according to the requirements of this model ($r^2 > 0.80$ and signal/noise > 2.0). The minimum correlation coefficient (r^2) was 0.82 with a minimum signal to noise ratio of 2.53.

Source 3 in this analysis was identified as a crustal/soil (28%). Crustal/soil was an easily identified source because it is characterized by the typical crustal elements such as Al, Ti, Ca, Mn and Fe. Crustal elements Al, Ti, Mn and Fe, similar to the winter period have maximal abundances in this source and they are very well correlated. Ca has main contribution in crustal/soil source[7]. The other strong and significant species contributing in this source are As, Ni, Pb, Cu and V.

Source 5 with strong Al, Cu, Mn and Zn[9] represents gasoline source (11%). The other present species are EC, OC_1- OC_4, and SO_4^{2-}. In this source OC dominate EC. Figure 4 shows difference between diesel and gasoline carbon thermal fractions during winter sampling period. It could be noticed presence of Ca mainly due to the mixture of soil during transportation.

Source 2 (14%) with strong OC_2, OC_3 and EC emissions represents diesel sources. EC is comparable with OC in contrast to the previous source in which OC dominated. OP in this source is higher than in gasoline source. Presence of Ca (also present in gasoline profile), is consequence of soil during transportation.

Source 1 is identified as a secondary aerosols profile (27%) with strong levoglucosan, mannosan, galactosan, Na^+, K^+, SO_4^{2-} and significant ion species NO_3^-. Secondary aerosols profile has a high concentration of SO_4^{2-} in summer period and shows strong seasonal variations.

Source 4 (20%) is also well and easy defined profile with strong wood and cellulose burning tracers levoglucosan, mannosan, galactosan and EC, OC_1, OC_2, OP, SO_4^{2-}, NH_4^+ and Se species. Other significant species in this profile are K^+, Cu and Pb. The evidence for identified this source with wood and cellulose burning is presence of water soluble potassium (K_w) and the fact that emissions of OC dominate emission of EC[7,10].

Comparison between winter and summer periods

Table 3 shows the comparison between distribution of sources for winter (heating) and summer (non-heating) periods.

Table 3. Comparison between distribution of sources for winter and summer periods

	Biomass burning	Secondary aerosols	Diesel	Gasoline	Soil/Crustal
Winter	52 %	2%	5%	5%	36%
Summer	20%	27%	14%	11%	28%

The results obtained show differences between source distributions during winter and summer seasons. While biomass burning is the dominant source during the winter period (52%), soil/crustal is the dominant source (28%) together with sec. aerosols (27%) during the summer.

Secondly, the sum of diesel and gasoline (traffic source) is higher during the summer (25%) than during the winter period (10%). There are also differences in EC/OC pattern during those two periods.

The main difference is concerned with the secondary aerosol source which is more dominant during the dry summer period because the atmosphere is more efficient in producing secondary SO_4^{2-} from the emitted SO_2 in the summer.

4. CONCLUSIONS

PM_{10} chemical composition data collected at an urban background sampling site in Belgrade were studied using the Unmix method to infer the possible emission sources. Five common sources: biomass burning, soil/crustal, secondary aerosols, diesel and gasoline have been resolved during two periods (winter and summer) showing significant seasonal variation. It is concluded that Unmix was an effective method of identifying possible emission sources out of ambient concentration data. The Unmix model is a useful source apportionment tool but it also has some level of complexity that requires caution, experience and cooperation to be sure that the identified source solution is the best one. With the limited number of aerosol samples (42 samples during winter period and 49 samples during summer period) taken into consideration, the results presented are just indicative. Use of some more advanced receptor modelling methods such as PMF analysis would improve resolution of possible emission sources.

5. ACKNOWLEDGEMENTS

This research was conducted within the WeBIOPATR project (2006-2009) funded by the Research Council of Norway through the Programme of Research and High Education of Norway and Western Balkan Countries.

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3 Pollution trends and levels

3.1 Estimating domestic wood burning emissions in Nordic countries using ambient air observations, receptor and dispersion modelling

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The major emission source of primary $PM_{2.5}$ in Nordic countries such as Norway, Sweden and Finland is wood burning for domestic heating. In Norway alone it is estimated that 80% of $PM_{2.5}$ is emitted through this source. Though direct measurements of wood burning emissions are possible under controlled conditions, emission inventories for domestic heating are difficult to calculate. Emissions vary from stove to stove as well as wood type, wood condition and burning habits. The consumption rate of wood burning is also strongly dependent on meteorological as well as societal conditions. As a result the uncertainty in wood burning emission inventories used in dispersion modelling is considered to be quite high.

As an alternative method for estimating the emissions resulting from wood burning for domestic heating this paper makes use of ambient air measurements, chemical analysis of filter samples, receptor models, dispersion models, and simple inverse modelling methods to infer emission strengths. The methodology is applied in three Nordic cities, notably Oslo (Norway), Helsinki (Finland) and Lycksele (Sweden). In these cities daily filter samples over several months have been collected. The filter samples have been chemically analysed for a range of elemental and specific markers including OC/EC and Levoglucosan. The chemical analysis has been used as input for a range of receptor models, including UNMIX, PMF, PMF-2 and COPREM. From these calculations the source contributions at the measurement sites, with particular emphasis on wood burning, have been estimated.

Such source apportionment studies provide source contributions at the receptor site only. To relate these to emissions, dispersion models are required. The receptor modelling is compared to dispersion models, using the existing emission inventories. This comparison of the dispersion models with the receptor models indicates, for example, that in Oslo and Lycksele the dispersion models overestimate the contribution from wood burning. To further assess the differences between the receptor and dispersion modelling a simple inverse modelling technique, using multiple linear regression, is applied to the total $PM_{2.5}$ concentrations, measured at all monitoring stations, to assess the contribution of wood burning. The inverse modelling results have been found to agree with those from the receptor modelling for Oslo. Though both the receptor and inverse modelling point to an overestimation of the wood burning emissions of $PM_{2.5}$ it is not possible to assign this solely to errors in the emissions inventory as dispersion model error can be significant.

An assessment of the uncertainty in the various methods is made. Uncertainty in the dispersion modelling is found to be of a similar order to the uncertainty in the wood burning emissions inventory and so no firm conclusions concerning the quality of the emissions inventories can be made. It was found that Levoglucosan as a wood burning tracer was essential for the identification of the wood burning source. It is recommended to improve plume rise and urban canopy meteorological descriptions in the dispersion models before these models will be of sufficient quality to allow quantitative assessments of emission inventories.

3.2 Black smoke air pollution trendline in representative urban habitats in Serbia for the period 1999-2008

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Black smoke pollution monitoring is conducted in Serbia within the Network of urban sampling sites for the imission measurement, according to the Programme of Air Quality Control in Serbia. In this paper, results of black smoke measurement are presented for urban settlements with characteristic air pollution sources: Belgrade (highly urban), Kostolac (thermo-energetic complex), Smederevo (heavy industry), and Užice (unsuitable topography).

A mildly increasing trend-line of black smoke air pollution is noted in all settlements. Only in Užice mean annual values were continuously beyond immision values given by law (50μg/m^3), during most of the research period, due to settlement's location and lack of a centralized heating system.

3.3 Content of lead in relation with size of respirable particulates during seasonal campaigns in Belgrade

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This paper presents the study of lead content in respirable fraction of airborne particles in Belgrade. Samples were collected at one monitoring site in Belgrade during four seasonal campaigns at least three weeks long, from November 2007 until August 2008. Samples of particles fractions PM_{10}, $PM_{2.5}$ and PM_1 were collected over 24-hour period (morning to morning) at sampling site located at an residential urban background site in New Belgrade affected by high traffic density roads in its vicinity. The results indicate average Pb concentration in PM_1, $PM_{2.5}$ and PM_{10} of 0.018, 0.0318 and 0.043 $\mu g/m^3$ respectively. Correlation was investigated between lead concentrations and total mass concentration in respective PM fraction, and NO, NO_2 and SO_2 that have been recorded in the framework of municipal monitoring at the same sampling site. The results show that PM_{10}, $PM_{2.5}$ and PM_1 as well as content of Pb in particulate fractions were higher during heating period (autumn and winter season) than in non-heating period (spring and summer). During non-heating season lead content is equally distributed in all three fractions. Average content of lead during heating period is about four times higher in PM_1than in the larger PM fractions. Particle size fractions are categorised as <1, 1-2.5 and 2.5-10 μm aerometric diameter.

3.4 A contribution to analyses of air pollution caused by particulate matter in Bor (Serbia)

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ABSTRACT
Particulate emissions are of concern because the presence of fine ($PM_{2.5}$) and ultrafine ($PM_{0.1}$) particles assume higher risk for human health. Such particles can penetrate deeper into the respiratory organs and, at the same time, the probability for such penetration and deposition in the respiratory system is greater. Work is ongoing in Europe and the USA in order to determine exactly what component or components of the particulate matter are causing the reported effects. This paper presents results of the analyses of air pollution caused by presence of respirable particles in the Bor town area. The analyses were undertaken on data collected in 2009 and in the past few years.

1. INTRODUCTION

The Municipality of Bor is located in a mountainous and forested area in the south-eastern part of Serbia, close to the Bulgarian and Romanian borders. It has a total population of 65 000 people of which 40 000 live in the city of Bor. Main economic activity comprises mining and metal processing. The area has been a major centre for mining and processing of copper and other precious metals for almost a century. The mining activities have left a strong mark on the surrounding landscape, most strongly characterized by the huge open-cast mines. The industrial activities in Bor, in particular those by the mining and smelter complex, have resulted in substantive negative impacts on the environment in the region (air, water, and soil) as well as raising serious concerns about associated health effects of the pollution at large. The smelting process liberates sulphur as sulphur dioxide. This may be used to produce sulphuric acid, which is produced on-site in an acid plant. Not all the sulphur dioxide produced is required or consumed in the acid plant. As a consequence, a large amount of sulphur dioxide is discharged directly into the atmosphere together with toxic metals. Taking into account the location of the industrial complex and dominant wind directions, these pollutants are spread over the town of Bor and the surrounding area. The inhabitants of Bor municipality are exposed therefore to high levels of air pollution, which can pose serious risks to their health [7].

The prevailing winds were predominantly from west - northwest and therefore tend to carry pollution away from the main centres of population (the wind rose at time interval from 1998 to 2008 is also shown at Figure 1.). During rainy periods the typical east or south-east winds are of more concern. Low or zero wind conditions occur regularly (more then 50% of time). Light and variable winds are likely to cause very high localized concentrations of pollutants.

In the Mining and Metallurgy Institute Bor, Department for Chemical and Technical Control (CTC), there is a group for measuring of meteorology parameters and air quality control. The results presented in this paper cover some experimental programmes performed by CTC during 2004-2009 at 2 locations (locations 1 and 4 in Figure 1).

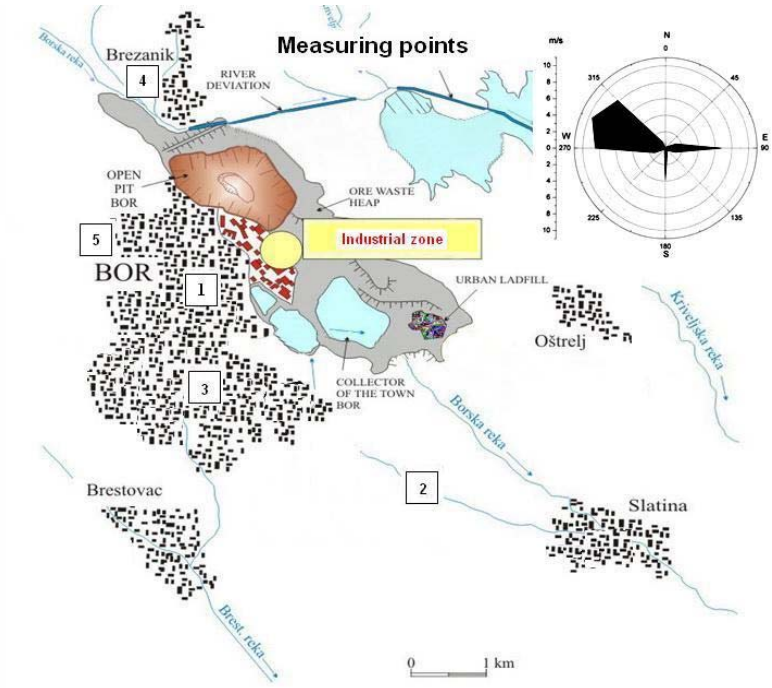

Figure 1. Map of the Bor municipality area with measuring points (1. Park, 2. Jugopetrol, 3. Institute, 4. Brezonik, 5. Hospital)

2. METHODOLOGY

The mass concentrations of SO_2 presented in this paper were monitored by means of SO_2 analyzers: AF22M [1], (location 1 during 2004-2006), HORIBA APSA-370 [4] (location 1 during 2009) and GFS-312E [3] (location 4 during 2007-2009). These instruments provide continuous and reliable measurement of sulphur dioxide in ambient air. Measurement is based on the principle of UV-fluorescence following the method specified in ISO10498. It is possible to perform automatic analysis by measuring the concentration of SO_2 in ambient air in the concentration range from 0 to 10 000 $\mu g/m^3$ using this method. The instruments are designed for long term, continuous measurement, logging and data output.

The mass concentrations of particulate matter presented in this paper were monitored by means of portable, direct reading, airborne particle sampler Osiris [2] (location 1 during 2004 - 2006) and GRIMM EDM180 [6] (location 1 during 2009). Dust monitoring was based on the optical light scattering technology where each single particle is sized and counted. This devices were designed for the simultaneous real time measurement of PM (PM_{10}, $PM_{2.5}$ and PM_1) according to European Standards EN 12341 (for PM_{10}), and EN 14907 (for $PM_{2.5}$). PM_1 values were also reported although no EN standard currently exists.

Also, the mass concentrations for PM_{10} are monitored by means of Beta-Attenuation Mass Monitor BAM1020 [5] (location 4 during 2007-2009), which is controlled by an advanced microprocessor system that makes it fully automatic.

The monitoring data used in this paper have been available originally on the basis of 15-min. averages. All other parameters have been computed from this database. For calculation of daily averages, a minimum 80% of 15-min. averages was required, otherwise the value is considered as missing. One-hour averages used for statistical considerations have been calculated from the 15-min averages. Sulphur dioxide and PM mass concentrations divided into annual, winter (October-March), and summer (April-September) averages are gathered in Table 1.

3. RESULTS AND DISCUSSION

The annual average values range form 44 to 227 $\mu g/m^3$ for SO_2, 32.7 to 45.7 $\mu g/m^3$ for PM_{10}, 15.9 to 23.2 $\mu g/m^3$ for $PM_{2.5}$ and 5.7 to 9.6 $\mu g/m^3$ for PM_1. Variation of the daily means can be demonstrated by the coefficients of variation, i.e. the standard deviation divided by the mean. The variability of SO_2 mass concentrations at measuring locations is very different, between 91% and 212%. The variability of PM mass concentrations at measuring locations changes between 53% and 111% for PM_{10}, between 80% and 104% for $PM_{2.5}$ and 100% for PM_1. Time series of 24-h average SO_2, PM_{10}, $PM_{2.5}$ and PM_1 mass measured at the selected locations are presented in Figures 2 and 3.

Strong fluctuations of the concentrations can be observed. Especially SO_2 and PM_{10} were characterized by strong amplitudes mostly related to changes in weather conditions. Excursions over daily limit values of concentrations of SO_2 and PM_{10} usually occurred due to very high concentrations in the period of several hours during the day. However, the mass concentrations of SO_2 (see Table 1.) were clearly higher at location 1 compared to concentrations at location 4. Mass concentrations of SO_2 and PM_{10} at the measuring point 1 (Park) are proportional during almost the whole measuring period (as shown in Figure 2). The same conclusion can be made for mass concentrations of PM_{10}, $PM_{2.5}$ and PM_1. These results refer that the area in the vicinity of the measuring point 1 are influenced by the same source of pollution, in this case Copper Smelting Plant Bor.

Mass concentrations of SO_2 and PM_{10} at the measuring point 4 (Brezonik) do not have the same trend during the year, they are even inverse in some periods (Figure 3). This measuring point is not at the dominant direction of the wind from the metallurgy complex, which is the main source of SO_2 pollution, so the influence of other pollution sources (such as traffic, ore waste heap or individual stacks in these periods is dominant. Nevertheless, the influence of the metallurgy complex on air pollution at this measuring point should not be neglected, since it is dominant in some periods [8].

Table 1. Average daily concentration, standard deviation (SD) and range of SO_2, PM_{10}, $PM_{2.5}$ and PM_1 at the selected measuring locations

Measuring location	SO_2 (µg/m^3)		PM_{10} (µg/m^3)		$PM_{2.5}$ (µg/m^3)		PM_1 (µg/m^3)	
	Mean (SD)	Max/Min	Mean (SD)	Max/Min	Mean (SD)	Max/Min	Mean (SD)	Max/Min
1.Park								
Year (2004)	86 (78)	914/11	41.1 (39.2)	204.5/2.85	23.2 (24.2)	89.8/1.6	9.6 (9.7)	36.6/0.6
Winter (2004)	68 (48)	892/11	40.7 (41.6)	204.5/2.8	23.0 (23.4)	88.9/1.4	9.9 (9.3)	36.6/0.6
Summer (2004)	103 (102)	914/11	36.6 (37.0)	138.1/12.5	22.4 (34.2)	123.7/7.7	7.5 (27.6)	89.8/2.9
Year (2006)	227 (292)	2441/10	32.7 (36.4)	204.3/1.9	15.9 (12.8)	49.3/3.3	5.7 (5.7)	27.2/0.4
Winter (2006)	255 (355)	2441/14	32.6 (47.5)	204.3/1.9	10.3 (10.9)	46.2/3.3	6.8 (7.0)	27.2/0.4
Summer (2006)	209 (246)	1370/10	41.7 (15.1)	77.7/17.7	21.3 (12.1)	49.3/4.6	3.5 (1.6)	6.9/1.0
Summer (2009)	150 (154)	730/3	33.4 (17.8)	86.7/11.0	21.4 (11.7)	52.8/4.0	17.5 (9.7)	46.8/3.0
4. Brezonik								
Year (2007)	44 (61)	328/5	42.5 (32.6)	293.6/8.8				
Winter (2007)	43 (64)	328/11	53.2 (41.5)	293.6/8.8				
Summer (2007)	45 (59)	217/5	32.4 (15.9)	111.0/10.3				
Year (2008)	68 (144)	1642/10	45.7 (29.9)	188.3/11				
Winter (2008)	92 (199)	1642/10	52.8 (34.9)	188.3/11				
Summer (2008)	45 (35)	196/10	35.2 (15.3)	84.9/14.7				

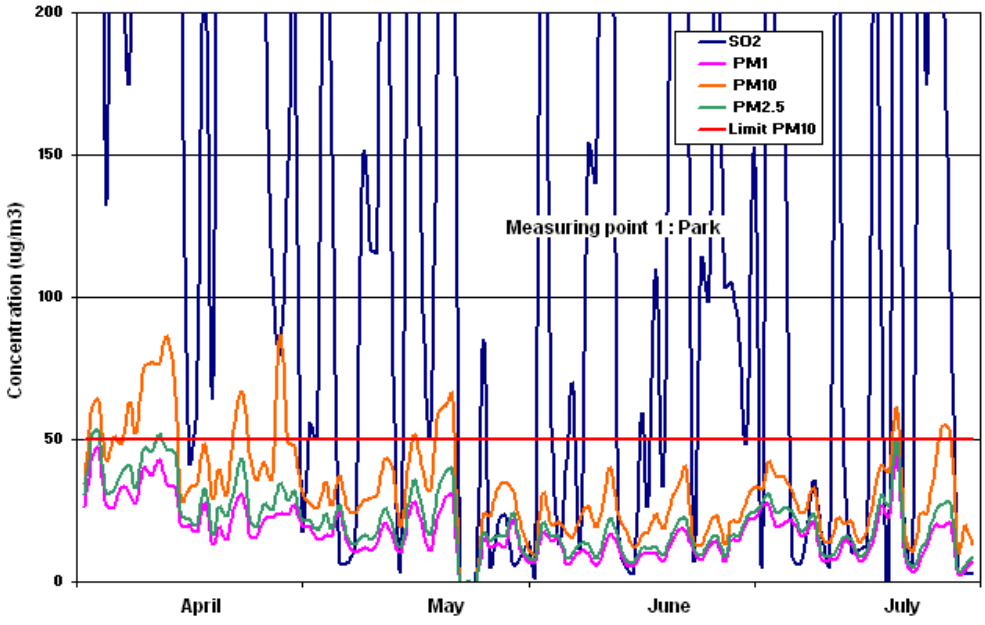

Figure 2. SO_2 and PM mass concentrations at the measuring point 1: Park (2009 year)

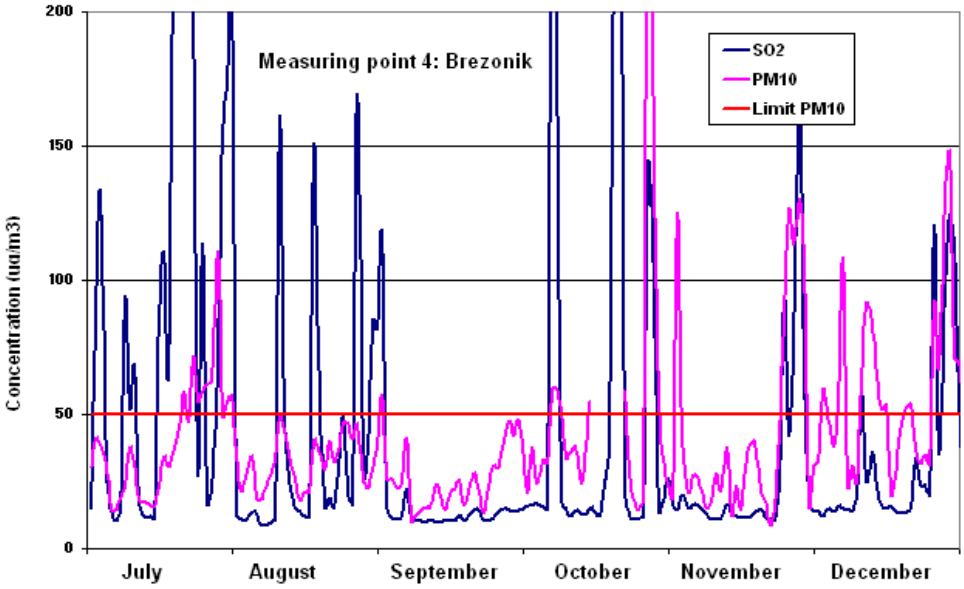

Figure 3. SO_2 and PM_{10} mass concentrations at the measuring point 4: Brezonik (2007 year)

4. CONCLUSIONS

Monitoring of mass concentrations of PM_{10} and PM_1 in the air as is very important from the aspect of risk assessment to human health. Measurement of concentration of PM (PM_{10}, $PM_{2.5}$ and PM_1) at the measuring sites in the urban area of Bor leads to the conclusions:

Presented results indicate that the dominant source of coarse and fine particles at Bor town is Copper Smelting Plant Bor. The most significant factors for the distribution of pollutants are meteorological parameters of wind speed and wind direction.

Excursions over daily concentration limit values of PM_{10} (50 $\mu g/m^3$) usually occur due to very high concentrations for several hours during the day. This is in good correlation with the detected values of SO_2 concentrations [8]. Therefore, while most of the particle pollution is below the limit value, a large pollution intensity for a few hours, one or more times during the day, can lead to an excess over the daily average limit value.

The share of PM_{10} particles in TSP (Total Suspended Particles) is generally more than 80% so that , a PM_{10} level exceeding the limit value is usually observed when the TSP pollution is above its limit value.

Further work in this area should focus on the model calibration for prediction of concentrations of sulphur dioxide and particles in real time, in order to provide short-term forecast of air quality.

5. ACKNOWLEDGEMENTS

This paper is supported by the Grant of the Ministry of Science and Technological Development of Republic of Serbia, as a part of a project TR21009 within the framework of Technological development programme.

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APSA-370 Ambient Sulfur Dioxide Analyzer - HORIBA, **URL:** www.horiba.com/process-environmental/products/ambient/BAM1020, **URL:** www.metone.com/documents/BAM-1020_6-08.pdf

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4 Exposure and health

4.1 Indoor air quality in European schools: Preventing and reducing respiratory diseases (SEARCH)

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There are many environmental health issues in the WHO European region. Stakeholders, working with and between ministries and involving intergovernmental, international organizations and civil society organizations, make decisions that contribute to sustainable development. The abstract is about an E&H research project, namely SEARCH project, implemented the CEE region during 2006-2009.

The ***SEARCH project*** is a *regional partnership* of the Regional Environmental Center for Central and Eastern Europe. The environment and health research institutes, ministries, environmental authorities, schools and the European environment and health experts are involved in the cross-sector research project.

The main focus of the project is connected to the implementation of the E&H policy in the EU Member States and in the WHO European Region. It means the regional participation in implementation of the Children's Health and Environment Action Plan, Priority Goal 3, Prevention and reduction of respiratory diseases of children due to out-door and indoor air pollution, by complex research in schools.

The ***objectives*** of the project are the followings:

1. To assess the associations between the school environment and the children's health

2. To make recommendations for improving the quality of school environment at the 5th European Environment and Health Ministerial Conference in Italy, in 2010.

3. To transfer awareness raising initiatives for the prevention of respiratory diseases, particularly among children, that have already been successful in Italy and Hungary.

The research has two main parts, the first is the exposure assessment: measurement of the indoor air quality in the school, assessment on school building and maintenance, assessment on the home environment. The second is the assessment of the children's health status: use of the symptom questionnaire and lung function measurements.

The SEARCH international project is ***implemented in*** Albania, Bosnia and Herzegovina, Hungary, Italy, Serbia and Slovakia. There are two associated countries Austria and Norway. The outcome of the project will be presented and disseminated in Italy during the 5th Environment and Health Ministerial Conference, in 2010.

Donors of the SEARCH project are the Italian Ministry for the Environment, Land and Sea and the Hungarian Ministry of Health. The supporters of the associated project are the Austrian Federal Ministry of Agriculture, Forestry, Environment and Water management, the Norwegian Ministry for the Environment and NILU.

4.2 Contribution of school indoor concentrations to total PM exposure in children

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ABSTRACT
The aim of the present study is to characterize PM mass concentration values inside classrooms, as well as to determine children exposure to PM, and particularly, the contribution of indoor school PM concentrations to the daily exposure. It also intends to contribute for general knowledge on PM concentration and exposure levels highlighting the importance of their estimation for the definition of air quality standards. This study is part of a wider project: SaudAr – The Health and the Air we Breath - and has been conducted in a town with 100000 inhabitants located in the central region of Portugal. The PM_{10} daily personal exposure of 60 children was calculated using a microenvironment approach applied to a period of 4 weeks, 2 in winter and 2 in summertime, with the objective of taking into account the seasonal variability of PM levels. Indoor and outdoor mass concentrations of PM in schools were assessed by gravimetric methods. The concentrations in the other environments were determined by air quality modelling.

1. INTRODUCTION

Air pollution is the environmental factor with the highest impact on health in Europe and is responsible for the largest burden of environment-related diseases (EEA, 2005). Inhalable particulate matter (PM) is considered a key contributor to this problem. Concern focuses not only on ambient air quality but also on air quality in indoor environments such as homes, workplaces, schools, etc. In fact, nowadays the indoor microenvironments are quite significant health determinants since people spend 80 to 90% of their time in these spaces (WHO, 2001). School age children, a particularly vulnerable population subgroup, spend a significant fraction of their day inside classrooms, being the time spent in this microenvironment only surpassed by the time spent at home. Therefore the air quality in classrooms contributes considerably to the total exposure of children to air pollutants, and consequently to their health.

It is generally accepted that the indoor concentrations of particles derive both from outdoor and indoor sources. Nevertheless, the relative importance of each source depends on various variables such as the ventilation rate; outdoor air pollution levels; type of indoor activities; size of particles; etc. (Branis et al., 2005). According to Monn et al. (1997), Luoma and Batterman (2001) and Branis et al. (2005) in indoor environments where no specific source of pollution is found (such as smoking or the combustion of fuel for heating and/or cooking), occupant-related activities may stand for the main source of PM. This particulate matter may be composed of cloth fibres, hair fragments, soil particles, skin cells, resuspended particles by the occupants' activity, and emissions from materials handled, such as paper, fungi spores, and fibres.

In contrast to the implemented EU ambient air policies, under the Air Quality Framework Directives and the New Directive on Ambient Air Quality and Cleaner Air for Europe, an integrated EU policy on indoor air quality is not yet available. To address the environmental risk factors that most affect the health of European children the Children's Environment and Health Action Plan for Europe (CEHAPE) was adopted by European Ministers in 2004, having as one priority goal to ensure clean outdoor and indoor air. Currently, indoor air quality is fragmentally tackled in sector oriented policies through several EU Directives. These EU directives explicitly include an indoor air quality aspect, or indirectly regulate indoor air quality, but none of them establishes fixed indoor air quality standards (Avgelis and Papadopoulos, 2004; EC, 2007). Nevertheless, according to WHO (2007) the existing air quality guidelines and recommendations are potentially applicable for indoor air and should therefore be used in the absence of a specific guideline or limit value for indoor air quality.

2. METHODOLOGY

PM Measurements

The study was conducted in 4 periods of the winter and summer of 2006 and 2007 in Viseu, Portugal – 16/01/06 to 28/01/06; 19/06/06 to 25/06/06; 15/01/07 to 21/01/07 and 28/05/07 to 03/06/07. During the period of the field campaigns two lecturing rooms in two elementary schools were chosen for the measurements. School 1 is located in the city centre while school 2 has a suburban location. The rooms have approximately 80 m^2, are naturally ventilated through large glazed windows (no forced ventilation or air conditioning systems are in use in the buildings) and have a mean occupancy of 20 children. Both rooms were equipped with standard school furniture made of wooden chipboard and metal and blackboards for chalk. Floors were covered with hard surface materials (wood and linoleum).

In school 1, indoor and outdoor PM_{10} and $PM_{2.5}$ were registered for the time period of the campaigns while for school 2 only PM_{10} was measured. Indoor PM_{10} and $PM^{2.5}$ mass concentrations were determined gravimetrically with low volume samplers ($1m^3h^{-1}$) and quartz filters (Whatman QMA). The inlets of the impactors were situated 120 cm above the floor. PM_{10} and $PM^{2.5}$ outdoor mass concentrations were measured gravimetrically with high volume samplers and glass fibre filters (Whatman EPM 2000). Filters were exposed along 24 h and changed once a day, at 7.30 a.m.. The filters were equilibrated for at least 48 h before each weighing, and weighed in a room with controlled temperature and humidity, 20 ± 1 ºC and 50 ± 2 %, respectively.

PM Modelling

In order to determine PM_{10} concentrations over the study domain, the air quality modelling system MM5/CHIMERE has been applied over Portugal for the period of the field campaigns. This air quality modelling system is based on the chemistry-transport model CHIMERE (Schmidt et al., 2001; Bessagnet et al., 2004), forced by the mesoscale model MM5 (Grell et al., 1994). The MM5/CHIMERE modelling system has been widely applied and validated in several air quality studies in Portugal (Monteiro et al., 2005; Monteiro et al., 2007) and is presently used as the Portuguese air quality forecasting system. The modelling system was applied first at the European scale (with 50 x 50 km

resolution), then over Portugal using the same physics and a one-way nesting technique, with 10 x 10 km, and finally over Viseu, at 3 x 3 km horizontal resolution. Table 1 presents the domains definition and the physical options selected for the MM5/CHIMERE application.

Table 1. MM5 and CHIMERE simulation characteristics

		European domain (D1)	Portuguese domain (D2)	Viseu domain (D3)
MM5	Dimensions (X,Y)	96 x 81 cells	73 x 109 cells	40 x 40 cells
	Horizontal resolution	54 km	9 km	3 km
	Vertical resolution	32 sigma levels	32 sigma levels	32 sigma levels
	Physics	MRF PBL scheme RRTM radiation scheme Grell cumulus scheme Graupel moisture scheme	MRF PBL scheme RRTM radiation scheme Grell cumulus scheme Graupel moisture scheme	MRF PBL scheme RRTM radiation scheme Grell cumulus scheme Graupel moisture scheme
CHIMERE	Dimensions (X,Y)	46 x 67 cells	29 x 58 cells	36 x 36 cells
	Horizontal resolution	50 km	10 km	3 km
	Vertical resolution	8 levels	8 levels	8 levels
	Chemical mechanism	Melchior	Melchior	Melchior

Personal Exposure

Different methodologies can be applied to determine the individual exposure, using direct measurements or estimations based on exposure concentration data and the time of contact. The general approach for exposure estimation can be expressed by:

$$Exp_i = \sum_{j=1}^{n} C_j t_{i,j} \qquad \text{(Equation 1)}$$

where Exp_i is the total exposure for the person *i* over the specified period of time; C_j is the pollutant concentration in each microenvironment *j* and $t_{i,j}$ is the time spent by the person *i* in microenvironment *j*.

Within this study, the individual exposure was estimated using the microenvironment approach and calculated according to Equation 1. The input data required for the exposure quantification was determined separately for each individual under the study. For this purpose, two main tasks have been carried out: a) the definition of the daily activity profile of each child for a typical winter and summer school week, which allowed the identification of the microenvironments frequented by those children and the time spent in each one; and b) the air quality characterisation of those microenvironments. The daily activity profile was established through personal enquiries to parents and children. The air quality assessment in the identified microenvironments, both outdoor and indoor, has been performed using a multi-strategy approach: measurements during field campaigns and air quality modelling simulations. For the microenvironments where measurements were not possible to take, PM_{10} concentrations have been obtained through air quality modelling. These microenvironments were geo-referenced and outdoor concentrations were obtained directly from modelling while for indoor concentrations the relations presented in Table 2 were used. Using these data daily personal exposure to PM_{10} was calculated for each child for a week in summer and winter time in 2006 and 2007.

Table 2.Indoor-Outdoor (I/O) relations considered in the exposure module for PM_{10}. (USEPA, 1997; Gulliver and Briggs, 2004).

Home	Other indoors	In vehicle
$C_{it}(day) = 48 + 0{,}51C_{out}$ $C_{in}(night) = 20 + 0{,}52C_{out}$	$C_{in}(day) = 48 \cdot (1 - 0.14) + 0{,}51C_{out}$ $C_{int}(night) = 20 \cdot (1 - 0.14) + 0{,}52C_{out}$	$C_{vehicle} = 13{,}1 + 0{,}83C_{out}$

3. RESULTS AND DISCUSSION

The obtained time activity profiles show that the school children spend more than 95% of their time indoors. This percentage slightly decreases in summer and at the weekend. Also, the children living in a suburban location tend to spend more time outdoors than urban children.

The results of the indoor and outdoor PM mass concentration measurements are summarised in Table 3.

Table 3. Indoor and outdoor PM mass concentrations ($\mu g.m^{-3}$) and PM indoor/outdoor (I/O) ratios.

	School 1						***School 2***		
	PM_{10} in	**$PM_{2.5}$ in**	**PM_{10} out**	**$PM_{2.5}$ out**	**PM_{10} I/O**	**$PM_{2.5}$ I/O**	**PM_{10} in**	**PM_{10} out**	**PM_{10} I/O**
whole period	102.7 ± 34.3	43.8 ± 11.3	49.8 ± 21.2	35.7 ± 10.7	2.1	1.2	81.0 ± 22.9	42.3 ± 7.5	1.9
winter	120.9 ± 41.7	50.5 ± 15.3	55.6 ± 32.1	34.0 ± 19.8	2.2	1.5	99.0 ± 26.8	45.7 ± 19.2	2.2
summer	70.3 ±32.3	34.9 ± 13.0	42.0 ± 8.7	38.0 ± 18.6	1.7	0.9	53.9 ± 18.9	37.3 ± 5.8	1.4
weekdays	113.3 ± 36.7	47.6 ± 13.9	50.7 ± 25.7	36.3 ± 19.2	2.2	1.3	85.0 ± 30.6	42.2 ± 16.0	2.0
weekends	24.8 ± 11.1	21.1 ± 8.1	30.9 ± n.a.	24.2 ± n.a.	0.8	0.9	34.7 ± 14.1	45.4 ± n.a.	0.8

Regarding the mean values for the whole period, the PM_{10} concentration obtained in school 1 (urban location) is higher than in school 2 classroom (suburban location). In both schools the indoor concentration levels are significantly higher in winter than in summer. During weekdays, the PM_{10} concentrations in the classrooms are significantly higher than in the outdoors for the same location, having I/O ratios over 2.0. This ratio is lower for $PM_{2.5}$ and decreases for both pollutants in weekends. During the summer, the difference between indoor and outdoor pollution levels is lower. This fact can be explained by the presence of indoor emission sources and low ventilation rates at wintertime, while open windows during summertime promote better conditions to indoor/outdoor air exchange. At weekends, the indoor PM values are similar to the ones measured outdoors, confirming the existence of indoor PM sources in weekdays. The PM_{10} mass concentrations found inside classrooms show no correlation with outdoor values. The indoor $PM_{2.5}$ values on weekdays, although higher than the outdoor levels, show some correlation with the outdoor concentrations ($R=0.50$ (p-value<0.05) in winter and $R=0.80$ (p-value<0.01) in summer). The linear regression indicates that in winter $C_{in} = 41.9 + 0.43C_{out}$ and in summer $C_{in} = 20.1 + 0{,}49C_{out}$. This analysis indicates that the $PM_{2.5}$ indoor contribution to total mass concentration is 2 times higher in winter than in summer.

The modelling simulations results are in agreement with the measurement values. They show that the outdoor legislated daily value of PM_{10} is often exceed, mainly in winter and in the most urbanised area of the town.

Based on the obtained results for the estimated exposure to PM_{10}, the children have been exposed to a mean value of 56.3 $\mu g.m^{-3}.h$ in school 1 and 50.5 $\mu g.m^{-3}.h$ in school 2. The contribution of the exposure in the classrooms is quite high (>50% of total exposure) compared with the time spent in this microenvironment (~30%).

4. CONCLUSIONS

It was found that mass concentrations of PM_{10} and $PM_{2.5}$ were much higher in classrooms than in ambient air, in accordance with the results of Wheeler et al. (2000) and Roorda-Knape et al. (1998). A strong seasonal variability was observed, being PM levels higher in summer. This fact can be explained by higher ventilation habits in summer. It can also be concluded that PM_{10} in classrooms is generated by indoor sources while $PM_{2.5}$ has an important outdoor contribution, particularly in summer. The comparison between weekdays and weekends suggests that the main indoor source of PM is human activity.

Although personal exposure results are calculated only for a 4 weeks period, they indicate that the children are exposed to a mean air quality value of approximately 50 $\mu g.m^{-3}$ during a typical school week. Hence, it is quite probable that the annual mean value of 20 $\mu g.m^{-3}$, recommended by WHO, is exceeded by any of the studied children. The microenvironment that contributes the most to PM exposure is clearly the classroom. Both the indoor PM concentrations found and the time spent by children in indoor environments indicate that the definition of guidelines or limit values for indoor air quality are of extreme importance due to the contribution of the children exposure in those microenvironments may have on their health. The definition of management strategies to decrease indoor PM concentrations in microenvironments such as schools arises as an important goal in the near future.

5. ACKNOWLEDGEMENTS

The authors are grateful to Calouste Gulbenkian Foundation for the SaudAr project's financial support. The authors are also grateful for the financial support under the 3rd EU Framework Program and the Portuguese 'Ministério da Ciência, da Tecnologia e do Ensino Superior' for the Ph.D. grant of J. Valente (SFRH/BD/22687/2005) and the Post-Doc grants of J. Ferreira (SFRH/BPD/40620/2007), J.H. Amorim (SFRH/BPD/48121/2008) and A.M. Costa (SFRH/BPD/48128/2008). The support from the ACCENT Network of Excellence (GOCE/CT/2004/505337) is also acknowledged.

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4.3 The importance of population susceptibility to air pollution: gene candidate approach

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ABSTRACT
The effects of environmental exposures might be transmitted to cellular level through mechanisms that could vary between individuals. Gene polymorphism in GSTM1/GSTT1, both deletions in the gene, showed the significant influence in genetic association studies of air pollution. In order to analyze the association of GSTT1/GSTM1 polymorphism with respiratory and cardiovascular disease in regard to air- pollution, for the first time we detected the presence of GSTM1/GSTT1 deletion in two different environmental risk factors' populations, Belgrade and Obrenovac. The groups consisted of 71 (Belgrade)/89 (Obrenovac) participants. Genotyping was performed by multiplex PCR. The frequencies of "null" genotypes for GSTM1/GSTT1 were not significantly different between the two investigated groups (47.89%/44.94%, 15.49%/17.98%, respectively). In conclusion, the frequencies of detected "null" genotypes in investigated two population subsets of Serbian origin was similar and in range with the frequencies in other Caucasian populations.

1. INTRODUCTION

Genetic epidemiology can contribute to establishing the causal nature of environmentally modifiable risk factors for disease development and thus contribute to appropriate preventive strategies. Technological excellence in genomics and medicine does not automatically lead to benefits in human health, which could require a true understanding of the etiology of complex or multifactorial diseases, and which, we argue, require a true understanding of the role of the environment. The effects of environmental exposures might be transmitted to cellular level through mechanisms that could vary between individuals. A uniform exposure would elicit different effects depending on an individual's genetic makeup.

One of the human cell defense systems against the damaging effects of oxidative stress is the glutathione S-transferases (GSTs). GSTs consist of a super family of dimeric, phase II metabolic enzymes which play an important role in individual response to environmental factors through both, detoxifying cytotoxic agents and protecting cellular macromolecules. Several GST genes exhibit polymorphic traits that directly result in changes in quantity or activity of enzymes (Garte, S., 2001). These enzymes play an important role in detoxifying cytotoxic agents and protecting cellular macromolecules. In addition, one of the defense systems against the damaging effects of oxidative stress is the GSTs. At least eight distinct classes of soluble GST that are highly expressed in the mammalian liver have been already identified: alpha, mu, pi, sigma, theta, kappa, omega and zeta (Awasthi, et al., 1994). Several GST genes exhibit polymorphic traits that directly result in changes in quantity or activity of enzymes (Garte, S., 2001). Polymorphisms in the GST gene may impair the capacity of defense against oxidative stress and lead to the development of a wide variety of diseases

(Ryberg, et al., 1997). Subjects with at least one functional allele for GSTM1 are grouped into the positive conjugator types, and called GSTM1-positive. The deleted genotypes, that lead to the inactive form of the enzyme, have been named GSTM1 null (Landi, S., 2000). The polymorphism in the GSTT1 gene loci is also caused by a gene deletion (Pemble, et al., 1994). This results in virtual absence of enzyme activity in individuals with GSTT1 and GSTM1null genotypes. Therefore, these enzymes may be related to the risk for lung cancer (Seidegard, et al., 1986; Nazar-Stewart, et al., 1993; Hirvonen, et al., 1993), respiratory diseases and atherosclerosis (Bridges, et al., 1990).

Gene polymorphism in GSTM1 and GSTT1, both deletions in the gene, showed the significant influence in genetic association studies of air pollution (Yang, et al., 2008). Particulate air pollution was previously associated with cardiovascular mortality and morbidity. Indeed, several studies have focused on the putative relationship between GSTT1 and GSTM1 "null" genotypes (deletion) and either coronary artery disease development or cardiovascular risk factors prevalence (Abu-Amero, et al., 2006). In order to analyze the association of GSTT1 and GSTM1 polymorphism with respiratory and cardiovascular disease in regard to air- pollution, the aim of this work was to determine null genotypes frequency in preliminary sample from two close populations with different environmental risk factors, Belgrade and Obrenovac.

2. METHODOLOGY

The studied groups consisted of 71 (Belgrade) and 89 (Obrenovac) participants (77.5% males) who underwent annual medical check-up at the Occupational medical centers. The participants were free of history or presence of any chronic disease, cancer or renal failure. Each participant gave written informed consent to participate in the study.

Peripheral venous blood was collected in 5 ml tubes with EDTA and the specimens were stored at -20°C until DNA isolation. From both cases and controls, genomic DNA was isolated from peripheral leukocytes by proteinase K digestion, phenol/chloroform extraction and ethanol precipitation, dissolved in TE buffer (pH 7.5) and stored at +4°C until genotype analysis (Kunkel, et al., 1977).

A multiplex polymerase chain reaction (PCR) method was used to detect either the presence or absence of GSTM1and GSTT1 gene polymorphisms in the genomic DNA samples simultaneously in the same tube; β-globin gene was co-amplified and used as an internal control (Chen, et al., 1996). This technique does not distinguish between heterozygote and homozygote GSTM1- and GSTT1-positive genotypes, but it does conclusively identify the null genotype (Helzlsouer, et al., 1998). Genomic DNA(100 ng) was amplified in a total volume of 20 μl reaction mixture containing 100 ng of each GST primers (GSTM1: forward 5'-GAA CTC CCT GAA AAG CTA AAG C-3' and reverse 5'-GTT GGG CTC AAA TAT ACG GTG G-3', GenBank accession no. NM_146421; GSTT1: forward 5'-TTC CTT ACT GGT CCT CAC ATC TC-3' and reverse 5'-TCA CCG GAT CAT GGC CAG CA-3', GenBank accession no. NM_000853); 50 ng β-globin gene primers (forward 5'-CAA CTT CAT CCA CGT TCA CC-3' and reverse 5'-GAA GAG CCA AGG ACA GGT AC-3'); 200 μmol/l deoxynucleoside triphosphates; 1 U of DreamTaq polymerase in 10 × DreamTaq

buffer composed of 1-2.5% of both KCl and $(NH_4)_2SO_4$ to provide high specificity of primer annealing and 20.0 mmol/l MgCl2, pH 8.8. PCR was performed on ABI 9700 (Applied Biosystems, Foster City, CA). After initial denaturation of 3 min at 94°C, 34 cycles were performed: 30 sec at 94°C (denaturation), 45 sec at 60°C (annealing) and 45 sec at 72°C (extension), followed by a final step of 5 min at 72°C. The GSTM1 (215-bp), GSTT1 (480-bp) and β-globin (268-bp) amplified products were visualized by electrophoresis on ethidium-bromide-stained 1.8% agarose gel (Figure 1.). For deletions of GSTM1 and GSTT1 no amplified products can be observed, whereas the β-globin specific fragment confirms the presence of amplifiable DNA in the reaction mixture.

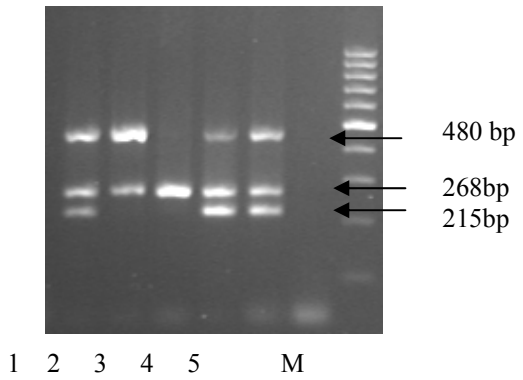

Figure 1. Detection of GSTM1 (215-bp) and GSTT1 (480 bp) genotypes by multiplex PCR

Absence of the PCR product indicates "null" genotype. M-100bp ladder, GSTM1 null genotype, lane 2; GSTT1 null genotype, lane 3; internal PCR control, β-globin gene fragment (268-bp)

3. RESULTS AND DISCUSSION

The frequencies of "null" genotypes for GSTM1 and GSTT1 were not significantly different between two investigated groups (47.89%/44.94%, 15.49%/17.98%, respectively). The frequency of double deletion was also similar (7.04/7.87). For the first time, we detected the presence of GSTM1 and GSTT1 deletion in our population.

The distribution of GSTM1 and GSTT1-null genotypes varies among different ethnic groups. It is of great interest to determine the presence and frequecy of gene polymorphisms in certain population in aim to associate it with the local environmental factors and development of the disease. Approximately 50% of the European and Asian populations are homozygously deleted for GSTM1 "null" allele (Kliencke, et al., 1990). It has been reported that GSTM1 deletion genotype prevalence ranging from 47 to 58% among Caucasians. Relatively few data exist about GSTM1 polymorphism in the black and mulatto populations (Ford, et al., 2000; Lin, et al., 1994). According to our knowledge, the data for Serbian population did not exist until this study. According to this study results the frequency of GSTM1 "null" allele is similar to lower boundary frequencies shown so far in Europeans (Sivonova, et al., 2009).

Large ethnic differences in the prevalence of the homozygously deleted GSTT1 genotype have been observed. The null genotype of *GSTT1* increased from north to south and west to east of Europe. In Asia the highest level of *GSTT1* null genotype was reported. The prevalence of the null genotype was highest among Chinese (64.4%), followed by Koreans (60.2%), African-Americans (21.8%) and Caucasians (20.4%), whereas the prevalence was lowest among Mexican-Americans (9.7%). Interestingly, the prevalence of the deleted genotype in Caucasians differed significantly when 257 individuals drawn from a nation wide organization were compared with 185 people from the New England area (23.7 versus 15.7%). These results indicate that there are major differences in the prevalence of this trait attributable to ethnicity and that ethnic origin even among Caucasians should be considered in studies of gene-environment interaction involving this polymorphism (Nelson, et al., 1995). So, we determined the frequency of *GSTT1* null genotype in population of Serbia and it seems to be similar with the frequencies which were reported for geographically close European populations (Sivonova, et al., 2009; Palli, et al., 2005; Lan, et al., 2001).

4. CONCLUSIONS

In conclusion, the frequencies of detected "null" genotypes in the two population subsets of Serbian origin investigated was similar and in range with the frequencies in other Caucasian populations.

5. ACKNOWLEDGEMENTS

This work was supported by Serbian Government Research Grant (TR23040).

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4.4 Integrative air pollution health risk assessment: gene-environment interactions study

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ABSTRACT
The overall estimated burden of disease due to outdoor air pollution may account for ~1.4% of total mortality, 0.5% of all disability-adjusted life years and 2% of all cardiopulmonary diseases. Certain population subgroups are more affected than others. To analyze quantitatively the impact on health of outdoor air pollution in particular areas, an information is needed on air pollution concentrations and exposure, the population groups exposed, background incidence of mortality and morbidity, and concentration–response (CR) functions (1). Genetic factors interact with environmental ones to cause most complex (respiratory and cardiovascular) diseases. An integrative approach with definition of both, areas and populations under the highest pollution burden and medical data of increased incidence of certain diseases in specific areas, makes the basis for the implementation of genetic approach in defining diverse responsiveness to the pollution. The project which is going on under the funding of Serbian Ministry of Science have implemented genetic epidemiology in health risk assessment.

1. INTRODUCTION

The overall estimated burden of disease due to outdoor air pollution may account for approximately 1.4% of total mortality, 0.5% of all disability-adjusted life years (DALYs) and 2% of all cardiopulmonary diseases. According to data from WHO in the year 2006. the cardiovascular disease was the leading cause of death, with about 30% of all death cases (www.who.int/entity/heatlhinfo/statistics/bodgbddeathdalyestimates.xls). In Serbia, more than 57% of all deaths were cardiovascular diseases during 2006 year (men 52%; women 62.8%) (Ministry of health; http://www.minzdravlja.info/downloads/Zakoni/Strategije/pdf). Individuals respond differently to exposure to air pollution, and features contributing to these variations have been accumulated under the concept of susceptibility. Increased susceptibility to air pollution has been linked to a large number of factors. To analyze quantitatively the impact on health of outdoor air pollution in either city, region or country, an information is needed on air pollution concentrations and exposure, the population groups exposed, background incidence of mortality and morbidity, and concentration–response (CR) functions (WHO, 2006).

Certain population subgroups are more vulnerable and affected, including the young and the elderly (Annesi-Maesano et al., 2003; Gauderman et al., 2004). Even in healthy adults who have undergone controlled exposure to an air pollutant, there is much variability in the measured effects. Genetic factors interact with environmental ones to cause most complex diseases, such as respiratory and cardiovascular, which incidence is increasing by elevated air pollution. However, genetic studies have generally ignored environmental factors as well as *vice versa*. The biological mechanisms by which air pollutants exert

their health effects include both inflammatory and oxidative processes in the body. Gene polymorphisms influence responsiveness to pollution, as found in both inflammatory cytokines and antioxidant systems. The variability in a response to certain pollutants is by some degree affected by gene polymorphisms, which are present in the candidate genes associated with disease. Thus, an integrative approach with definition of both, areas/populations under the highest pollution burden and medical data of increased incidence of certain diseases in those areas, makes the basis for the implementation of genetic approach in defining diverse responsiveness to the pollution. On the basis of present knowledge there is a strong rationale to perform gene-environment interaction studies in local surroundings aiming to define the present level of air-pollutants and their effect on health through the light of genetic basis of selected population.

The importance of such approach is illustrated through the official efforts and financial support of National Institute of Health (US) for proposed research programs for the period from 2007-2010. On February 8, 2006, Health and Human Services Secretary announced that the President's 2007 budget proposal included $40 million for the National Institutes of Health to plan and implement a Genes and Environment Initiative (GEI). Approved by Congress, federal funding began in fiscal year 2007 and will continue until 2010, with $26 million annually going to genetic analysis and $14 million annually designated for the development of new tools to measure environmental exposures that affect health. Priority exposure classes included ozone, particulate matter and diesel exhaust, metals (e.g., arsenic, cadmium, mercury), volatile organic compounds (e.g., benzene), PBDEs, PAHs, as well as molds and allergens. Final aim of such projects is an improved health impact assessment (HIA).

Genetic approach

Implementation of GEI by the Genetics Subcommittee began with a Genome-Wide Association (GWA) Study component comprising: 1) genotyping facilities to perform high-throughput genotyping for GWA studies; 2) a coordinating center to provide analytic support, data quality assessment and quality control, and logistical management; and 3) investigative groups that will address scientific questions using existing DNA samples from well-characterized subjects using GWA approaches. Curated data are made available in a central, controlled-access database, the database of Genotype and Phenotype (dbGaP), established by the National Center for Biotechnology Information (NCBI) for free and broad research use.

State of art in Serbia

It was already mentioned that in past generally genetic studies have not been incorporated in environmental research, as well as the measurement of environmental factors are often very limited in genetic studies. An integrative approach in further research and implementation of the results in health risk assessment becomes necessary. It has a task to connect and provide interactive engagement of researches from different fields and to provide time and cost benefits comparing to separate research. This kind of projects are still in pioneering phase since there are no national institutions or projects of national and strategic interest, which could provide the infrastructural and informational support and centralized data bases for broad research use. The project running in

Institute of Nuclear Science Vinca supported by Serbian Ministry of Science and Technology has an aim to implement genetic epidemiology in health risk assessment. As it was said, the absence of institutional support the difficulties in gathering the data for environmental factors, medical history of participants arisen. Also, it seems that there is the lack of information and education of population, since the response of population to participate in this project was very low, 2/3 of subjects have not accepted to participate.

An illustration of institutional support would be the description of US The National Human Genome Research Institute's Office of Population Genomics, which was established to facilitate the application of genomic knowledge to health. The office will promote multi-disciplinary research in epidemiology and genomics, by applying genomic technologies in clinical studies to existing population, and developing new population resources for investigation of both genetic and environmental contributions to complex diseases (http://www.genome.gov/19518660). The step before would be the foundation of The National Human Genome Research Institute in Serbia.

Public Health Significance of Applied Genomic Research on Diseases with Environmental Causes

Applied genomic research has a role to play in three areas: 1) to help stratify disease risks and target interventions to achieve not only individual health promotion goals but overall population health benefits; 2) to identify unknown environmental risk factors for disease or confirm suspected environmental risk factors using such evolving tools as toxigenomics, gene-environment interaction analysis, and "Mendelian randomization;" and 3) to characterize disease occurrence in populations in terms of transmission, natural history, and etiologic heterogeneity and also, to identify biologic targets for intervention such as drugs and/or vaccines.

The major objective of applied genomic research for conditions with environmental causes is not necessarily discovering new genetic "causes" of disease but supplementing and improving existing approaches to treatment and prevention. We define "applied genomic research" as clinical and epidemiologic research that characterizes genetic variants in populations, assesses gene-environment interaction, and evaluates genetic tests for screening and prevention (research that answers the question "What do you do with a gene when you find one?") (Khoury et al., 2006).

Genetic analysis can also be used to increase our understanding of the natural history of environmentally induced diseases, suggesting population-level interventions. For example, it was reported that asthmatic children in Mexico with the glutathione S-transferase M1 (*GSTM1*) null genotype experienced a significant ozone-related decrement in pulmonary function, while children with the normal *GSTM1* genotype did not (Romieu et al., 2004). Furthermore, it was reported that supplementation with the antioxidant vitamins C and E mitigated ozone-related decline in forced expiratory flow, a protective effect that was stronger in children with the *GSTM1* null genotype. If confirmed in other studies, these results will shed some light on the biologic basis of an environmentally induced condition. Asthmatic children with a genetic deficiency of *GSTM1* may be more susceptible

to the deleterious effects of ozone on the small airways and may derive greater benefit from antioxidant supplementation (Romieu et al., 2004).

Perhaps most importantly, these findings suggest that a simple intervention—antioxidant vitamin supplementation—could be administered to all children with asthma, producing general benefits for all and specific benefits for those susceptible to ozone. Without such genotype-specific analyses, an important potential intervention could have been overlooked.

4. CONCLUSIONS

The long term rationale of such studies appears to be that an accumulation of knowledge regarding susceptibility genes will allow us to identify high risk population subgroups. Although the most clinical applications of genomics are not ready for widespread use, there is an increasing need to develop, evaluate, and integrate genomic tools into clinical and public health research. This in turn may subsequently allow the development of intervention strategies aimed at such high risk groups including modification of lifestyle habits and increased surveillance for those at most risk.

5. ACKNOWLEDGEMENTS

This work was supported by Serbian Government Research Grant (TR23040).

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4.5 Toxicological endpoints of airborne carbonaceous particulate matter

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Abstract

Combustion products of fossil fuels represent a complex mixture containing particles, semi-volatile matter and gases. The airborne particles with a diameter less than 2.5 μm ($PM_{2,5}$), and with a high content of fine black elemental carbon are often called soot. These particles may contain many different chemicals, and some of them are well recognized toxic agents. Except for chemical composition of the carbonaceous matter, the size of the particles plays significant role in their toxicity. There are epidemiological and experimental data associating air pollution with cardiorespiratory diseases, cancer and reproductive disorders in humans. Relative risks associated with long term exposures are relatively small and difficult to detect, but the number of exposed population is huge, so the overall impact is very important. As combustion emissions account for over a half of fine particulate matter in the air, efforts for further investigation on recognizing their toxicity should be made.

1. Introduction

The main source of air pollution by carbonaceous matter are fossil fuels combustion processes. Major emission sources include coal combustion and traffic (various types of motor vehicle fuels, primarily gasoline and diesel). Except those, very important, primarily indoor source of pollution is tobacco smoke.

Combustion products of coal (soot and tars) represent a complex mixture containing particles, semi-volatile matter and gases Depending on the source and time period, these mixtures are consisted of many various gases, solid and liquid particles, including organic material, salts such as sulfates and nitrates, metals, and biological materials (1).

The airborne particles with a diameter less than 2.5 μm ($PM_{2,5}$), and with a high content of fine black elemental carbon are often called soot Except for the elemental carbon, which is relatively biologically inert substance, these particles may contain many different chemicals, and some of them are well recognized carcinogenes. The mutagenicity and carcinogenity of airborne combustion particles are initially attributed to polycyclic aromatic hydrocarbons (PAHs). PAH is a term encompassing a wide range of compounds that are emitted from a number of sources. It consists of two or more aromatic rings made entirely of carbon and hydrogen. The physical and chemical properties of individual PAH vary considerably. Recent studies discovered that wide range of other polycyclic aromatic compounds contribute to the toxicity of combustion products. These substances include substituted aromatic hydrocarbons such as nitroarenes (nitro-PAH)and nitro-PAH lactones (2).

Particles bearing these compounds are inhaled and deposited in the airways in accordance with well understood physical and physiological principles. The

aerodynamic diameter of particles in the ambient aerosol will control the pattern of their deposition in the lungs. Coarse particles mainly stay at upper respiratory tract, $PM_{2,5}$, because of their relatively small size, reach the terminal airways in the lungs, and smaller, ultrafine particles and gases may trough the lungs be absorbed into systemic circulation (3). The aim of this is paper is to review the adverse health effect of the carbonaceous particles from the epidemiological point of view along with the supporting experimental studies on toxicological endpoint.

1. Results of epidemiological observations

Epidemiological studies have shown that there is a consistent link between outdoor and indoor concentration of soot and adverse health effects.

In the 1990s, two large American cohort studies on air pollution demonstrated a strong association between particulate matter (PM) concentrations and cardiorespiratory mortality (4, 5). Subjects of these studies were controlled for relevant individual confounders like smoking and occupational exposure. After adjusting for the risk factors, statistically significant association between air pollution and mortality was found. Air pollution was positively associated with death from lung cancer and cardiopulmonary disease, but not with death from other causes considered together. Mortality was the most strongly associated with the fine particulates, including sulfates. Although the effects of the other, unmeasured risk factors cannot be excluded with certainty, these results suggest that fine-particulate air pollution, or a more complex pollution mixture associated with fine particulate matter, contributes to excess mortality in certain U.S. cities (6).

Air pollution is also recognized as the cause of increased incidence of allergic respiratory diseases, like asthma (7, 8).

The effect of the greatest significance on exposure to carbonaceous matter is the development of the lung cancer. The links between exposure to fossil fuels combustion products and the development of cancer has been recognized among professionally exposed population many centuries ago. The classical examples are Pott's observations of high incidence of scrotal cancer amongst chimney sweepers, and von Volkmann’s report of increased skin cancer in workers exposed to coal tar. Kennaway and colleagues explained it as a carcinogenic effect of polycyclic aromatic hydrocarbons (PAH) derived from coal tar. Polycyclic aromatic compounds came in focus of the research in air pollution in recent decades, and more than 500 carcinogenic compounds were detected (9). The International Agency for Research in Cancer (IARC) has classified a number of common mixtures of substances that include PAH compounds as carcinogenic to humans (category 1). Thus, professional exposition of workers to the fumes during coal gasification, coke production and aluminum production significantly increases the risk of cancer development, so these substances have been classified as category 1 carcinogens. The association between tobacco smoke and bronchial cancer is also typical example of combustion products carcinogenic effect (10).

Except for specific subgroups like smokers and professionally exposed persons to the carcinogenic substances, the carcinogenic effect of combustion products is investigated for general population. Air pollution may be a logical explanation for

the higher incidence of lung cancer noticed in urban versus rural areas The mixture of chemicals that makes up ambient air should be considered to be carcinogenic in the same way as the industrial mixtures, but the risk of cancer associated with exposure to ambient air is expected to be considerably lower because of the much lower concentrations of carcinogenic compounds found in ambient air.

Several studies evaluated the role of air pollution on lung cancer development since the 1960s, but it was very difficult to obtain statistically significant data to prove the link, because of various confounding factors. Except for cardiorespiratory mortality, studies leaded by Dockery (4) and Pope (5) demonstrated strong connection between air pollution and death from lung cancer. Additional follow up of the mortality of approximately 500 000 adult men and women from 1982 to 1998 indicated a significantly increased mortality risk ratio for lung cancer with each 10 $\mu g/m^3$ increase of $PM_{2.5}$ (11). In these studies, long term exposure was estimated from metropolitan annual average ambient concentrations and comparisons in air pollution exposure were based on inter-city concentration differences. No information on exposure to pollutants was available at the individual level. Studies conducted in Europe trying to prove the link between air pollution and lung cancer, paid grater attention on providing information on confounders and exposure to traffic at individual levels also (12, 13). The results of the one of the latest and the most important prospective study in Europe on air pollution and risk of lung cancer were published in 2006 (14). To estimate the relationship between air pollution and lung cancer, a nested case-control study was set up within EPIC (European Prospective Investigation on Cancer and Nutrition). Cases had newly diagnosed lung cancer, accrued after a median follow-up of 7 years among the ex-smokers (since at least 10 years) and never smokers. Matching criteria were gender, age (±5 years), smoking status, country of recruitment and time elapsed between recruitment and diagnosis. Residence in proximity of heavy traffic roads was used as an indicator of exposure to air pollution. In addition, exposure to air pollutants (NO_2, PM_{10}, SO_2) was assessed using concentration data from monitoring stations in routine air quality monitoring networks. Results demonstrated a nonsignificant association between lung cancer and residence nearby heavy traffic roads.

When interpreting the findings regarding the impact of air pollution on the general population, it should not be forgotten that diesel exhaust is classified by IARC as category 2A: a probable human carcinogen (15). Epidemiological studies of the effects on people exposed to high concentrations of diesel exhaust have not produced clear cut evidence of its carcinogenicity. The greatest exposures to vehicular fuels and exhausts occur occupationally. Several studies have indicated that diesel exhaust contributes to occurrence of the human lung cancer (16). Problems of confounding by cigarette smoking and difficulties of exposure assessment have made many epidemiological studies in this area difficult to interpret, so it may be stated results suggest that long-term employment in jobs involving substantial exposure to diesel exhaust is statistically associated with a small increase in risk for lung cancer.

2. Supporting experimental studies on mechanisms of toxicity

Results of epidemiological studies raise question on the recognition of specific toxic agents responsible for the adverse health effects and possibility of lowering their emission. Air pollution is a complex mixture containing thousands of different combustion products, including a variety of recognized genotoxins. The organic extractable mass from carbonaceous soot particles emitted from several well studied combustion sources (coal, diesel and tobacco) induces tumors in animals and mutation in cells. The organic fraction includes many polycyclic aromatic compounds (PAC) which are powerful mutagens and carcinogens. The importance of these compounds in establishing current views of links between exposure to chemicals and the development of cancer has been reviewed by many authors (2). Extensive mechanistic studies have shown that many PAH compounds - including some that occur in ambient air - are complete carcinogens, i.e. they can both induce cancer by producing mutations in DNA and promote cancer by affecting the proliferative capacity of affected cells. These effects are referred to as genotoxic and epigenetic effects, respectively, which seem to be two independent processes. Genotoxic effects depend on intracellular conversion of PAH compounds to diol-epoxides during the metabolic process of conjugation to water soluble substances which could be excreted by the kidney. The epigenetic effects of PAH compounds involve binding to the aryl hydroxylase (Ah) receptor in the cytoplasm, translocation of the PAH-Ah complex into the nucleus, binding to a nuclear transcription factor and activation of genes that regulate the expression of factors that control cellular growth and differentiation. PAH compounds may also affect the production of cancer by triggering an inflammatory response and generating intracellular oxidative stress by free-radical production.

Except for chemical composition of the carbonaceous matter, the size of the particles plays significant role in their toxicity. Harrison et al. (17) suggested that lung cancer linked to air pollution in the large cohort studies can be explained not just on the basis of the ambient concentration of relevant lung carcinogens (arsenic, chromium, nickel, PAH), but rather an overall effect of the particulate matter itself. They found that the cancer rates predicted and observed were rather similar, indicating that known chemical carcinogens are responsible for the lung cancers due to $PM_{2.5}$.

Experimental studies on the mechanisms linking PM and lung cancer are progressing (18). In vitro studies suggest that particles impact genotoxicity as well as cell proliferation via their ability to generate reactive oxygen and nitrogen species. This may happen because of the physicochemical characteristics of the particle surface, or due to their ability to stimulate cellular oxidant generation via various mechanisms, including an inflammatory response as an essential process. However, in vitro studies need confirmation by in vivo experiments, which is not always the case. Typical example is the lung cancer as a toxicological endpoint of PACs. Diesel exhaust contains a wide range of PACs that are accepted as carcinogens in experimental animals. Whilst exposure to high concentrations of diesel particulates (diesel soot) produced lung tumors in rats, this did not occur in hamsters or in mice (15). The explanation may be overload of the rat's particle clearance mechanisms. Overload may be a phenomenon specific to the rat,

evidence in other rodents is less good, and may reflect a different pattern of handling of particles from that seen in primates. Observed type of tumor is not seen in man. Also, it is possible that despite the accepted genotoxicity of some compounds, a threshold of effect occur in practice, as a result of defense systems that prevent low levels of genetic material changes to produce the cancer.

3. Conclusion

There are epidemiological and experimental data associating airborne carbonaceous matter with cardiorespiratory diseases, cancer and reproductive disorders in humans. These effects are connected with chemical composition of the mixture and the physical characteristics of particles. Although the relative risks associated with long term exposures are relatively small and difficult to detect, huge number of persons is exposed, so the overall impact is not negligible. As combustion emissions account for over a half of fine particulate matter in the air, efforts for further investigation on recognizing their toxicity should be made.

4. Acknowledgements

This work was supported by the Serbian Ministry of Science and Technological Development, project no. TR21009.

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4.6 Assessment of in vitro genotoxicity of air samples from cities in Slovakia on human cells

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Abstract

Ambient air quality in Slovakia is regularly monitored for „basic„ air pollutants, i.e. sulphur dioxide, oxides of nitrogen, carbon monoxide, total suspended solids, ozone, and particulate matters (PM). Additionally to these pollutants, heavy metals (HMs), volatile (VOCs) and semivolatile organic pollutants (SVOCs) have been measured and analysed in the PHARE project EU/93/AIR/22.

PM has been reported to be associated with increased respiratory, cardiovascular, and malignant lung diseases. Aim of the study was to investigate the potential mutagenic effects of air samples from 12 localities of Bratislava, Košice and other parts of Slovakia during the course of a year. Air samples from 4 sites (in Bratislava and Košice) were sampled 4 times a year. The other 8 localities were sampled twice a year (winter and summer samplings only).

We have applied the alkaline comet assay modified with endonuclease III to investigate the potential mutagenic effects of air samples from 12 localities in Slovakia during the course of a year. As target cells, freshly isolated human peripheral lymphocytes and transformed human liver HepG2 cells were used. DNA strand breaks and oxidised pyrimidines were measured after the treatment with different concentrations of extracts from the 48 air samples. 32 samples were used to test the toxic activity of organic compounds present in air samples (dichloromethane extracts). 16 samples were used for evaluation of aqueous extracts from filters to detect effect of HMs and PM.

As a positive control, H_2O_2 was used to induce significant DNA breakage and oxidative DNA damage. B(a)P was used as another positive control for testing the degree of DNA damage and metabolic capacity of the cells. To exclude the possibility that DNA degradation is merely the consequence of cytotoxicity, we determined the cytotoxic effect of all extracted air samples on the cells by trypan blue exclusion.

Our analyses show that 2/3 of samples extracted by dichloromethane induced DNA damage in HepG2 cells and almost 1/3 in lymphocytes. 3/4 of aqueous extracts induced a strong positive effect in HepG2 cells, none of them in lymphocytes. Comparing results from all localities and from different samplings during the course of the year, we found winter samples to be more mutagenic than summer samples. Although we found some discrepancies, most of our results correlated with both chemical analysis and cancer risk assessment results.

Key Words

Comet assay, air pollution, primary human lymphocytes, transformed human liver HepG2 cells, oxidative DNA damage, genotoxicity testing

Introduction

Ambient air pollution has been implicated as an important cause of various health problems, including cancer (Møller et al., 2008). Air pollution contributes a lot to the increasing mortality of lung cancer. A study by Stewart and Kleihues (2003) showed that the mortality of lung cancer was correlated with levels of specific pollutants such as benzo[a]-pyrene, metals and particulate matter. Particles with diameter less than 10μm (PM_{10}) are reported closely related to the incidence and mortality of human diseases and can cause asthma, reduction in lung function, and respiratory inflammation (Ostro et al., 2006). They can also affect cardiovascular system, nervous system and immune system, and promote cancer (Ballester et al., 2006; Samoli et al., 2005; Lewis et al., 2005). PM_{10} is a complex mixture consisting of a large number of chemicals, including polycyclic aromatic hydrocarbons (PAHs), strong acids, sulphates and nitrated organic compounds, metals, etc. The quality of Slovakia's ambient air is regularly monitored for common air pollutants, i.e. sulphur dioxide, oxides of nitrogen, carbon monoxide, total suspended solids, ozone, particulate matter. In this study, a variety of additional analyses were carried out, including measurement of heavy metals (HMs), volatile (VOCs) and semivolatile organic pollutants (SVOCs) as well as particulate matter, risk assessment and finally potential genotoxic effect. Samples of air from 12 localities in Slovakia were assessed (Dusinska, 1997) during the course of a year.

Method

For genotoxicity testing, air samples from two localities in Bratislava and Košice were taken 4 times in different seasons during the year; 8 localities in other industrial and rural cities were sampled only twice – in winter and summer.
Organic compounds from four campaigns were extracted from filters using dichloromethane. As dichloromethane extracts are better suited for further fractionation and chemical analysis it is considered to be the best choice for a general solvent system for extraction of complex environmental mixtures (Crebelli et al., 1988, Krisha et al., 1983, Lewtas, 1990, Nielsen 1992).

DNA strand breaks and oxidised bases were measured with the modified alkaline comet assay using the DNA lesion-specific enzyme endonuclease III (Collins et al., 1996).

32 samples were used to test for the mutagenic potential of organic compounds present in air samples (dichloromethane extracts), and 16 samples were used for evaluation of aqueous extracts for possible gemotoxicity of water soluble compounds and metals. DNA strand breaks and oxidised bases were measured after short-term and long-term treatment with different concentrations of extracts.

Two types of human cells were used - primary human lymphocytes (from a single healthy donor), freshly prepared for each experiment, and transformed human liver HepG2 cells.

Results and discussion

DNA strand breaks and oxidised pyrimidines were measured after the treatment with different concentrations of extracts from the 48 air samples. 32 samples were used to test the toxic activity of organic compounds present in air samples

(dichloromethane extracts). 16 samples were used for evaluation of aqueous extracts from filters to detect effect of HMs and PM.
As a positive control, H_2O_2 was used to induce significant DNA breakage and oxidative DNA damage. B(a)P was used as another positive control for testing the degree of DNA damage and metabolic capacity of the cells. To exclude the possibility that DNA degradation is merely the consequence of cytotoxicity, we determined the cytotoxic effect of all extracted air samples on the cells by trypan blue exclusion The lymphocytes had a normal background level of endogenous DNA damage, which did not vary significantly during the course of a year. Lymphocytes were incubated with extract at various dilutions in medium without serum for 1 hour; HepG2 cells were treated for 20 hours during the exponential phase growth. As a positive control, in each experiment, a standard dose of H_2O_2 (100 □M, 5 min, 4°C) was used to induce significant DNA breakage and oxidative DNA damage. B[a]P was used as another positive control (at concentration 10 □g/ml).

Both mutagens (B[a]P and H_2O_2) induced DNA damage in HepG2 cells as well as in human lymphocytes. In the case of B[a]P damage was saturated at a concentration of 5-10 μg/ml, probably because enzymes present in the cells were not able to metabolise higher amounts of B[a]P. We did not detect any oxidative DNA damage after treatment with B[a]P. Results with H_2O_2 confirm that this agent induces DNA breaks as well as oxidative DNA damage (oxidised pyrimidines detected with endonuclease III). Treatment with the solvent DMSO shows no significant damage at 2% or less.

To exclude the possibility that DNA degradation is merely the consequence of cytotoxicity or cell death, we determined the cytotoxic effect of all air samples. Lymphocytes were treated with different concentrations of extracted air samples for 1 hour and cell killing was determined by trypan blue exclusion. Concentrations used in genotoxicity studies were not cytotoxic (the viability of cells was in all cases higher than 85%).

% DNA in tail was used as the parameter for evaluation of positive effect, since tail intensity is directly related to DNA break frequency. A range of 1-10 % DNA in tail above the control level we consider a negative response - a consequence of normal variation. 11-15 % DNA in tail above the control level is considered an equivocal response (+-). 16-30% DNA in tail (above control) is considered a weak positive response (+), indicating that the test substance induces a significant level of DNA breaks and is potentially mutagenic. 31-45% DNA in tail induced above the control (++) indicates a strong positive response (as typically produced by a strong mutagens) and damage higher than 46% DNA in tail reflects very strong DNA-damaging activity (+++). Using these criteria we evaluated samples from all localities and campaigns.

In organic samples extracted by dichloromethane we found a positive DNA-damaging effect (strand breaks) in 20 from 32 samples using HepG2 cells and in 9 samples using lymphocytes. In this project, carcinogenic metals like As, Cd, Ni and Cr were analysed. In 13 from 16 samples of aqueous extracts induced a strong positive effect in HepG2 cells and 4 samples using lymphocytes.The higher DNA-damaging effect was significant in 6 from 12 localities (testing with human lymphocytes) and in 10 from 12 localities (with HepG2 cells). Our results show that air from certain areas, mainly in big industrial cities in Slovakia, can be genotoxic. Comparing all campaigns and localities, especially winter and summer

sampling, we found a tendency for winter samples to be more damaging. The mechanisms of ambient particulate matter-related adverse health effects are still incompletely understood. Knaapen et al., (2004) demonstrated that the PM_{10} was associated with free radical activity.

The modified comet assay seems a good tool for studying potential genotoxicity especially in combination with lesion specific enzyme to detect specific DNA lesions and using human cells (DCollins et al., 1997a, b; Dusinska and Collins, 2008). The HepG2 cell line retains many of the functions of normal liver cells ibcluding high metabolic capacity. The main advantage of the choice of human cells is that it is possible to extrapolate from the results to estimate the potential genotoxic risk of a mixture of air pollutants in man. Although we found some discrepancies, several results correlated with both chemical analysis and cancer risk assessment results.

Acknowledgement

This work was supported by EC contract Phare EU/93/AIR/22 and by the Slovak Grant Agency of Ministry of Health and by NILU internat Healtheffect project.

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4.7 Influence of the air pollution to disease worsening and mortality of patients with chronic obstructive pulmonary disease and asthma

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ABSTRACT
Objectives: despite a recent progress in the treatment of chronic obstructive pulmonary disease (COPD), causes of the disease worsening have not been fully ellucidated. Methods: retrospective study including 3 groups of patients: group 1 - patients admitted to intensive care unit (ICU) for asthma worsening; group 2- patients who died from COPD worsening in the ICU; group 3 - patients who died from COPD in non-ICU departments in the aforementioned institution in a recent two-years period. The number of hospital admissions and letal outcomes was correlated with mean concentration of NO_2, SO_2, CO and soot measured during 4 consecutive days preceding these events at 20 locations in Belgrade. Results: in the analysed period, 34 patients were admitted in the ICU for asthma worsening; in the same period hospital deaths for COPD worsening in the ICU and non-ICU departments occurred in 77 and 75 patients respectively. As regards to non-ICU hospital deaths for COPD worsening, of all analysed factors, the only significant difference existed related to concentration of CO between days with and without letal outcomes (1.47 ± 08 vs. 1.24±0.6; P 0.03) Unlike that, the only significant difference for ICU hospital deaths for COPD worsening, was registered for SO_2 concentration (18.4 vs. 16.1; P 0.006). Related to asthma worsening, none of the analysed pollutants was found as significant. Conclusion: based on the obtained results, air pollution might influence COPD and even asthma worsening in a way that requires further prospective controlled studies on greater number of patients. 75 patients died for COPD worsening in non-ICU departments; in the same period

1. INTRODUCTION
According to GOLD, outdoor air pollution is widely accepted as one of the risk factors for COPD occurrence, together with tobacco smoke, occupational dusts and indoor air pollution (1). Nevertheless, out of the many inhalation exposures, only tobacco smoke, occupational dusts and chemicals can cause COPD on their own (2,3,4).

The role of outdoor air pollution in causing COPD is unclear, but appears to be small compared with that of cigarette smoking. As it has been clearly demonstrated that infection (bacterial and viral) plays a major role both in the COPD pathogenesis and exacerbations, the analysis of the influence of other factors is additionally complicated.

We set out to determine whether and in which way air pollution contributes to disease exacerbation and mortality of hospital patients with chronic obstructive pulmonary disease and asthma.

2. METHODS

A retrospective study was made that included 3 groups of hospitalized patients in the [1]Institute for Lung Diseases (ILD), Clinical Centre of Serbia, Belgrade in a recent two-year period. Group 1 included patients admitted to intensive care unit (ICU) for asthma worsening; group 2 included patients who died from COPD worsening in the ICU, whilst group 3 consisted of patients who died from COPD in non-ICU departments.

The data about the course of the disease and treatment outcome were acquired from the original patients' dossiers.

The mean concentration of NO_2, SO_2, CO and soot were measured at 20 locations in Belgrade and the data included here were obtained from the original official reports.

All the data were entered into a single Excel database. Statistics applied are a one way Anova test, independent samples test, Pearson correlation.

The number of hospital admissions and lethal outcomes was correlated with mean concentration of NO_2, SO_2, CO and soot measured during 4 consecutive days preceding these events.

3. RESULTS

In the analysed period, 34 patients were admitted in the ICU for asthma worsening; in the same period hospital deaths for COPD worsening in the ICU and non-ICU departments occurred in 77 and 75 patients respectively.

The mean concentrations of the air pollutants in days with and without non-ICU hospital deaths for COPD worsening are presented on Table 1. Of all analysed factors, the only significant difference related to the concentration of CO between days with and without lethal outcomes (1.47 ± 08 vs. 1.24±0.6; P 0.03)

Air pollution in days with and without ICU hospital deaths for COPD worsening is presented in Table 2. Unlike non-ICU hospital deaths, the only significant difference for ICU hospital deaths for COPD worsening was registered for SO_2 concentration (18.4 vs. 16.1; P 0.006).

The mean concentrations of air pollutants in days with and without asthma worsening are presented in Table 3. As regards to this patient group, none of the analysed pollutants was found to be significant.

*Table 1. Mean concentrations of pollutants in days with and without non-ICU hospital deaths (four days preceding the lethal outcome); *: P< 0.05*

		mean	SD	minimal	maximal
soot	with	38.5	19.2	13.3	125.1
	without	35.5	16.8	12.5	142.2
NO_2	with	36.6	13.7	8.1	82.5
	without	34.7	11.9	7.5	93
SO_2	with	18.7	9.4	6.7	41.1

	without	16.2	9.5	5.2	55
CO*	with	1.4	0.8	0.6	4.5
	without	1.2	0.6	0.5	4.5

*Table 2. Mean concentrations of pollutants in days with and without ICU hospital deaths (four days preceding the lethal outcome); *: P< 0.05*

		mean	SD	minimal	maximal
soot	with	35.7	15.4	15.2	83.5
	without	35.8	17.3	12.5	142.2
NO_2	with	33.8	12.9	7.7	85.1
	without	35.0	12.1	7.5	93.0
SO_2*	with	18.4	9.0	7.7	46.1
	without	16.1	9.5	5.2	55
CO	with	1.2	0.6	0.6	4.5
	without	1.2	0.6	0.5	4.5

Table 3. Mean concentrations of pollutants in days with and without asthma worsening preceding hospital deaths (four days preceding the lethal outcome)

		mean	SD	minimal	maximal
soot	with	31.9	7.7	15.4	55.7
	without	36.0	17.3	12.5	142.2
NO_2	with	33.4	6.2	21.9	45.5
	without	35.0	12.3	7.5	93.0
SO_2	with	14.8	9.6	6.8	42.1
	without	16.5	9.5	5.2	55.0
CO	with	1.0	0.3	0.6	2.2
	without	1.2	0.6	0.5	4.5

4. DISCUSSION

Despite sufficient literature data about the influence of the air pollution to COPD exacerbations, all aspects of this problem have not been fully elucidated. The results of the current study are in line with our previous analysis that did not confirm a significant influence of the air pollution by itself to asthma exacerbations (although strong correlation existed between asthma exacerbations and meteorological factors) (5).

One point should be addressed when discussing the isolated influence of the air pollution to COPD and asthma worsening: the key point in asthma pathogenesis is inflammation, which in the same time may cause COPD worsening. On the other hand, meteorological factors can significantly influence the degree of inflammation in small airways, which is why the analysis of the isolated influence of the air pollution to the aforementioned conditions carries a certain bias.

The current study revealed a possible influence of CO and SO_2 concentrations on COPD worsening or death. The possible mechanisms of that influence were addressed in some recent studies, suggesting that some fluid imbalance in the small airways, together with pollutant exposure, could cause airway obstruction with segmental increase in airway resistance and rise in distal pressure (6, 7). In

an urban environment with high pollution, as in our study, the concentration of heavy (positive) ions is higher than the concentration of light (negative) ions. The fusion of heavy ions and pollutant particles causes local irritation, airway inflammation, and increased epithelial permeability (8).

On the other hand, it is also well known that the influence of ions coincides with (or even precedes) the incoming cold front that was shown to be associated with the spontaneous pneumothorax (SP) occurrence. As SP and asthma share some common pathophysiological aspects (inflammation of the small airways that causes blebs isolation – the main mechanism in the SP onset), it becomes clear that it is not easy to analyse the influence of the air pollution without taking account of meteorological factors. Furthermore, one earlier analysis in the same geographic location as in our study (9), revealed situations with fog (cold, wet weather phasis 6hv) as unfavourable for both acute respiratory infections and asthma.

The explanation of these findings is more complex. Although it was confirmed that the frequency of asthma exacerbations was higher on misty or foggy nights than on clear nights, it is not clear whether this frequency is related to airborne water droplets, or to the meteorological condition that causes mist or fog (10). Because a higher atmospheric temperature on misty or foggy nights indicates a larger saturated amount of airborne water droplets, other recent studies suggest that mist and fog may be a stimulus for bronchoconstriction (11, 12).

In brief, the current study indicated the possible contribution of some air pollutants to asthma and COPD worsening and death. Further controlled studies are necessary in order to demonstrate if it is possible to delineate the influence of the external pollution from meteorological factors.

5. ACKNOWLEDGEMENTS

This paper is supported by the Grant of the Ministry of Science and Technological Development of Republic of Serbia, as a part of a project TR21009 within the framework of Technological development programme.

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5 Air quality management

5.1 Co-benefit and co-control studies in Norway

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ABSTRACT
Today's air quality management requires integrated and coordinated measures where urban air quality planning includes also greenhouse gas (GHG) emissions and climate change issues. Several studies evaluating different strategies were recently performed in Norway, looking at different geographic areas in and outside Norway.

In both developing and industrialized countries, abatement of air pollution and mitigation of climate change have generally been treated separately. The tools that have been made available for investigating scenarios for reducing local impacts and health effect improvements can also be used in order to investigate cost effective actions aimed at reducing greenhouse gas emissions. These approaches would lead to a co-benefit as it will both improve the health of people and give climate benefits at best possible costs.

Approaches prepared for co-benefit studies in Norway as well as plans for co-control projects in China are presented in this paper. These approaches also have lead to specific developments and focus on issues previously not included in traditional air pollution abatement studies.

INTRODUCTION

During recent years focus has shifted from local air pollution and its threat to health and environment, toward global threats due to greenhouse gas (GHG) emissions and their impact on climate. In both developing and industrialized countries, abatement of air pollution and mitigation of climate change have generally been treated separately. There are, however, large benefits in considering the control options together; such approaches would mostly lead to increased health and/or climate benefits and decreased costs.

As global warming has recently taken most of the focus in the political decision processes, local and regional challenges seem to have been set aside. Today's air quality management requires integrated and coordinated measures where urban air quality planning includes also greenhouse gas (GHG) emissions and climate change issues. Several studies evaluating different strategies were recently performed in Norway, looking at different geographic areas in and outside Norway.

NILU has recommended decision makers take a balanced view, as it is possible to reduce both GHG emission and local pollution simultaneously. International experience shows that climate change mitigation can result in a simultaneous reduction in air pollution. IPCC states in its fourth assessment report that "integrating air pollution abatement and climate change mitigation policies offers potentially large cost reductions compared to treating those policies in isolation".

Possible co-benefits

The IPCC recommends a co-benefit thinking in the climate change mitigation. To support this argument, a number of technologies and measures in the energy supply, transport, building and industry sector have been identified to also help abate urban air pollution.

Focusing on co-benefit actions is now and will in the future, be an important part of NILU's research both in the local and regional air quality management planning. It is necessary also in the study of climate change, including the study of mitigation steps and their effects.

A stringent global climate policy will lead to considerable improvements in local air quality and consequently improves health. Measures to reduce emissions of greenhouse gases to 50% of 2005 levels, by 2050, can reduce the number of premature deaths from the chronic exposure to air pollution by 20 to 40%. (Bollen et al 2009).

Climate policy will already generate air quality improvements in the OECD countries in the mid-term; whereas in developing countries these benefits will only in the longer run show to be significant (OECD, 2008).

The integrated long-term cost-benefit approach balances the means to lower simultaneously the adverse impacts of climate change and air pollution and shows significant climate benefits only after 2050. In summary, these simulations and results from the literature review suggest that for countries giving priority to GHG mitigation, the local air pollution co-benefits provide an additional incentive by off-setting a proportion of the GHG mitigation costs. These co-benefits could be larger than currently estimated since most estimates omit the possible co-effects of GHG mitigation on indoor air pollution, which is expected to be large in countries such as India and China (IPCC, 2007).

The NILU planning tool

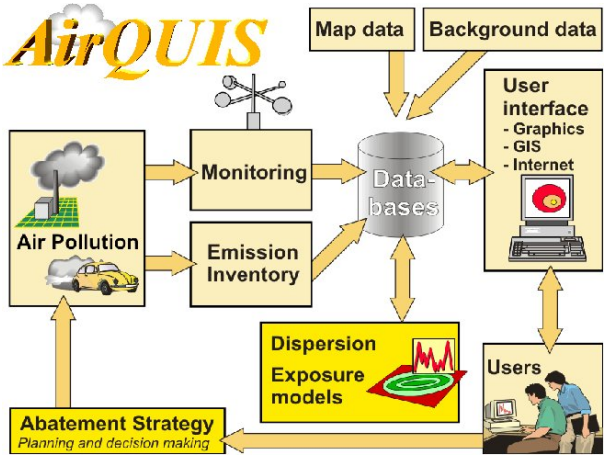

Figure 1: The NILU developed air quality planning tool; AirQUIS.

The NILU planning tool AirQUIS has been developed by NILU to handle a number of air pollution tasks and challenges. It is based on a Geographical Information System (GIS). The main objective of a modern environmental surveillance platform like AirQUIS is to enable direct data and information transfer and obtain a remote quality control of the data collection.

The system combines monitoring, data presentation and modelling in one package. It also includes a module for emission inventorying, which enable to connect fuel consumption, energy use and industrial processes with emission rates. The system can estimate classical air pollutants as well as greenhouse gas emissions. The planning tool thus enable the user not only to present and evaluate the present situation, but also to undertake environmental planning for a sustainable future both when local impacts and health effects are concerned and when GHG emissions are to be evaluated. The GIS platform, on which the system is operated, provides easy access to the data and gives a perfect and easily understandable data presentation tool.

Norwegian studies and actions

Background for measures employed in Norway is to be found in several commitments. In addition to the need to comply with air quality directives, Norway undertakes to reduce global greenhouse gas emissions by the equivalent of 30% of its own 1990 emissions by 2020, and intends to cut the global emissions equivalent to 100% of its own emissions within 2030. In other countries, most notably in China, authorities are also increasingly looking to measures that simultaneously improve local air quality and reduce GHG emissions.

Measures to achieve these goals include moving from fossil based energy to more use of bio fuels. This however may change the environmental challenges. While the GHG emissions will be reduced, emissions of particulate matter, nitrogen oxides and polyaromatic hydrocarbons may increase and give rise to more local air pollution as well as to more harmful pollution composition, and increase exposures of human populations. Combination of criteria pollutant changes and GHG emissions may lead to increasingly harmful effects on our built cultural heritage.

Carbon capture and storage technologies have been in focus for some time, and are subject to scrutiny from the point of view of their wider environmental impacts. Studies of co-benefit of different policies, most notably in the area of air pollution and climate change abatement, have further need for methodological developments. These include development and application of integrated assessment taking into account various geographic scales, improved exposure assessment for human population and establishment of exposure-response relationships, as well as further studies to increase our knowledge on local and regional aerosol formation and its influence on climate forcing and weather patterns.

Integrated studies

The integrated and co-ordinated projects where urban air quality planning included also greenhouse gas emissions and climate change issues was presented based on a discussion that NILU introduced in a seminar in The World Bank meeting in May 2006.

One of the main issues is to what extent GHG mitigation costs would be partially covered by the co-benefits in terms of reduced local air pollution. The bottom-up emission inventories applied in local air pollution mitigation and air pollution improvement studies enable GHG emissions to be specified for individual sources or groups of sources. This will in turn enable GHG emission strategies to be specified enough to enable the costs of these actions to be estimated. The approach will thus lead to a better understanding of the most cost effective actions both for reducing local impacts and reducing GHG emissions.

Scenarios Oslo

Studies have been performed in Oslo in order to evaluate the exposure to people for alternative scenarios identified in order to reduce the air pollution impacts.

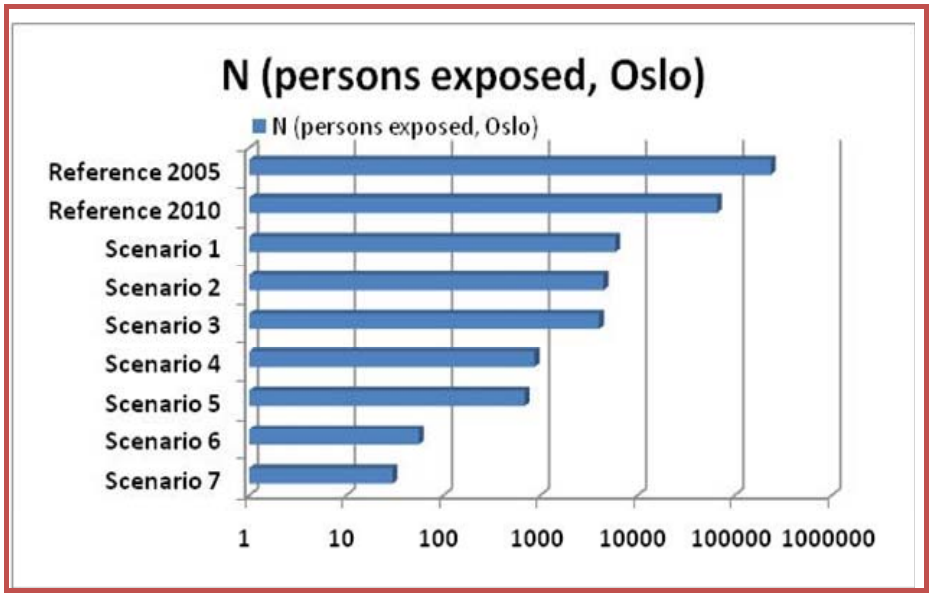

Figure 2: The number of people exposed to the 8th highest daily grid value of PM_{10} ($\mu g/m^3$) exceeding 50 $\mu g/m^3$ (National Target). Reference year 2005 and 2010 have been compared to seven different scenarios for reducing PM_{10} exposures.

Simultaneous estimates of GHG emission reduction potential have been part of these studies. A traffic volume increase from 1990 to 2005 of 3% in energy per car resulted in a 17% increase in GHG emissions.

Norwegian Climate Policy and Carbon Capture

The Norwegian Government is committed to develop Carbon Capture and Storage (CCS) technologies, and hopefully contribute to make this technology commercially viable at a global scale.

Carbon Capture and storage programmes are already being undertaken in Western Norway. NILU has been working on the effects of local impacts from possible amine emissions. There may be several local negative effects of reducing compounds impacting global climate.

The consumption of energy used for the CO_2 capture has also been a hot issue lately together with the emissions that comes from the production of this energy. It is known that there will be more than 50 different substances that are produced within the process. Some of these will probably be cleaned and taken out as liquid or solid waste, follow the CO_2 stream for deposition and be emitted to air. After emission these products will enter into the photochemical processes and additional components will be formed

NILU emphasizes that an evaluation of the potential impact for health and the environment from a CO_2 capture plant based on amines should be mandatory. An evaluation should at least look into a theoretical exercise for establishing possible effects of the different types and quantities of amine emissions. The need for collecting emission data and knowledge of health and environmental impacts of these emissions should be a requirement in the emission permit to the capture plants.

From fossil fuel to bio fuels

Moving from fossil based energy to more use of bio fuels may change the environmental challenges. The GHG emissions as CO_2 will be reduced, but emissions of PM, PAH and NO_x may increase and give rise to more local air pollution.

Relative to a gas fired power plant with cleaning equipment a bio fuel based power plant at the same capacity will emit more pollutants.

Climate change and our Cultural Heritage

Traditionally our cultural heritage; monuments and buildings have been impacted by pollutants linked to local sources and compounds such as SO_2 and NOx. Combining these pollutants with greenhouse gases and climate change will accelerate the impacts. It will speed up the deterioration and will require more maintenance.

CDM an instrument for limiting GHG emissions

With the Kyoto Protocol becoming legally binding from 16 February 2005, the Clean Development Mechanism (CDM) is becoming a key instrument for limiting greenhouse gas emissions (GHG) and promoting sustainable development.

For both developing and developed countries to benefit from the CDM, it is important to establish increased awareness and understanding of its various aspects. Building capacities in the baseline methodology and assessment of GHG emission reductions/sequestration benefits of CDM projects are keys to the successful development and implementation of the CDM.

The following types of GHG mitigation or sequestration projects and activities can be eligible for CDM**:**

- Renewable energy technologies
- Energy efficiency improvements - supply side and/or demand side
- Fuel switching (e.g., coal to natural gas or coal to sustainable biomass)
- Combined heat and power (CHP)
- Capture and destruction of methane emissions (e.g. from landfill sites, oil, gas and coal mining)
- Emissions reduction from such industrial processes as manufacture of cement
- Capture and destruction of GHGs other than methane (N_2O, HFC, PFCs, and SF_6)
- Emission reductions in the transport sector
- Emission reductions in the agricultural sector
- Afforestation and reforestation
- Modernization of existing industrial units/equipment using less GHG intensive practices/technologies (retrofitting)
- Expansion of existing plants using less GHG intensive-practices/technologies (Brownfield projects)
- New construction using less GHG-intensive practices/technologies (Greenfield projects)

Seven basic stages have been identified in the development of a CDM project.

Co-control and co-benefit projects China

NILU proposed a new project for China together with Norwegian institutions and CAI Asia developing a programme for co-control. The project places a strong emphasis on assisting Chinese institutions in building technical capacity and expertise, specifically on the co-control of air quality, energy and climate change. By building capacity for co-control, this project will make it easier for China to reduce local air pollution and contribute to greenhouse gas reductions. This is fully in line with Norwegian priorities for development cooperation, which has made climate change and environmental protection a cornerstone of its development cooperation.

The proposed project is a national level project, with demonstration of co-control policies concentrated on cities in Western China, while a training component will cover the national, provincial and local levels.
The **objectives** of the project are:

- To provide policy guidance and advice on integrated control of air pollution and GHG emissions in the 12^{th} and 13^{th} 5 year periods (FYP).

- To demonstrate the viability of the co-control approach in addressing environmental challenges related to air quality and energy management at the regional and local level.
- To enhance the capacity of MEP and other related institutions, at national, regional and local level to formulate and carry out simultaneous cuts in air pollution and GHG emissions in the 12th and 13th five year periods.

The objectives will be achieved through **three main project components:**

1. National level policy analysis, suggestions and support on co-control
2. Demonstration and pilot cases of integrated AQM and co-control at the urban level, in selected cities in Western China.
3. Capacity building for integrated AQM and co-control at national, regional and local level, with an emphasis on Western China Provinces.

NILU also performed studies in China related to cost effectiveness in the city of Guangzhou.

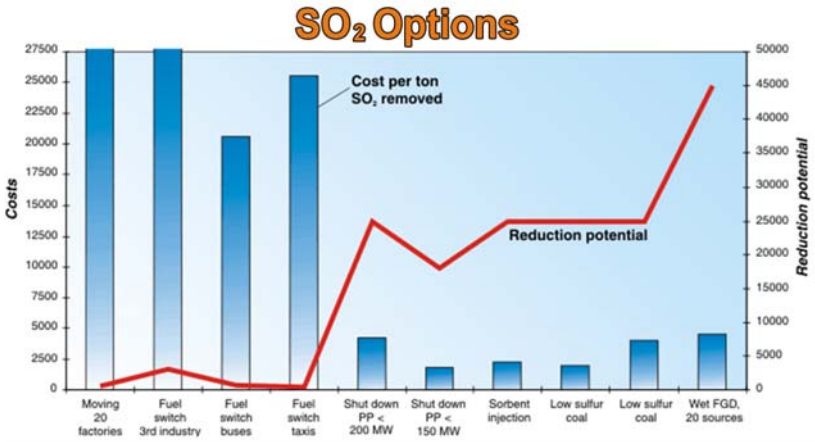

Figure 3: Ten mitigation actions identified in order to reduce the SO_2 concentrations in Guangzhou summarized the cost of actions relative to the reduced potential for SO_2 exposure in the city.

A cost-benefit study was undertaken in three cities in the province of Shanxi, China. Comparisons of cost-benefits were performed for various identified control actions in order to reduce SO_2 and TSP exposure and health impacts in the three cities. The project was implemented through the cooperation between Chinese and Norwegian expert in order to develop a "Master Plan against Air Pollution in Shanxi Province" (Shanxi Province, 2005).

The modeling exercise conducted through the Sino-Norwegian project provides a unique opportunity to understand impacts of city level pollution abatement tools in one of China's most energy intensive cities. The cost-benefit analysis is quite unique given that the health economics approaches are relevant in order to evaluating the cost/benefit of interventions. Even if the Chinese national health data might be sparse, inconsistent, and in areas questionable the study has done well in finding alternative data sources and compared data with other international databases (Aunan et al, 2004).

The studies in Shanxi have shown that there are actions where the cost of implementing these actions are less than the cost-estimated benefits gain in improved health effects in the population. The scenario-based and pollution sources-oriented health benefit evaluation of air pollution in the city of Taiyuan in Shanxi province have proven very useful. Even though selection of optimal control scenarios for Taiyuan requires further cost-benefit analysis, this study does provide decision-makers with evidence about not only the significance of control and prevent environmental pollution, but also give indications of what measures are most effective (Zhang et al, 2009).

Areas of further development

NILU have identified further needs for development in order to continue the work related to integrated assessment, co-benefit studies and co-ordination of climate change and local air pollution issues. Some of these issues are:

- Exposure-response on human health
- Local and regional influence of aerosols on climate forcing and weather patterns
- Development and application of combined integrated assessment at various scales
- This requires competence on:
- Emission inventories, air quality and atmospheric science
- Climate and pollution policies
- Integrated assessment modelling, e.g. cost effectiveness / optimisation of abatement measures

The issues presented in this paper are important issues in order to improve the tools for integrated assessments, and this work will continue in Norway as well as at NILU.

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5.2 Correlation between PM_{10} and black smoke in Belgrade

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Particulate matter air pollution is typically monitored in the ambient air as total suspended particulate (TSP), particles less then 10 microns (PM_{10}), and black smoke (BS). Particles included in PM_{10} or even smaller particles, so called fine particles that are below 2.5 microns in diameter ($PM_{2.5}$) are of greater health concern than particles of all sizes (TSP), since smaller particles are more likely to penetrate into the deep lung. PM_{10} is used as a summary indicator of air quality, due to its importance as a health determinant. It is likely that individual pollutants other than PM_{10} can have additional impact on health alone or in combinations, but it is currently unclear how to estimate them.

The paper presents correlation between PM_{10} and BS measurements in a Belgrade urban monitoring site, considered a traffic related site. The monitoring equipment is located in a street running along the center of the old part of the city, with a legal speed limit of 50 km/h. In order to estimate the correlation between PM_{10} and BS, 24 hour mean concentrations were used for period January 2006-December 2008. We tested correlation during seasons, heating period (November-March) and for the whole year. We tested linear relationship in the equation given by Y=a* X+b, i.e. PM_{10}= a * BS + b, where parameters **a, b** coefficient of correlation **r** were determined. Results are presented in tables and charts and it can be seen that during winter (cooler part of the year) there is functional correlation **r** = 0.677 of medium strength between mass concentration of PM_{10} and levels of BS, which is very similar to the whole year where **r** = 0.625.

5.3 Air dust concentration in the vicinity of ash disposal site, depending on the size of pond ("Water Mirror")

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ABSTRACT

Thermal power plants Nikola Tesla "A" and "B" (TENTA and TENTB in the next text) located in Obrenovac near Belgrade use lignite in power production. Use of coal with high ash content leads to increasing environmental problems with gaseous emissions but also with the disposal of ashes residues. Total sizes of ashes/slag depots are 600ha and 382ha for TENTA and TENTB respectively; active cassettes have dimensions ~200ha and ~130ha. Active cassettes of the disposal sites are covered by rather large waste ponds, which sizes vary depending on working condition of sluice system and on meteorological conditions. The waste ash, in liquid configuration 10 L water per kg of ash, is transported to the disposal sites by the use of conveyer tubes. The sluice system is consisted of nozzle net for damping disposal sites, but there are situations when this system is out of working for the long time due to technical problems or due to negative air temperatures. Size of ponds in such situations could be importantly reduced. An investigation was initiated to find relation between sizes of ponds and air dust concentration in the vicinity of ash disposal sites. Results of the investigation are expecting, greater sizes of dried disposal site surfaces in combination with stronger winds give greater dust emission and greater air dust concentration.

INTRODUCTION

If surfaces of ashes and coal depots are sufficiently dry, i.e. if surfaces of ashes/slag depots are not protected with pond strong wind is able to roll "greater" particles (known as surface creep) or to lift some of them to the distances up to approximately 1m downwind (saltating particles). Saltating, sand sized particles sandblast the surface and eject fine particles which remain suspended in the air for long period by air turbulence and which can be transported to the great distances downwind (Fig.1).

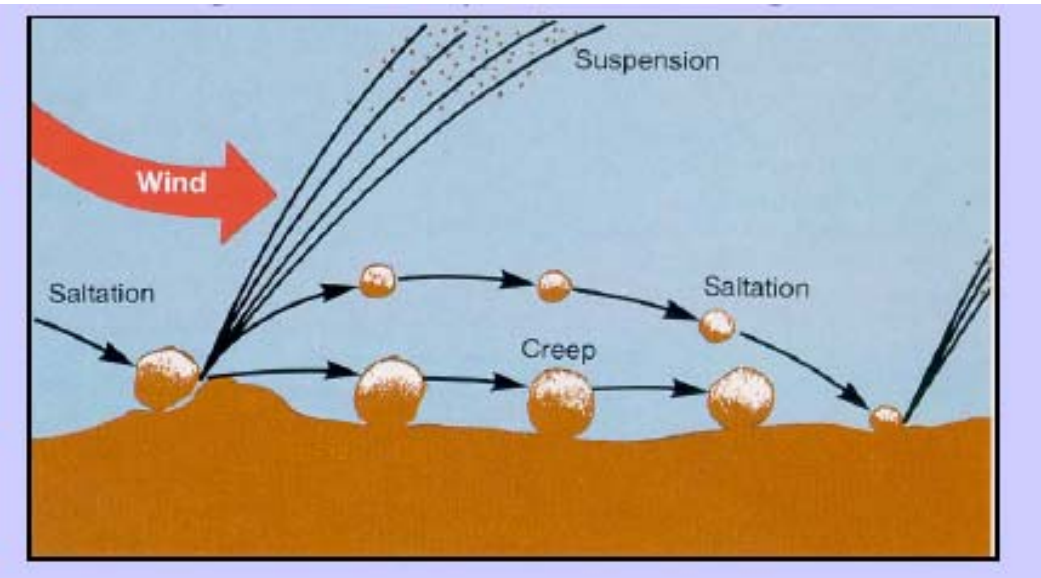


Fig. 1. Saltation of dust. Source: http://en.wikipedia.org/wiki/saltation_(geology)

Several authors have pointed out saltating (sandblasting) as the most important mechanism for lifting dust aerosols to the atmosphere. It is parameterized with formula Shao and Raupach (1993):

$$q = A\frac{\rho}{g}\sum_{u_*} u_*\left(u_*^2 - u_{*tv}^2\right) \qquad (1)$$

where q is the instantaneous horizontal (saltation) mass flux (g cm^{-1}), A a unit less parameter (usually assumed to be equal to 1), ρ density of air (g cm^{-1}), g acceleration of gravity (cm s^{-2}), u_* wind shear velocity (cm s^{-1}) and u_{*tv} is threshold shear velocity (cm s^{-1}).

The wind shear velocity u_* is related to wind speed at height z under neutral condition (wind speed greater or equal to 6 ms^{-1}) by:

$$U(z) = \frac{u_*}{k}\ln\left(\frac{z-D}{z_0}\right) \qquad (2)$$

where $U(z)$ is wind speed at height z, k von Karmann's constant (0.4), z_0 roughness height (cm) and D displacement height (cm). The threshold shear velocity u_{*tv} is the minimum friction wind speed assumed to give dust emission; it is related to soil roughness and soil characteristics.

Because of sandblasting by saltation-sized particles, vertical dust flux F_a (g cm^{-2} s^{-1}) is linearly related to q by a constant K (cm^{-1}) Marticorena at all (1997):

$$F = K \cdot q \qquad (3)$$

The value of K is typically on order 10^{-5}-10^{-6} and it is strongly dependent on depots surface texture, crusting and moisture.

Numerical experiment

In order to calculate lifting of dust from ash depots, dry surfaces of disposal sites were divided into numerous numbers of smaller cells dust sources, characterized by its dimensions 100m x 100m, coordinates and surface texture (parameters u_{*tv}, z_0, D and K). On his way, the disposal area sources are represented as a sum of numerous smaller surfaces which are treated in the model as the point dust sources. Several sizes of dried surfaces were taken into consideration, that is, active cassettes were covered with ponds of different sizes and shapes.

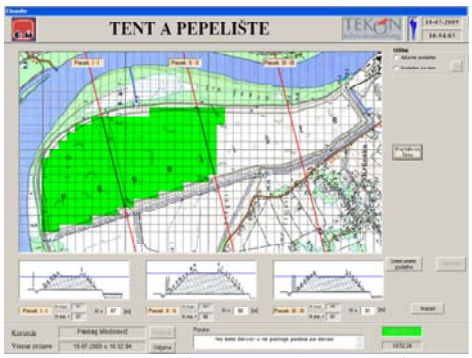


Fig. 2. Ash disposal site TNTA, dry 100% of active area white painted ~ 130 ha

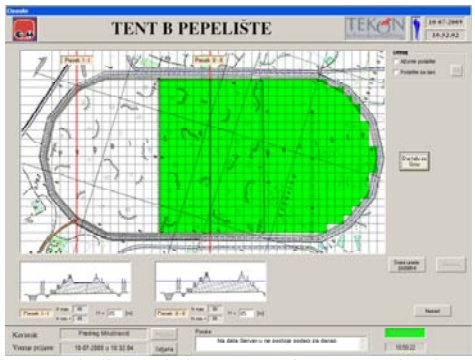


Fig. 3. Ash disposal site TNTB, dry 100% of active area white painted ~ 200 ha

In this experiment sizes of ponds were varying, from 0% of active cassette size fig.2 and fig.3 to 25% of its size fig.4 and fig.5. to 50% of its size fig.6 and fig.7 and at last to75% of its size fig.8 and fig.9. Shapes of ponds were not considered in this paper.

Some the other characteristics of ash disposal sites TNTA and TNTB are presented in Tables 1 and 2.

Surface	382 ha active ~ 130 ha
Height	18-25 m
Volume	112.000.000 m^3

Table 1. Ash/slag disposal site TentA

Surface	600 ha active ~ 200 ha
Height	29 m
Volume	174.000.000 m^3

Table 2. Ash/ slag disposal site TentB

The experiment was performed so to simulate dust emission from ash disposition sites in case when ash deposits have not adequate water protection. This experiment was designed on the base of using adverse meteorological conditions after disposal sites started to emit dust - wind speed greater than 9.14ms^{-1} (10 ms^{-1}, 15ms^{-1} and 20 ms^{-1}).

Calculating domain was 53.5km x 32.5 km, with dimensions of network cells 100m x 100m. Values of parameters u_{*tv}, z_0 and D were taken from literature $u_{*tv} = 0.29 cms^{-1}$, Okin G.S. Gillette D.A. (2004), $z_0 = 33.3 \mu m$ and

$D = 1mm$ from Zender et al (2002). On the bases of eq. 2 and taking previous values of the parameters, threshold wind speed at 10 meters level was calculated $U_t(z) = 9.14ms^{-1}$. The idea of this work was to recognize importance of adequate maintaining a pond of ash disposal sites and of adequate maintaining its size. We did not discuss in details mechanism of dust lifting, parameters figured in the model equations were downloaded from literature, but dew to emphasize importance of this problem we varied parameter K taking its lower and upper limits 10^{-6} and 10^{-5} respectively.

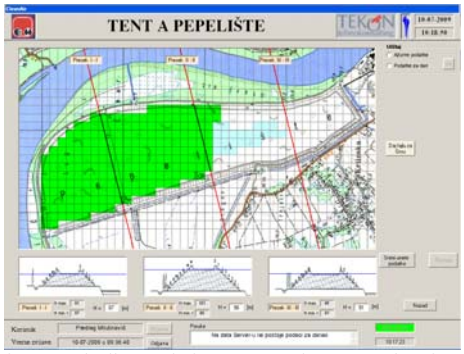


Fig. 4. Ash disposal site TNTA, dry 75% of active area white painted, blue pond

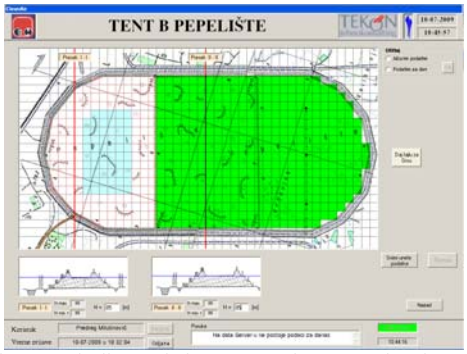


Fig. 5. Ash disposal site TNTB, dry 75% of active area white painted, blue pond

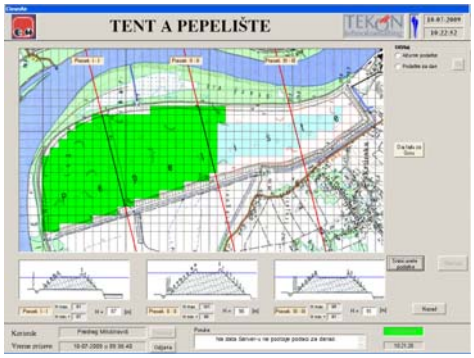


Fig. 6. Ash disposal site TNTA, dry 50% of active area white painted, blue pond

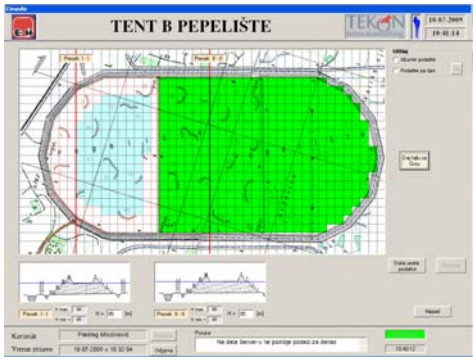


Fig. 7. Ash disposal site TNTB, dry 50% of active area white painted, blue pond

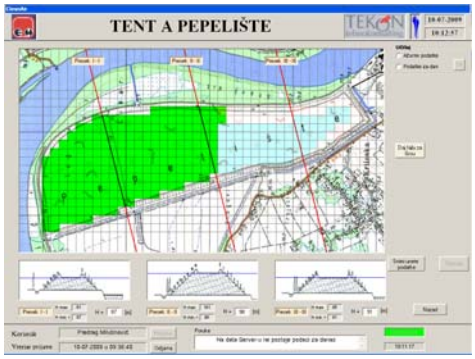


Fig. 8. Ash disposal site TNTA, dry 25% of active area white painted, blue pond

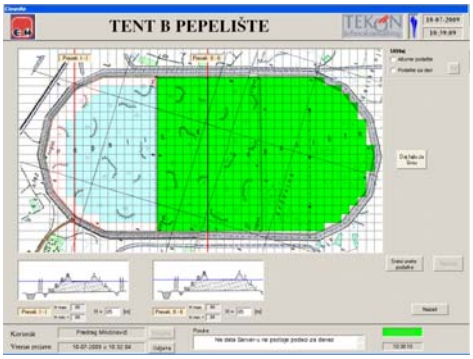
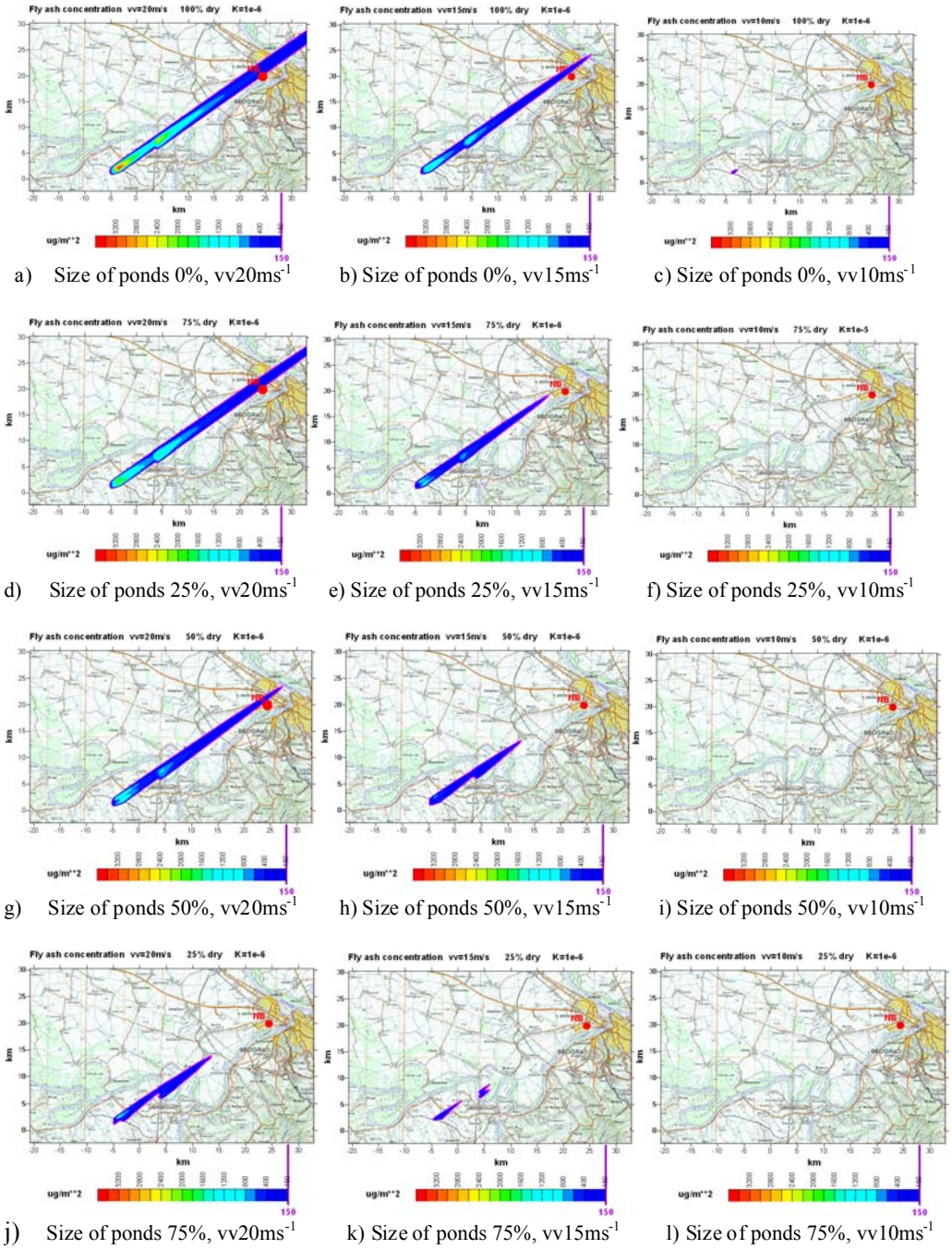


Fig. 9. Ash disposal site TNTB, dry 25% of active area white painted, blue pond

Results

Two sets of experiments were realized varying parameter K due to simulating lower and one order greater dust lifting from ash disposal sites and due to more powerful of presentation their influence to the environment, depending on their

ponds size. Lifted dust flux reached a maximum of 2520 μg m^{-2} s^{-1}. for wind speed 20ms^{-1} and lower value of K, 845 μg m^{-2} s^{-1} and 65 μg m^{-2} s^{-1} for wind speeds 15 m s^{-1} and 10 m s^{-1} respectively. Taking higher value of K dust fluxes were one order greater i.e. 25205μg m^{-2} s^{-1}, 8447 μg m^{-2} s^{-1} and 652 μg m^{-2} s^{-1}.



a) Size of ponds 0%, vv20ms^{-1} b) Size of ponds 0%, vv15ms^{-1} c) Size of ponds 0%, vv10ms^{-1}

d) Size of ponds 25%, vv20ms^{-1} e) Size of ponds 25%, vv15ms^{-1} f) Size of ponds 25%, vv10ms^{-1}

g) Size of ponds 50%, vv20ms^{-1} h) Size of ponds 50%, vv15ms^{-1} i) Size of ponds 50%, vv10ms^{-1}

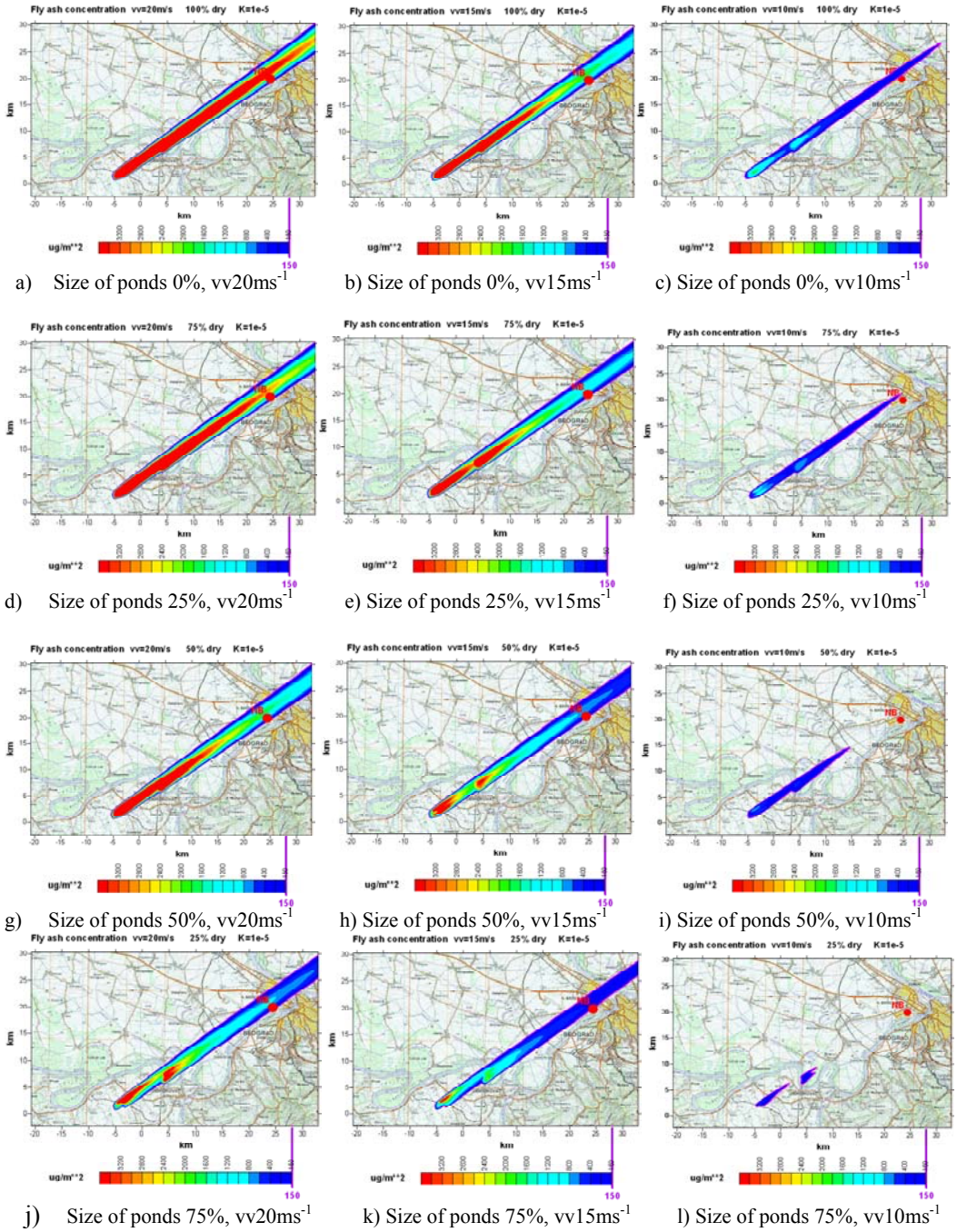
j) Size of ponds 75%, vv20ms^{-1} k) Size of ponds 75%, vv15ms^{-1} l) Size of ponds 75%, vv10ms^{-1}

Fig.10. Air dust concentration for K=1e^{-6} and for various wind speeds vv (20ms^{-1}, 15ms^{-1} and 10ms^{-1}) and for various sizes of ash disposal sites ponds (0%, 25%,50% and 75% of a size of disposal sites active cassette surface)

Taking, from the environmental point of view the most adverse meteorological situation, wind speed of 20ms^{-1} and 100% dry disposal active cassette surface (no presence of pond) and taking lower values of the parameter K, maximum ash concentration 2 meters above surface reached 3300μg$\cdot$m^{-3} (fig 10.a)). In the same

time for the 25% of size of dried surface of disposal sites, maximum ash concentration was 960µgm^{-3} and on the remote places ash concentrations were under limit value of 150 $\mu g \cdot m^{-3}$ for populated area (fig 10.j)).

Using higher limit of K=1e^{-5}, maximum air dust concentrations are one order greater but these results also illustrate reduction negative influences of ash dispose sites to the environment when size of pond grows (fig.11.a)-l1.l)).



a) Size of ponds 0%, vv20ms^{-1} b) Size of ponds 0%, vv15ms^{-1} c) Size of ponds 0%, vv10ms^{-1}

d) Size of ponds 25%, vv20ms^{-1} e) Size of ponds 25%, vv15ms^{-1} f) Size of ponds 25%, vv10ms^{-1}

g) Size of ponds 50%, vv20ms^{-1} h) Size of ponds 50%, vv15ms^{-1} i) Size of ponds 50%, vv10ms^{-1}

j) Size of ponds 75%, vv20ms^{-1} k) Size of ponds 75%, vv15ms^{-1} l) Size of ponds 75%, vv10ms^{-1}

Fig.11. Air dust concentration for K=1e^{-5} and for various wind speeds vv (20ms^{-1}, 15ms^{-1} and 10ms^{-1}) and for various sizes of ash disposal sites ponds (0%, 25%, 50% and 75% of a size of disposal sites active cassette surface)

Comments and conclusions

Presented results confirmed expectations that greater sizes of ash disposal surfaces in better way restrain negative influences of ash disposal sites to their environment. In this paper surfaces of ash depots were assumed to be described with parameters taken from literature u_{*tv}, z_0 and D. Value of parameter K also was taken from literature, but its value arbitrary varied as lower and upper limit taken from literature too. Obviously, for chosen ash deposit sites of TNTA and TNTB it is necessary to investigate in details size distribution of particles and of disposal sites surfaces like roughness, threshold shear velocity and especially their texture because final results depend very much of values of parameter K. Appropriate meteorological measurements, continuous monitoring of ponds shapes and sizes are necessary to better understanding importance of appropriate maintaining disposal sites ponds due to minimizing environmental problems with ash disposal sites of TNTA and TNTB. At last both models, of dust lifting and of atmospheric dust dispersion, have to be calibrated in field experiments and using measured values of dust concentrations in numerous points of monitoring network at representative locations of TNTA and TNTB.

ACKNOWLEDGEMENTS

This work has been supported by the Ministry of Science and Technological Development of the Republic of Serbia funded through the 15005 – TR project.

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5.4 Qualitative assessment of air quality using additional US EPA guidelines

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ABSTRACT

The paper shows a new methodological approach for qualitative assessment of air quality value in urban environments. The approach is based on the Standard US EPA, 451/K-94-001, with a qualitative assessment of air quality determined on the basis of an annual air quality index calculation. The methodology used in the paper is based on statistical methods as well as on an annual air quality index calculation method. Calculation of the index is based on the original relation of average measured annual immission concentrations of pollutants and their impact on population's health using the equation given by the Standard, US EPA 451/K-94-001. The air quality value obtained by this method allows for continuous assessment of air quality over a long time period, providing a basis for epidemiologic conclusions and determination of areas in which health risk assessment is needed. It also represents the possibility of assessing the need for adequate air protection measures. An air quality assessment for the city of Nis is given in terms of standard air pollutants for the period from 1994 to 2008 using this method.

Key words: air pollution, air quality, air quality index, modelling, health risk.

INTRODUCTION

Identification of air pollution level, air quality evaluation and assessment of adverse effects on human health and the bio-system is prospective if regular observation of pollutant presence in the air is implemented by using efficient standard methods and generally adopted systems for air quality control.

In world practice, air quality evaluation is based on positive legal regulation by the World Health Organisation, the European Union, as well as application of regional legal regulations in several countries (USA, Canada, Russia, France, England, etc.) with the aim of ensuring an air purity level safe for human health and the environment.

Some European countries use a method for air quality assessment based on an "air quality index" calculation. Introduction of an air quality index became necessary after the connection between air quality (air pollution) and human health had been established. The air quality index provides a qualitative evaluation of air quality in order to inform the population about air pollution levels and effects on health. The air pollution level is defined by a range of measured transient concentrations of pollutants, as defined by individual country standards. Air pollution levels are represented by an index. Calculation of the index is regulated by individual laws in each country. The index values obtained are represented by a colour scale depending on the index/human health ratio. Information about the qualitative evaluation of air quality is very important for high-risk populations (senior citizens, children, sick persons, etc.). High-risk populations are alerted to higher

levels of air pollution via the air quality index and adequate protective measures can be taken accordingly.

Air quality index in the EU countries most often use ranges from 1-6 and 1-10. The US Environmental Protection Agency (US EPA) also established an air quality index which is defined by the Standard US EPA 451/K-94-001. The air quality index based on EPA recommendations represents a relation between transient and/or daily concentrations of pollutants and their effect on human health in general (Table 1). An index scale for determining air quality has been created based on daily pollutant concentrations and their effect on human health, (Fig. 1) [1].

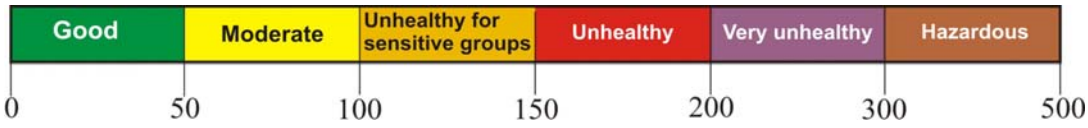


Figure 1. Air quality index scale prescribed by the Standard US EPA

Methodology

When the air quality index scale ranges from: 0 to 50, air quality evaluation is good; from 51 to 100, air quality – moderate; from 101 to 150, air quality – unhealthy for high-risk groups; from 151 to 200, air quality – unhealthy; from 201 to 300, air quality – very unhealthy and from 301 to 500, air quality – hazardous.

An adequate method for forming a correlation between average annual concentrations of pollutants and air quality index is applied in this paper, prescribed by the Standard US EPA 451/K-94-001. Moreover, this paper introduces a new air quality classification which fulfils all methodological conditions for good classification.

Correlation of average concentrations of pollutants with the air quality index is conducted by using statistical methods, plus analysis and incorporation of average pollutant concentration levels and their effects on general health of exposed population, according to the index scale given in the US EPA method.

New terms for representing air quality are introduced here based on a proper classification depending on its effect on human health in general. Nevertheless, an effort was made to meet the following principles of correct classification: principle of determination of division object category, principle of simplicity, principle of relative speciality of each part of the division, principle of unity of specific parts of the division, and principle of division speciality.

Results and discussion

The aim of the research is the creation of a new methodological approach for qualitative and quantitative evaluation of annual air quality. Qualitative and quantitative evaluation of annual air quality is based on identification of the effect of certain pollutant concentrations on the health of the exposed population. Such evaluation represents a basis for frequency analysis, effect analysis, and indeterminacy analysis when estimating potential territorial health risk from air pollution.

For potential territorial health risk estimation, measured and/or predicted concentrations of pollutant immissions are used. Health risk assessment is conducted in parts of the analysed territory where pollutant immission concentrations exceed the threshold level.

Application of the air quality index, coordinated with given annual levels of air pollution enables adequate direction of health risk assessment and forms the basis for epidemiologic inferences in the analysed territory. Therefore, the aim of this paper is focused on forming a correlation of air quality index and air quality on the one hand, and the effect of certain levels of annual concentrations of pollutants on human health on the other. Table 1 shows the original overview of the correlation between specific levels of annual pollutant immission concentrations and air quality index. The EPA Standard is given in Table 2.

Table 1. Correlation of annual pollutant immission concentration and air quality index

Level	Concentration of pollutants **(μg/m^3)**					Index gauge
	Soot	CO	SO_2	NO_2	HCHO	
I	0,0-11,80	0,0-1,43	0,0-11,80	0,0-24,00	0-0,05	0 - 50
II	11,81-50,00	1,44-3	11,81-50,00	24,01-60	0,06-0,10	51 - 100
III	50,01-77,77	3,01-3,95	50,01-77,77	60,01-84,00	0,11-0,14	101 - 150
IV	77,78-105,00	3,96-4,91	77,78-105,00	84,01-120,00	0,15-0,20	151 - 200
V	105,56-209,72	4,92-9,70	105,56-209,72	120,00-150,00	0,21-0,24	201 - 300
VI	209,73-279,17	9,71-12,89	209,73-279,17	150,01-180,00	0,25-0,29	301 - 400
VII	279,17-348,61	12,90-16,86	279,17-348,61	180,01-210,00	0,30-0,35	401 - 500

Table 2. Air quality index scale, air quality and its effect on human health

Air quality index scale	Air quality	Effect on human health
0 to 50	Good	No effect
51 to 100	Moderate	No effect (Minor health issues for extremely sensitive persons)
101 to 150	Unhealthy for high-risk groups	Health issues for the high-risk part of the population
151 to 200	Unhealthy	Health hardness for active population
201 to 300	Very unhealthy	Significant health issues for the whole population
301 to 500	Hazardous	Possibility of serious effect on health

The correlation of annual air quality index, air quality and its effect on human health provides the opportunity to compare the effect of pollutants on air quality and the health risk from air pollution. Likewise, calculation of annual air quality

index can be used for air quality mapping. If the index is used for air quality mapping, we will obtain certain fields of air quality which can be indicated in a suitable colour according to air quality scale given by US EPA (Fig. 1). The concentration limits shown in Table 1 define the air quality fields obtained.

Since the applied air classification given by US EPA does not meet the principles of good classification, this paper introduces a new classification of air quality on the basis of index value as follows: good when air quality index ranges from 0 to 50, moderate from 51 to 100, adverse from 101 to 150, extremely adverse from 151 to 200, bad from 201 to 300, and extremely bad from 301 to 500.

The air quality index for the city of Niš for the period 1994 – 2008 has been calculated according to the air quality index equation given by US EPA Standard 451/K-94-001, incorporating annual levels of immision concentrations given in table 1. The calculated values of air quality index for standard pollutants in the named period are given in Table 3.

Table 3. Annual air index quality for the city of Niš, in the period 1994–2008

Substance	Year of air quality monitoring														
	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008
	Values of Air quality index														
SO_2	163,7	96,0	76,8	97,3	58,9	55,1	16,9	38,7	51,2	46,1	52,5	55,1	57,4	59	44,5
Soot	33,8	21,2	16,9	21,2	29,6	46,5	16,9		4,23	46,5	63,4	66	82,1	73	34,9
CO	30,4	45,1	17,8	108,8	138	47,2	/	/	80,8	121,9	/	/	/	/	140
NO_x	58,6	59,6	51,8	23,2	19,6	20,3	/	/	24,8	26,1	/	/	/	/	51,7
HCHO	2,73	2,81	/	3,9	3,8	12,5	/	/	6,5	5,9	/	/	/	/	8,4

The calculated annual values of air quality index given in Table 3, show that the air quality in the observed annual periods falls into good, moderate, and adverse categories. The highest values of air quality index have been calculated with respect to concentrations of SO_2 and CO, which suggests that these are the dominant substances for air quality and human health in the region of Niš.

The possibility of using air quality index in air quality mapping is shown in the example of SO_2 for the characteristic year 1994, when the largest concentrations were observed in the entire period of air quality monitoring in the region of Niš. Calculated values of air quality index for SO_2 at measuring points for 1994 are shown in Table 4. Positions of these measuring points are shown on the air quality map in Figure 2.

In addition, in 2008, high values of CO concentrations have been detected. The air quality index for CO in 2008 is shown in Table 5, and in Figure 3, air quality fields with positions of measuring points are shown, at which concentrations were monitored in 2008.

The map of air quality fields as represented through calculated values of air quality index, simply and practically indicates the parts of the analysed territory in which health risk assessment has to be performed. By calculating the air quality

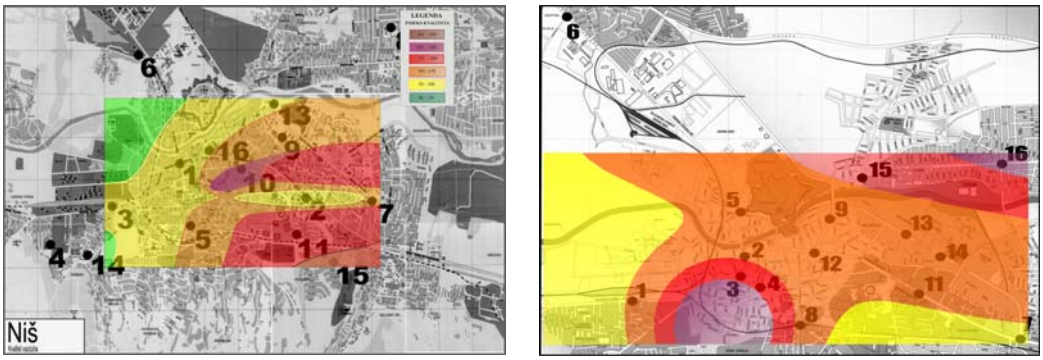
index, it can be determined in which year the air quality had a significant effect on the health of exposed population. Those conclusions can still be used as a basis for epidemiologic research.

Table 4. - Annual air quality index with respect to SO_2 in 1994 in the region of Niš

Controlled measuring point	1	2	3	5	6	7	8	10	13	15
Index values	80,7	74,3	123,8	144,98	118,58	161,94	90,92	254,62	113,30	423,46

Table 5 - Annual air quality index with respect to CO in 2008 in the region of Niš

Controlled measuring point	1	2	3	5	7	8	14	15	16
Index values	110,9	142,17	184,0	110,90	90,57	136,96	116,11	158,21	208,86



(a) (b)

Fig. 3 – Air quality fields in the city of Niš, (a) depending on concentrations of SO_2 in 1994 and (b) depending on concentrations of CO in 2008.

Conclusion

This research shows that the new aforementioned methodology for air quality assessment enables:

- Simplicity in monitoring air quality continuously for a long period of time
- Provision of information for annual levels of air pollution
- Acquisition of information about air quality effect on human health and formation of the basis for epidemiologic examinations
- Air quality mapping based on calculated air quality indices
- Evaluation of the need for health risk assessment in certain part of the analyzed territory

ACKNOWLEDGEMENTS

This work was supported by the Serbian Ministry of Science and Technological Development, projects No. 21009.

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5.5 Monitoring of Vehicular Lead Air Pollution in Belgrade during 2008

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Monitoring of vehicular lead air pollution has been conducted in 2008. On 14 representative intersections in Belgrade. On the basis of performed measurement results the city has been zoned (5 zones). The highest concentrations are registered in the central zone, while the lowest belonged to the suburban ones. The key reasons for this phenomenon are traffic frequency and the vehicle type, the intersection structure, as well as meteorological parameters.

5.6 Variations of PM_{10} mass concentration and correlation with other pollutants in Belgrade urban area

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In this paper, the PM_{10} levels measured at urban residential background site in New Belgrade in Omladinskih Brigada Street are presented. The aerosol samples were collected within four seasonal campaigns conducted in autumn: Nov 13-Dec 03, 2007, winter: Feb 07-28, 2008, spring: May 06-28, 2008. And summer: July 17- August 15, 2008. The concentrations measured using a European reference method (Kleinfiltergeræt) are compared with PM_{10} mass concentrations measured with Horiba automatic station, at the same sampling site and three more sites within Belgrade municipal monitoring network.

The results show that PM_{10} values in Belgrade urban area were high during autumn and winter campaigns (heating season) with a number of samples exceeding the limit value of 50 $\mu g/m^3$: 14 values out of 20 with maximum value 209 $\mu g/m^3$ during the autumn, and 14 values out of 19 with maximum value 196 $\mu g/m^3$ in winter season, although the average monthly concentrations were lower. During spring campaign, the number of exceeded limit values was three out of 22 and all values during summer campaign were below 50 $\mu g/m^3$.

PM_{10} values at all sites followed the same trend during each campaign. The highest concentrations at all monitoring sites are recorded during periods: Nov 20-Nov 25, 2007 and Feb 19-Feb 23, 2008.

This research was conducted within the WeBIOPATR project (2006-2009) funded by the Research Council of Norway through the Programme of Research and High Education of Norway and Western Balkan Countries.

5.7 Seasonal Variation of Benzo(a)Pyrene in Suspended-Particles in Belgrade City, Serbia

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are mostly formed during incomplete combustion or pyrolysis of organic material**.** Air samples for analysis of BaP in suspended-particle are collected at monitoring sites within municipal air quality monitoring network in period 2004-2008 according to ISO 9835:1993. In period 2004-2007 all samples were taken as total suspended particles (TSP) by PROEKOS, high volume sampler at height of 1.5-2 m above ground level over 24-hour periods, at Glass Fibre Filter WHATMAN. In 2008 solid fraction PM_{10} were taken by LECKEL, model LV3. Collected samples are prepared according to Compendium Method TO-13A using GC/MS. In this presentation we have taken in consideration results from the last five years (2004-2008). During winter season concentrations were higher at almost all measuring sites. There was found significance difference in level of BaP between sampling sites. In the period of 2005-2008 annual averages values were over limit value of 1.0 ng/m^3.

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are products of incomplete combustion formed during burning or pyrolysis of organic matter such as coal, oil, biomass, gasoline and diesel (Finlayson- Pitts and Pitts, 2000; EC, 2001). Also (PAHs) in ambient air can emitted from industrial combustions, aluminum production, cement manufacture, production of coal tare, coke and asphalt, petroleum catalytic cracking and restaurants. Atmospheric PAHs can exist in gaseous and particle phases, they are predominantly associated with particulate matter (PM). This suggests that particulate PAHs are regarded as significant hazardous substances to human health through breathing. Air pollution has adverse effects on respiratory and cardiovascular health such as acute reduction in lung function, aggravation of asthma, increased risk of pneumonia in the elderly, low birth weight and high death in newborns (Wilson et al., 2004) . Particulate matter have been suggested to pose a great risk to human health due to their high number concentration in urban environments and potential to penetrate (ultrafine particulate) from the lung alveoli into the blood circulation (Delfino et al., 2005). Chemical composition of airborne particulate matter (PM) in polluted atmosphere has become a topic of considerable importance over the recent years in relation to public health (Harrison et al. 2004).

Particulate matter form a highly complex mixture of different-sized solid and liquid particles. Mass concentration may not be the most appropriate exposure parameter for the assessment of health risks of atmospheric pollution (Forsberg et al., 2005). Many aromatic compounds, commonly identified in airborne particles, are suspected genotoxic agents and carcinogens, and some of them may also cause acute health effects (WHO/IPCS, 1998; EC, 2001). Thus, inhalation of

polycyclic aromatic hydrocarbons (PAHs) in particulate mixture is potentially a serious health risk.

Benzo[a]pyrene (BaP) has been regarded as a marker of the total and carcinogenic PAHs (EC, 2001). The European Commission has set an annual target value of 1 ng/ m^3 for benzo[a]pyrene in ambient air. Annual mean concentrations of BaP in major urban areas in Europe are in range 1-10 ng/m^3. In rural areas the concentrations are less than 1 ng/m^3. In order to estimate the carcinogenic risks for humans, the benzo(a)pyrene-equivalent (BaPE) carcinogenicity was evaluated by multiplying the concentrations of each PAH with their toxic equivalent factors (TEF) (Tsai et al., 2004) which can be used to calculate the relative carcinogenicity of ambient samples with a known distribution of PAHs. Carcinogenic PAHs like BbF and IcdP which are dominant PAHs in urban environments appear to play only a minor role in the carcinogenic activity. The relative contribution of DahA to the carcinogenic potential is stronger, even at much lower concentrations, due to its high TEF (Papageorgopoulou et al., 1999).

2. METHODOLOGY

The sampling sites were located in Belgrade, Serbia, within municipal air quality monitoring network.Total area of the city is about 360 km^2 and population is about 1710 000. Local urban monitoring network consists 17 semiautomatic, 6 stationary and 2 mobile automatic stations. The sites were influenced by variable contribution of traffic and in winter season by local heating. Some of them are an urban background site, which means that the sites are not directly exposed by traffic or other emissions. In period 2004 air samples for the TSP-PAHs were collected on 7 measurement sites, in 2005-2008 on 6 and in 2008 samples for PM_{10}-PAHs were taken on 13 measurement sites.

Air samples for the particulate and gas phases of PAHs in total suspended matter (TSP-PAHs) were collected for 24h using a High Volume Sampler Proekos, at height of 1,5-2 m, with approximately of volume 300 m^3 of air. Air is passing through GF/A glass fibre filter Whatman 110 mm diameter. Before sampling filters were heated in an oven on 105 ^oC for 1h and than put in isothermal box for cooling and weighing. An electrical balance Precisa XR 125 SB micro-balance sensitive 0.01 mg was used to measure weight. The coarse particle samples PM_{10}-PAHs has been collected since July 2008 by LECKEL, model LV3 on to glass fibre filter Whatman 47 mm diameter with approximately of volume 50 m^3 of air.

TSP-PAHs samples were prepared according to Compendium Method TO-13A: Determination of PAHs in Ambient Air Using GC/MS. All samples were extracted in Soxhlet extractor with a solvent solution of 250 ml (a mixture of 125 ml n-hexane and 125 ml acetone) for 18 h. The extract than concentrated using rotary evaporator with 100 µl toluene as keeper, until 0.5 ml and analysed on GC/MS. PM_{10}-PAHs samples were extracted with solvent solution of 50 ml (a mixture of 12.5 ml hexane and 12.5 ml acetone (1:1) in Multiwave 3000 with Rotor 8SOLV. The extract than concentrated as the same way as for TSP-PAHs samples.

Benzo(a)pyrene was determined using Gas Chromatograph model Agilent 6890 N with Mass Selective Detector model Agilent 5973 MSD and capillary column

DB-5 MS l, 30m 0.25 mm x 25 µm. The oven temperature was programmed to be from 70°C at a rate of 8°C/min to 310 °C and held for 5 minutes with helium as the carrier gas. It was used Semi Internal standard (deutered PAHs) for internal calibration. 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. The detection limit (DL) for each species was determined according to US-EPA Test Methods SW-846 (http://www.epa.gov/sw-846/pdfs/chap1.pdf). A known quantity of each standard substance was measured seven times, and the DL for each species was three times the standard deviation from the seven tests. The DL for each species, when converted to atmospheric concentration is 0.02 ng/m^3.

3. RESULTS AND DISCUSSION

The monitoring of BaP in Belgrade was first performed ten years ago. In this presentation we have taken in consideration and evaluation results from the last five years, from beginning of 2004 till the end of 2008. Fig.1 displays annual mean concentration of TSP in Belgrade urban area. All values were above 120 µg/m^3 which is target value for TSP. Maximum monthly value was 729.7 µg/m^3 in November 2005 on measurement site Mate Vidakovića Street and minimum monthly value was 135 µg/m^3 in April 2006 on measurement site Despot Stefan Boulevard 54/a. As we can see all mean values were between 150-230 µg/m^3.

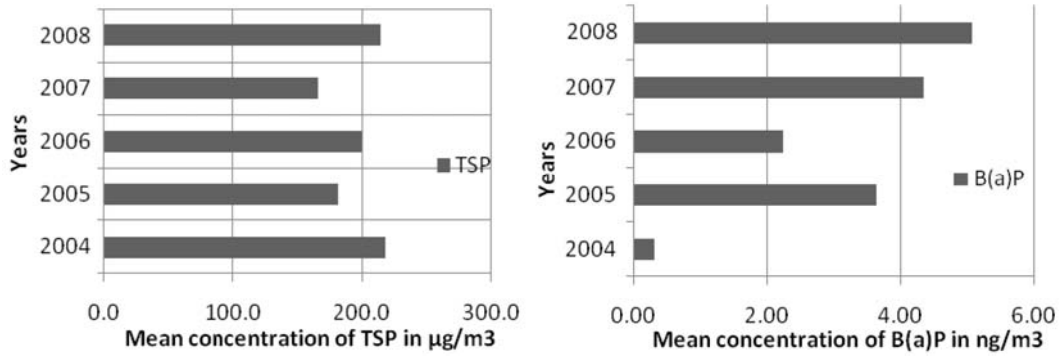


Figure 1-2: Annual mean concentration of TSP B(a)P in Belgrade urban area

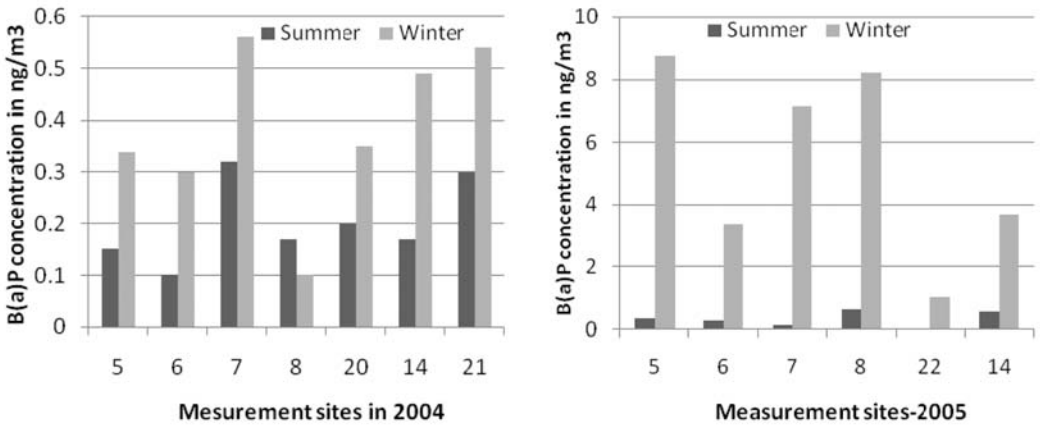
In Figure 3. there are present position of measurement sites 1-17. Measurement site 23 is near site 13. Measurement cites 18-22 are located in wider Belgrade Metropolitan area. 18 and 19 in vicinity of Thermal Power plant "Obrenovac", 20-22 in vicinity of Thermal power plant "Kolubara"and 23 is located 30 km on south in city of Mladenovac.

Measurement sites:

1- Despot Stefan Boulevard 54/a;
2- Sava Holy;
3- M.Pocerca;
4- G.Delčeva;
5- M.Vidakovića,
6- Queen Jelena;
7- JNA Place;
8- Mansion of Grga Andrijanović;
9- Čukarica, Prince Višeslav.;
10- Lj.Bogdana;
11- Ustanička;
12- O.Jovanović;
13- Obilićev venac;
14- Institute of Biology;
15- Doctor Subotić;
16- Ohridska;
17- New Belgrade, Parking service;
18- Obrenovac;
19- Grabovac,
20- Vreoci,
21- -Lazarevac;
22- Mladenovac;
23- Rail street (near to the site 13)

Figure.3 : Measurement sites within monitoring network in Belgrade city center

The concentrations of B(a)P increased from 2004 to 2008. Figure.2 displays annual mean concentration of B(a)P in Belgrade urban area. The highest annual mean value was in 2008. The highest monthly value was 35.7 ng/m^3 in November 2005 on measurement site 5 and minimum monthly values were 0.02 ng/m^3 on three measurement site 5, 6 and 8 in summer months. Annual mean concentration for B(a)P was under the target value set by European Commission 1 ng/m^3. in 2004. But later in period 2005-2008 annual mean concentrations were above target value. Figure 4-8 displays seasonal variations of B(a)P.



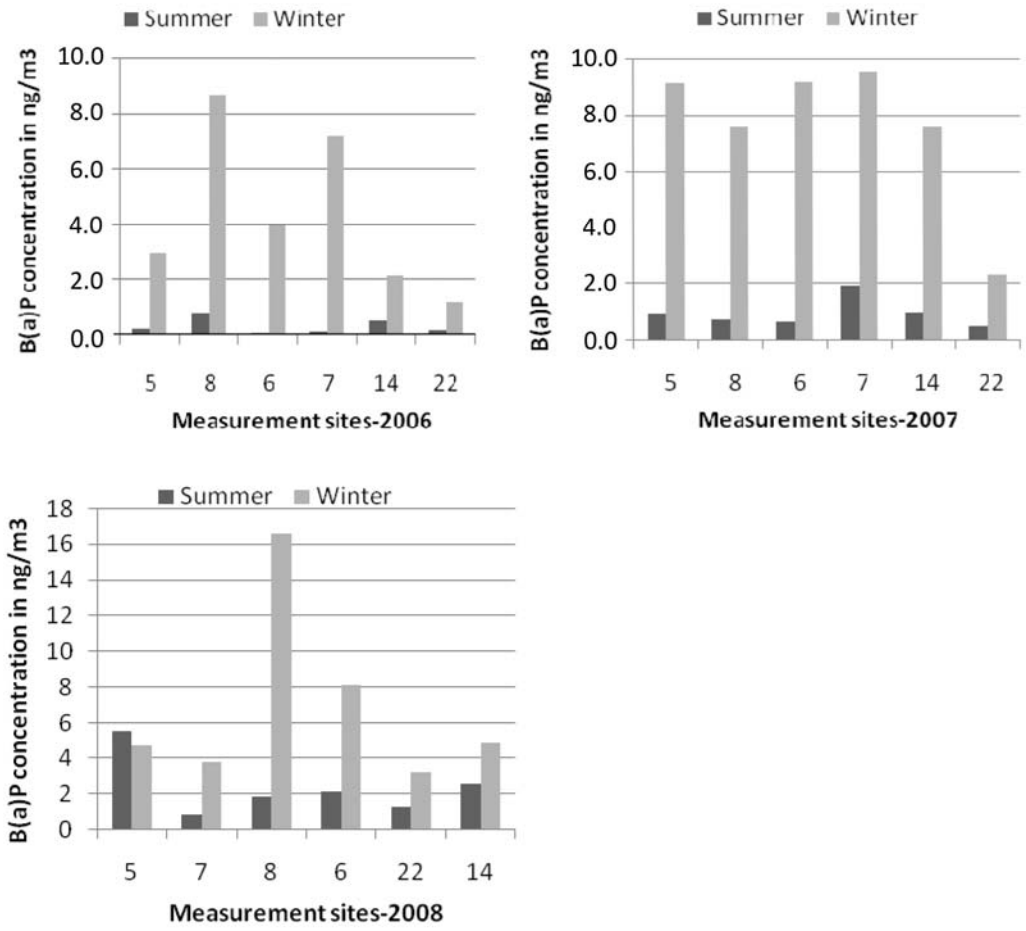


Figure.4-8.Seasonal variations of B(a)P in TSP in Belgrade urban area

In 2008, until May, it was sampling TSP. After that is has been collected PM_{10} on the same measurement sites. Thus, it seems that B(a)P data obtain from filters collected after May 2008 are not comparable with previous. For the other half of the 2008 year data is shown on Figure.9. Some new measurement sites were established in the meantime as we can see on schedule.

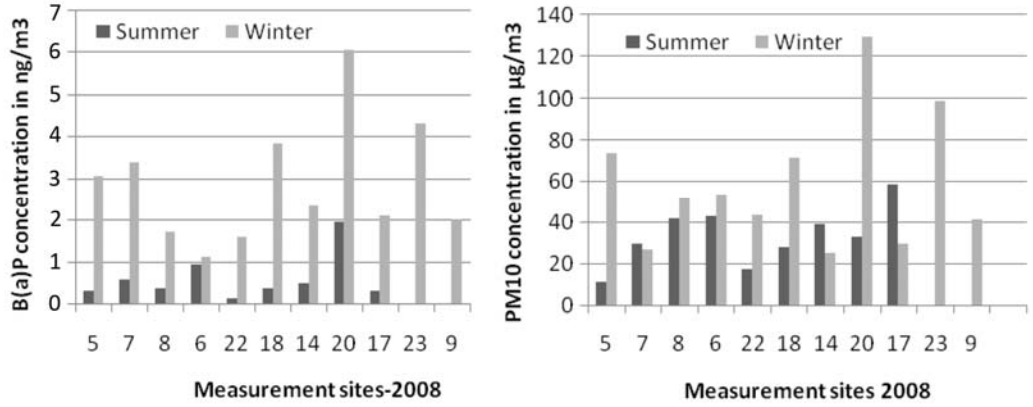


Figure.9-10: Seasonal variations of B(a)P in PM_{10} and PM_{10} in Belgrade urban area

The PM_{10} concentration were lower during warm season than cold season. On some sites concentration was above 50 $\mu g/m^3$ which is target value recommended

from EC. Maximum value was 150.2 μg/m^3 in December on Bulevar despota Stefan 142 site, and minimum was 3.8 μg/m^3 in September on Žarka Zrenjanina site. Also, the concentration of B(a)P in winter followed PM_{10} concentrations- all values were above target value for B(a)P. Maximum value was 9.09 ng/m^3 in December on measurement site Vreoci and minimum value was 0.05 ng/m^3 in August on site Mladenovac. In 2004 all values of B(a)P concentrations were under 1 ng/m^{3}and in 2008 60 % of measurement B(a)P concentrations were above limit value (Table1).

Table 1: Concentrations of B(a)P above limit value

Year	Number of measurement	Values above 1 ng/m^3	%
2004	**27**	**0**	0.0
2005	**42**	**21**	50.0
2006	**69**	**27**	39.1
2007	**67**	**41**	61.2
2008	**90**	**54**	60.0

4. CONCLUSIONS

The mean annual concentrations of TSP in period 2004-2008 were above target value in each year in Belgrade urban area. The concentration of TSP and PM_{10} were higher in winter than in summer. Trough the obtained results it can be conclude that concentration of Benzo(a)pyrene in particulate matter generally followed the patern of seasonal variations of TSP (and also PM_{10}), being the higest in winter and the lowest in summer. During winter season i.e. heating season concentrations were higher at almost all measuring sites because of strong influence of local heating. Future work will be to investigate the concentrations of BaP in smaller solid fractions in air pollution, PM_{10} (new measurement sites were established within municipal monitoring network in 2008), $PM_{2.5}$ and smaller ($PM_{1.0)}$ as the most important for adverse health effects.

5. ACKNOWLEDGEMENTS

The authors would like to thank the Institute of Public Health of Belgrade for the opportunity and support to carry out this measurements, Ministry of Science and Technological Development of Serbia, project TR21009 and WeBIOPATR project for supported results analysis.

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5.8 Analysis of influence of wind direction and speed to PM_{10} concentration in Pancevo

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Wind direction and speed have very significant influence on transport of emitted pollutants and their spatial and temporal dispersion. Analysis of relation between wind direction and speed on one side and PM_{10} concentrations on the other side may be important for planning measures for improvement of air quality.

The analysis of relation between these elements is graphically presented in this paper as wind roses and PM_{10} roses for measurement site Vojlovica in Pancevo, using wind direction and speed data from automatic weather station in Pancevo.

The relation between wind direction and speed and PM_{10} concentrations points out an importance of using forecasted values of these meteorological elements as one of the measures for improvement of air quality and health risk reduction.

5.9 Impact of dust emission from 300 m chimney from thermo power plant Kakanj on ambient concentration of PM_{10} in Kakanj area

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Impact of dust emission from large Thermo Power plants (TPP) on increasing ambient concentrations of PM_{10} is important. In this research, using mathematical model will be shown influence estimation of dust from TPP Kakanj on immision levels of PM_{10} in Kakanj area.

Data used in this research are from many years of measurements using automatic station in the city Kakanj, as well as from two mobile automatic stations. Parameters measured on these stations are: PM_{10} and meteorological data. We have also used meteorological data from station Turbici, which is placed on a hill near 300m TPP stack, and is representative for evaluation of transport of air pollution by wind.

The choice of mathematical dispersion model is important element of this research. We chose SELMA GIS with AUSTAL 2000 as a powerful combination, as it offers many advantages.

SELMAGIS is completely implemented into ESRI's geographical information system ArcGIS. Thus the user is able to use his specific air quality models and at the same time all functionalities of the GIS. Using GIS makes it possible to work under the same graphical user interface (GUI) for administrating input and output data, preparing input data (e.g. digitizing emission sources), run the dispersion models, evaluate and display results. Using GIS has the advantage that various possibilities of interfaces to geographical data bases exist, e.g. emission inventories, street maps and interfaces to other file formats. By this it is possible to get input data from different administrative data bases.

SELMAGIS consists of different modules, which have interfaces to each implemented dispersion model. The following modules are implemented: Digitizing Tool, Emission Factory, Meteorology Factory, Terrain Factory, Navigator for Dispersion Model, Evaluation and Visualization.

5.10 Modelling air concentrations of fly ash in Belgrade, emitted from thermal power plants TNTA and TNTB of Obrenovac

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ABSTRACT
Coal thermal power plants TNTA and TNTB of Obrenovac ("Nikola Tesla A and B") are located in the WSW (~234^o) wind rose direction, about 30 km away from the centre of Belgrade. There is an expectation that their three chimneys, 150m, 220m and 280m tall, with emissions of ~3 tonnes per hour and their ash and coal disposal sites (size ~ 300ha of total potential dust emission area and ~ 287 million m^3 of disposed ash and coal) could, in some meteorological conditions, be an important source of air pollution in Belgrade. Some results of fly ash air pollution modelling from these sources are presented, for assigned adverse meteorological conditions as well as for some real meteorological conditions, as recorded by a meteorological station recently established in the vicinity of mentioned power plants. Two kinds of simulations were performed, one of them using slow wind when emissions from chimneys dominate and the other using strong winds when dust emission from disposal sites is predominant. The results obtained using assigned meteorological data during these studies indicate that these sources could contribute to an increase in dust concentration, but on the other hand results obtained using real, but limited meteorological data base did not confirm such predictions.

1. INTRODUCTION

In routine operation, the chimneys of thermal power plants TNTA and TNTB release to the atmosphere, about 3t/h (estimated) of fly ash. The physical heights of the chimneys lie in the range 150-280 metres. The other characteristics of the chimneys are presented in table 1.

Table (1). Physical characteristics of Chimneys

Chimney	Height(m)	Diameter(m)	Temperature of exit gaseous estimated (^{o}C)	Vertical exit velocity estimated(m/s)	Source strength estimated(kg/h)
TENTA-1	150	10.5	170	10	1000
TENTA-2	220	16.9	170	10	1000
TENTB-1	280	30.0	170	10	1000

These air pollution sources are permanent. In cases where the ash and coal disposal sites are sufficiently dry - i.e. if surfaces of ashes/slag disposal sites are not adequately protected with pond/"water mirror" - strong winds could lift dust from these deposits so that they become sources of large-scale emissions of fine particulate matter. Characteristics of coal and ash disposal sites TNTA and TNTB are presented in Tables 2.-5.

Table 2. Coal disposal site TentA

Surface	13.2 ha
Length	470 m
Width	300 m
Height	5-20 m
Volume	300.000-1.300.000 m3 average 800.000 m3

Table 3. Coal disposal site TentB

Surface	8.4 ha
Length	300 m
Width	280 m
Height	5-21 m
Volume	200.000-800.000 m3 average 500.000 m3

Table 4. Ash/slag disposal site TentA

Surface	382 ha active ~ 130 ha
Height	18-25 m
Volume	112.000.000 m3

Table 5. Ash/ slag disposal site TentB

Surface	600 ha active ~ 200 ha
Height	29 m
Volume	174.000.000 m3

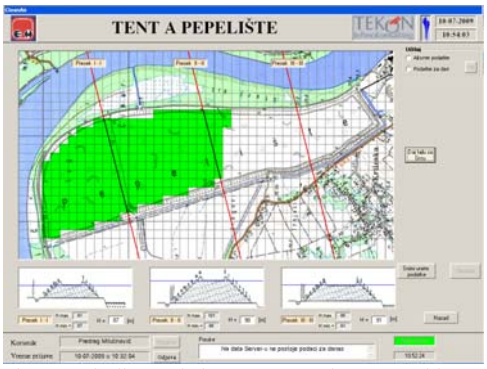

Fig. 1. Ash disposal site TNTA, active area white painted ~ 130 ha

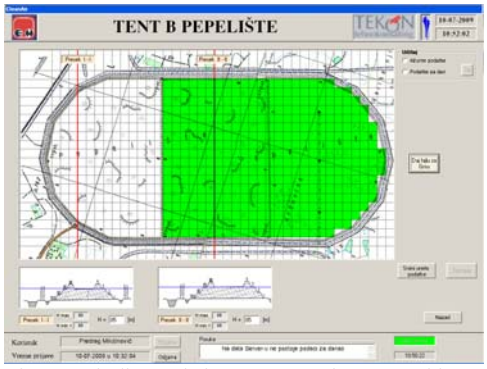

Fig. 2. Ash disposal site TNTB, active area white painted ~ 200 ha

1. Mathematical modelling of fly ash distribution assessment

The most commonly used mathematical model of ground-level concentrations of emissions from tall stacks is the Gaussian plume model Turner D.B. (1964):

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

where $C(x,y,z)$ is air pollution concentration at grid point (x, y, z), Q source strength, H effective height of source emission, σ_y,σ_z diffusion coefficients in y and z directions respectively and u is average wind speed.

To account for gravitational settling of "heavy" particles, heights of emission H are modified with the term T. J. Overcamp (1975):

$$\left(H-\frac{v_s x}{u}\right) \quad (2),$$

where v_s is terminal velocity and x is downwind distance.

In the case of heavy particles, the gravitational settling velocity v_s predicted by the Stokes equation dominates. Typical values for settling velocity v_s vary from 0.01 to 1 cms^{-1} depending on particle size. In this paper the deposition velocity was chosen to be 0. 8 ms^{-1}, Sehmel G. A. (1980).

These equations are applied to both the point sources (chimneys) and the area sources (coal/ash disposal sites).

The most important mechanism for lifting dust aerosols to the atmosphere from the ground is sandblasting. It can be presented with equation, D. Gillette (1979):

$$q = A\frac{\rho}{g}\sum_{u_*} u_*\left(u_*^2 - u_{*tv}^2\right) \quad (3),$$

where q is the instantaneous horizontal (saltation) mass flux (g cm^{-1}), A a unitless parameter (usually assumed to be equal to 1), ρ density of air (g cm^{-1}), g acceleration of gravity (cm s^{-2}), u_* wind shear velocity (cm s^{-1}) and u_{*tv} is threshold shear velocity (cm s^{-1}).

Because of sandblasting by saltation-sized particles, the vertical dust flux F_a (g cm^{-2} s^{-1}) is linearly related to q by a constant K (cm^{-1}) typically on order of 10^{-5} to 10^{-6} (Marticorena at all (1997)). The value K is strongly dependent on deposit surface texture, crusting and moisture.

2. RESULTS

Two kinds of numerical experiments were undertaken. The first was designed so to simulate air dispersion dust emitted only from three tall chimneys. Assigned meteorological data in this case were prepared so as to represent situations with three Pasquill-Gifford stabilities A, D and F; a wind speed of 1m/s was used.

The other experiment was performed so as to simulate dust emission from chimneys and also from four ash/coal disposition sites in case when ash deposits are without adequate water protection. This experiment was designed with adverse meteorological conditions when the disposal sites start to emit dust - wind speed > 10m/s (10.1 m/s, 15m/s and 20 m/s).

Finally, dispersion calculations were made using real meteorological data recorded by an automated meteorological station established in the vicinity of these dust sources. The dispersion calculations covered a period from February 23rd to June 29th. The domain for calculation was 53.5km x 32.5 km, with dimensions of network cells 100m x 100m.

The calculation results using assigned adverse meteorological conditions, wind direction from dust sources in TNTA and TNTB towards Belgrade and wind velocity of 1m/s, indicated that in case of Pasquill stability class F-very stable, the contribution to ground dust air pollution in Belgrade can reach significant values (Fig.5). In the other Pasquill dispersion classes A and D, the influence on air pollution is less, as in Fig. 3. and Fig. 4. Calculated ground – level concentrations indicate that lower chimneys in TNTA (150m and 220m tall) could have a greater contribution to air pollution in Belgrade than taller chimney of TNTB (280m tall).

Calculations made using real meteorological data recorded in the period from February to June 2009 did not confirm contribution of these dust sources to concentrations in Belgrade. However, the meteorological data base used was

sufficiently quality controlled, because the automated meteorological station was only recently established at thermal power plants place and it is still under an experimental working regime.

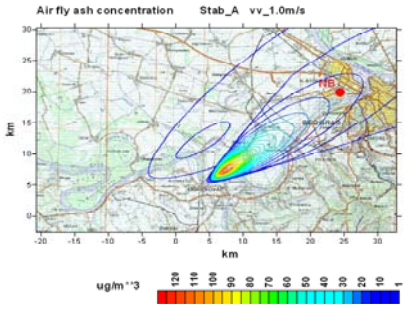

Fig.3. Chimneys Stability A

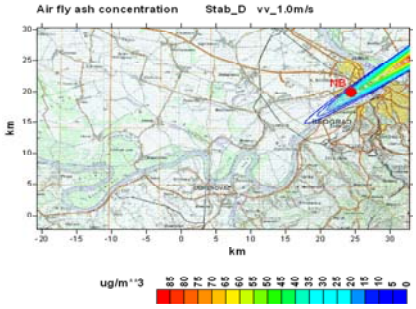

Fig.4. Chimneys Stability D

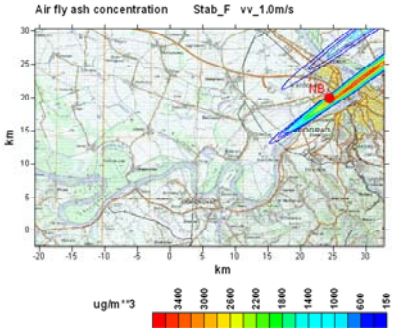

Fig. 5. Chimneys Stability F

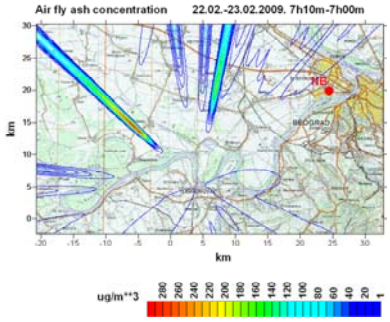

Fig.6. The worst real situation in the period 22.2.2009. 7h 10min - 23.2.2009. 7h

Combinations of assigned several classes of strong winds and sizes of ponds at dust disposal sites have the expected result that stronger winds and lower sizes of disposal site ponds give stronger dust emissions. Conversely, combinations of slower winds and larger ponds give weaker dust emission.

Combinations of wind speeds of 10.1, 15 and 20m/s were used in modelling with ponds covering ash disposal sites TNTA and TNTB of 25% (75% of deposit surfaces dry), 50% (50% dry), 75% (25% dry surfaces) and 100% dry ash disposal surfaces. Usually a pond covers about 50% of disposal site surfaces. Figures 7 and 8 represent two extremely opposite situations, totally dry disposal surfaces (100% dry) and relatively good covering depots with ponds (25% dry).
The impacts of these sources to the atmospheric dust concentration at distant places could be important, but the results of modelling presented here show that the influence of lower chimneys of TNTA could be greater than that of fly ash deposits Fig.5. and Fig.7.

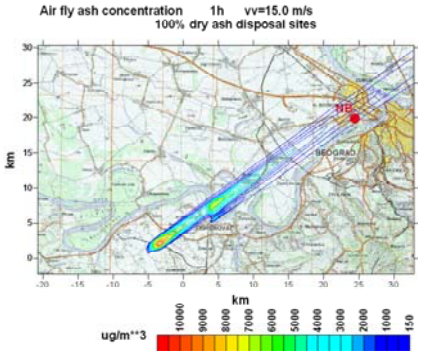

Fig.7. All dust sources Stability D vv=15m/s

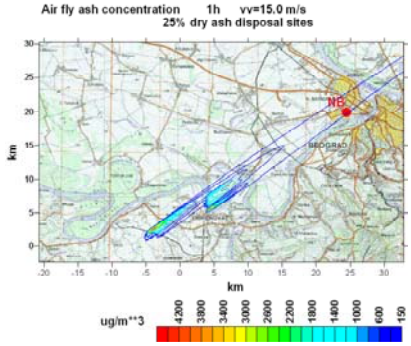

Fig.8. All dust sources Stability D vv=15m/s

2. Comments and conclusions

Under adverse meteorological conditions which remain rather constant (low wind speed, stable conditions), the model predicts that atmospheric dust concentration emitted from thermal power plants chimneys increase at greater downwind distances. On the basis of these results, it appears that the chimneys of TNTA and TNTB could influence the fly ash concentration in Belgrade.

Strong winds and low coverage of disposal sites with ponds results in huge increases in atmospheric dust concentration at short downwind distances, as well as considerably increased dust concentrations at large distances.

The frequency of adverse meteorological conditions appearing us an important question. *In situ* meteorological measurements did not record such situations, but meteorological measurement has only been established recently and the data series are very limited. Obviously, meteorological measurements at power plant sites have to be continued to improve meteorological characterization because the influence of distant thermal power plants of Obrenovac on air pollution in Belgrade has been recognised.

3. ACKNOWLEDGEMENTS

This work has been supported by the Ministry of Science and Technological Development of the Republic of Serbia funded through the 15005 – TR project.

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5.11 Deciding upon a national monitoring strategy considering scientificneeds and international obligations

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Monitoring of air quality serves several interlinked purposes, and to be cost efficient as well as scientifically sound it is important to look at these different perspectives together when designing an optimum national monitoring strategy. There are mainly two considerations, the monitoring obligation in accordance to international frameworks, and the scientific needs to understand emission, transport, deposition and exposure of air pollution. This is essential when deciding upon best abatement strategies for emission reductions.

In Europe there are two main regulative networks. For the member state of EU, the Directive on ambient air quality on cleaner air for Europe (EU, 2008) gives the requirements of measurements for the legislative pollutants (i.e. PM, SO_2, NO_x, O_3). The main concern is the local air pollution problems, but to evaluate the regional contribution to local air pollution it requires a close harmonization with the EMEP (European Monitoring and Evaluation) programme under the Convention of Transboundary Air Pollution (CLTRAP). The EMEP programme includes a suite of different parameters covering the topics concerning acidification, eutrofication, heavy metals, persistant organic pollutant, photo-oxidant and particulate matter. EMEP is developing a new monitoring strategy for the period 2010-2019 (UNECE, 2009), and an important aspect is the linkages of geographical scales, (local versus regional, intercontinental transport, global change). It also highlights the need to address the interaction of global change (including climate change) with air quality issues. Presently there is no international monitoring obligation for greenhouse gases, but there are strong recommendations of monitoring the most essential parameters in the Global Atmospheric Watch (GAW) Programme under the World Meteorological Organization (WMO, 2007).

Due to the significant interactions between the suite of chemical constituents and the associated physical properties of air pollutants, as well as the synergies in abatement measures, national and international monitoring efforts should be closely coordinated. Such an approach will ensure a sound observational basis that can give added benefits and avoiding duplication of efforts. In Serbia and Montenegro there is a potential for better harmonization of monitoring efforts and especially improve the regional EMEP network. This will also support the abatement strategies for local air quality as well as problems related to climate change.

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6 Poster Session

6.1 Study on the effect of fractional composition and ash particle diameter on ash collection efficiency at the electrostatic precipitator

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ABSTRACT
The electrostatic removal of solid particles from flue gases has a wide application in the range of the industrial processes. Electrostatic removal of solid particles from the flue gases operating on the principle that the gas is allowed to pass between two electrodes, one of which is grounded (plate collecting electrode), and the other is connected with the negative pole of high-voltage current (coronary electrode). The particles in the gas stream are electrically charged and are separated from the flue gas under the influence of electric field. Flue gas process parameters (volume flow, temperature, velocity) and the parameters of the electrostatic precipitator (length of electric field, migration velocity of the ash particle, particle size distribution, distance between plate collecting electrodes) have a big influence on the collection efficiency in an electrostatic precipitator. Many researchers analysing the influence of these parameters on particle collection efficiency in the electrostatic precipitators and often they give contradictory conclusions. Different mathematical models were used in order to show that geometric characteristics of electrostatic precipitators (length of collecting electrodes, distance between collecting electrodes, migration velocity) have influence on their collection efficiency. In one paper is shown comparison between the results obtained using theoretical models of Deutsch and Zhibin-Guoquan with the results of experimental examinations of electrostatic precipitator in laboratory controlled conditions. The results obtained using model of Detusch and Zhibin-Guoquan do not accord well with the experimental results of particles with diameter less than $10\mu m$. The newest model is a good approximation of the experimentally obtained results even for the particles with the diameter less than $10\mu m$. Experimental investigation of electrostatic precipitator and ash collecting in the electrostatic precipitator is done on the real industrial plant (at the thermal power plant „Gacko“ with block power of 310MW, Bosnia & Herzegovina). Thermal power plant „Gacko“ has two flue gas ducts with an electrostatic precipitator on each (total two electrostatic precipitators). Investigation of the electrostatic precipitator performance was done according to BAS ISO 9096. Within the measurement surface, measurements were made on 20 points per section.

In this article the electrostatic precipitator efficiency during ash particle removal with wide range of particle sizes from 1 to $250\,\mu m$ is evaluated. It is observed that ash removal degrees from the experiments has approximately equal value (95,93% to 97,78%), while ash particle removal degree calculated from the correlation equations of different references has a good suitability with the

experimental results. The models of Deutsch, Zhibin-Guoquan and Nóbrega-Falaguasta-Coury have good approximation with the results of experimental investigations on a real industrial plant (thermal power plant “Gacko”, power $310\,\mathrm{MW}$). The best accordance with the experimental results shows Deutsch equation, while the other theoretical models show less accordance with the experimental results. For the ash particles with the diameters less than $17.5\,\mu\mathrm{m}$ there is no good correlation between investigated theoretical models. The biggest deviation of the model is noticeable in the case of usage of the Deutsch equation.

6.2 Effective population exposure considerations

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ABSTRACT
If there is no access to measurements of real physical exposure of an average individual to air pollution, some estimates can help. We propose several considerations to that end, assuming that the only available data are those of the measuring stations. The focus in the present paper are two problems: assessing population exposure in areas where some measuring stations are placed in street canyons, and obtaining effective population exposure in an area covered by several stations that are placed in locations with different population densities.

1. INTRODUCTION

In order to estimate real exposure of a population to pollutants, it is common to resort to direct measurements which involve participation of individuals, with their consent to carry samplers around their usual daily business and routines. This method provides detailed individual data, and can be valuable, provided that each individual treats the sampler with equal care and that the chosen individuals are a representative sample of the population surveyed. If this method cannot be afforded, however, then one can rely on the data of the air quality measuring stations, and make estimates to deduce overall population exposure to various pollutants. This, of course, limits considerations only to exposure to pollutants whose sources are outdoors, excluding tobacco smoke and other typical indoor pollutants. For some purposes, however, the main points of concern are outdoor sources, and population exposure to them.

In that context, representativeness of measuring stations is critical. A measuring station can suffer from inhomogeneity of pollutant concentration distribution over an area that the station covers, giving unrepresentative results due to its location. Furthermore, the result it provides may have little relevance to real, or effective, population exposure, if the area around the location is poorly or not populated at all. These two issues are dealt with in the present paper.

2. PROPOSED METHODOLOGY

Monitoring in urban environments generally suffers from the problem of the representativeness of measuring points because of inhomogeneities in spatial distribution of pollutants caused by topography and/or uneven distribution of pollution sources. In the case of Belgrade, the main source of pollution is traffic. We thus focused on the instances of street canyons, as the major anomalies in pollution distribution in such an environment. Measurements obtained at such locations should be corrected so as to be more representative of the wider area of their location. This can be done by a correction factor, applied to concentrations of pollutants directly linked to traffic sources. We will try here to come to a procedure of estimating that correction factor in a simple way.

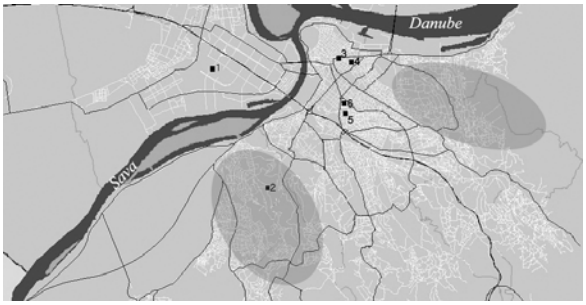

Figure 1. *Layout of the Belgrade metropolitan area with six air-monitoring stations: 3 – BDS station, 4 – CC station. Ellipses denote elevated terrain, both around 240 m altitude.*

We take NO_2 as the usual traffic pollutant, and compare its average concentrations for the year 2008 in one of the Belgrade street canyons (Bulevar Despota Stefana station, BDS) with the concentrations in the corresponding nearby urban background station with low traffic (Carlija Caplina station, CC) as reference. The BDS (canyon) average for 2008 is 48.07 μg/m^3 [Institue of Public Health, 2008] and the CC (urban background) average is 20.46 μg/m^3 [Hydrometeorology Service, Serbia, 2008]. Apparently, the canyon station result is 2.35 higher than the background reference. This would mean that the BDS station measurements should be corrected via multiplying by a correction factor of 0.426 (0.426= 1/2.35) in order to make them representative, or, rather, make them reflect the background concentrations. However, from the viewpoint of population exposure, this is probably not an appropriate value, because people in in this area do not live only in the urban background locations, outside street canyons or heavy traffic locations. The easiest compromise would be to take the value of 0.713, which is half-way between 0.426 (overcorrected) and 1 (uncorrected). However, this value is subject to estimate, and depends on the estimated distribution of population between the streets with busy traffic vs. low traffic in the area (background). In other words, the formula for calculating the realistic adjustment factor F_a (in terms of population exposure) should be, Equation (1):

$$F_a = F_c + (1 - F_c)F_p \qquad (1)$$

where F_c is the concentration ratio of the reference station to canyon station (0.426 in the above case) and F_p is the fraction of the population estimated to be exposed to the canyon concentrations. We propose the range of this factor to correspond to the values between two most probable extremes: half of the population (F_p= 0.5) and a quarter of the population (F_p = 0.25) exposed to canyon concentrations. The rationale for this is purely geometrical (Figure 2): buildings have outside windows that appear on two, three, or all four of their sides (A, B, or C in Figure 2). In the case of two sides, half of the population is exposed, and in the case of four sides, a quarter of the population is exposed to the impact of the street canyon. In the present case, for the area that the BSD station represents, we estimated that about 1/3 of the population is exposed to street canyon concentrations, which means F_p = 0.33. This yields the adjustment factor of F_a = 0.615 for the BDS station. The reason for such an estimate is the

architecture of the buildings, which is mixed between two and four-side windowed. Of course, more precise estimates would have to come from the statistics of actual individual exposure measurements, but we believe they would anyhow fall in the range mentioned. The range of uncertainty with this estimate is from F_a = 0.57 (if F_p= 0.25 is adopted) to F_a = 0.70 (if F_p = 0.5 is adopted), which is only about ±12% of the correction factor F_a.

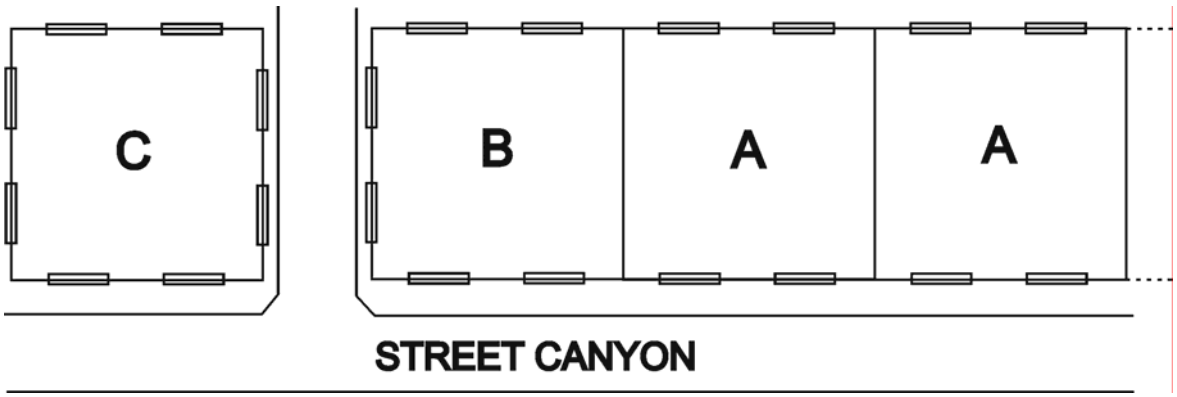

Figure 2. *A schematic of three types of exposure, based on the geometry of the buildings.*

The procedure can be summarised as in Table 1.

Table 1. Summary of the procedure of obtaining the correction factor Fa.

Canyon result	Background result	Ratio Canyon/Background	F_c	F_p (estimate)	F_a (eq. 1)
48.07 µg/m^3	20.46 µg/m^3	2.35	0.426= 1/2.35	0.33	0.615

Thus, in terms of population exposure, the effective average concentration in 2008 for the area in question is obtained by multiplying the measured BDS concentration with the correction factor, F_a:

Effective concentration= (BDS concentration)·F_a= 48.07 µg/m^3·0.615= **29.6** µg/m^3.

In order to have up-to-date assessments, the latest measurements from both stations (canyon and background) should always be used, or, their averages over a recent period that is of interest.

Another issue is the representativeness of a measuring point in terms of effective population exposure. If one wants to estimate an average effective concentration over an area to which the population of that area is effectively exposed, one needs to take into account the population density in the area. In this context, one must not neglect the effects of a possible highly populated region where even moderately high pollution can cause massive health effects, due to massive exposure. An opposite shortcoming would be introduced if measurements from a location with a lot of green areas, but with low population density, were taken as is. Such a measuring point would contribute to forming an unrealistically positive estimate of effects of the overall air quality, and should not be given the same statistical weight as the sites with higher population densities.

We believe that, for these reasons, the results should be statistically weighted by population density in a procedure of obtaining an assessment of effective population exposure in a complex urban area. A simple weight factor can be of the following type, equation (2):

$$W_{s,p} = \frac{D_{s,p}}{\sum_{s} D_{s,p}} \qquad (2)$$

where $D_{s,p}$ is the population density of the area represented by station s measuring pollutant p. The denominator holds the sum of all population densities taken into account.

By using the statistical weighting according to Equation (2), the results from several stations in a larger area can be summarized into a single effective concentration that the public in that area was exposed to. Also, if air quality indexing is used, which is more appropriate for health effect issues, this statistical weighting can be used in obtaining an effective air quality index over a larger area [Zujic et al., 2008].

3. CONCLUSION

Measuring and monitoring pollution in an area is an activity that provides results which may not be directly, especially not quantitatively, linkable to effective population exposure. Some measuring sites are in street canyons with high local traffic pollution levels, some are in green urban background, some are in areas with moderate pollution but high population density, others are in high pollution area with low population density, etc. All of these instances need to be covered appropriately and quantitatively in assessments of overall population exposure to pollutants. We propose here two simple methodologies that tackle the problem of measurements obtained in street canyons, and the problem of differences in population densities across a wider area that has several monitoring stations.

The problem with street canyon measurements is solved by comparing the results with a nearby urban background station results, and introducing a factor by which the street canyon results should be corrected. This factor also includes a purely geometrical (or architectural) estimate of the fraction of population that is directly exposed to street canyon pollution.

The problem with differences in population densities is solved by statistical weighting of the results by population densities in each of the areas that the results should be representative of.

4. ACKNOWLEDGEMENTS

This work was supported by the Serbian Ministry of Science and Technological Development, projects No. 142065 and 21009. We are also grateful to the Belgrade Institute of Public Health and Hydrometeorology Service of the Republic of Serbia for the data used in this study.

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6.3 Simulation of pollution levels of nitrogen oxides in a typical urban area of Banja Luka – Republic of Srpska, Bosnia and Herzegovina

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ABSTRACT
This paper presents a statistical analysis levels of NO_2, NO, NO_x and meteorological parameters of data collected by the air pollution laboratory operated by Institute of Protection, Ecology and Informatics. Levels of NO_2 NO, NOx in air samples from the urban zone of Banja Luka were determined at the locality "Center" in Banja Luka (capital of Republic of Srpska, in Bosnia and Herzegovina) which is highly populated area, with intensive traffic and industry. The site was selected to represent a typical urban area. These results were compared to standard limits for urban areas legislation and EU standards, which showed that this area is contaminated by nitrogen dioxide. Statistic analysis showed several patterns that suggest a significant relation between air pollution and meteorological parameters. Correlation between NO_2, NO, NO_x and t ^{0}C levels and was also carried out. Lower temperatures, and by that increase of heating and fuel burning, have a certain influence too, as the results of modelling of air pollution with meteorological parameters unmistakably show. In a sample of winter smog, besides nitrogen-dioxide, there are also other polluting materials in smaller concentrations (such as carbon-monoxide), which can cause acute intoxication and other problems. . This is the first time that such research has been performed in the vicinity of Banja Luka.

1. INTRODUCTION
Nitrogen oxides play a significant role in various chemical and photochemical reactions in ambient air and the products of these reactions reduce the visibility and adversely affect human health, materials, and vegetation. Sources of nitrogen oxides in the environment are natural or man-made. Initially, NO is emitted into the ambient air on the same way as well as anthropogenic activities. The speed of conversion and the formation of secondary pollutants depend on concentrations of ozone, OH-radicals, hydrocarbons, other air pollutants, and especially on insulation (Spicer, 1977).

2. METHODOLOGY
For determination of parameters of air pollution *Measuring station* LU3000 was used. Nitrogen dioxide, NO and NOx have been measured by equipment from *Thermo Electron Corporation Environmental Instruments Environmental instruments 27 Forge Parkway Franklin Massachusetts*. Monitoring of nitrogen oxides concentration was performed by the Model 42C Chemiluminescence NO-NO_2-NO_X Analyzer, APNA 360. For the level of pollution by NO_2 a chemiluminescence method was used, Ranges were: 0-0, 1/0-0,2/0-0.5/0-1.0/0-2/0-5/0-10 ppm. For monitoring of nitrogen oxides there is no CEN standard, and it is in preparation phase, but there is ISO/FDIS (ISO 7996:1985).

The Model 42C is based on the principle that nitric oxide (NO) and ozone (O_3) react to produce a characteristic luminescence with intensity linearly proportional to the NO concentration. Infrared light emission results when electronically excited NO_2 molecules decay to lower energy states (Navas et al., 1997).

Simultaneously data are obtained on average temperature, air pressure, and relative humidity, speed and wind direction, recorded at the meteorological monitoring site at the outer rim of the inner city every day for the entire duration of the study.

These results of imission of pollutant monitoring during 2006 were compared in accordance with current legal regulations regarding air quality, issues on pollution and air quality control. Based on both data and Regulations on limit values of air quality (RLV, 2005) and standards recommended by World Health Organization (WHO) and EU countries, an assessment of the current state will be given. It will be determined if the measured values satisfy recommended and limit values specified in law. The results will also be compared in accordance with Resolution on air protection in the Municipality of Banja Luka (RAP, 1989) which suggests limit values for measuring pollutants, showed in $\mu g/m^3$.

For the analysed parameters, the following were given - sum of measurements (Σ), number of measurements during a month (N), then average values (X), standard deviation (SD), minimum (min) and maximum (max) values and number of days (BD) when these measurements exceeded limit value (ELV) were recorded.
Standard deviation, that represents square root from variance (average square deviation) and most frequently used measure for dispersion, was measured.

For processing the statistic data while determining interdependence and relation between some parameters of air quality and meteorological ones - i.e. for modelling of pollution together with meteorological parameters - classification trees were used, which represent statistical technique that is most frequently used (originated from artificial intelligence) in the field of generating the rules out of data - data mining (DM). A DM machine can be used for future planning and DM's purpose is prediction. Modern software packages used for simulation of pollution of NO_2, i.e. modelling, are: *Sipina for Windows* and *SPSS* 15.0 used for correlations and regression NO, NO_2, NO_X and meteorological parameters.

3. RESULTS AND DISCUSSION

Mean annual of concentration NO_2 in a research field of Banja Luka is 46.08 $\mu g/m^3$.

The highest values of nitrogen dioxide were in September (83.18 $\mu g/m^3$), December (66.42 $\mu g/m^3$) and November (63.36 $\mu g/m^3$), the lowest in July (12.56 $\mu g/m^3$) while the maximum value - 193.13 $\mu g/m^3$ - was in February, and minimum - 0.44 $\mu g/m^3$ - in July. It is stated that the mentioned area belongs to air quality class III, which represents more seriously polluted air with an influence on human health, flora and fauna, corrosion and damage to tangible goods. However, the September value of 83.18 $\mu g/m^3$ belongs to class IV, which

represents area with very contaminated air which endangers human health, causes progressive deterioration of fauna and flora, corrosion and damage to tangible goods (RAP, 1989). From April to July, the air quality was satisfactory, based on presence of nitrogen dioxide, and it classified the area under research into class I of air quality. The maximum limit for hourly sampling period is 200 $\mu g/m^3$ and it should not be exceeded more than 25 days during a year and on average in 3 years, but in Banja Luka it was exceeded 31 times, which is 7 times more than recommended. For 24-hour sampling period the maximum limit is 90 $\mu g/m^3$ and it should not be exceeded more than 7 times in a calendar year - but in Banja Luka it was exceeded 20 times in this period of examination, which is even 3 times more than recommended.

Linear interpolations between NO_2 and NO_X, NO_2 and t ^0C, NO_2 and NO are shown in Figure 1, 2 and 3. Research shows that variation of NO_2, NO and NO_x dominantly depends on both industrial activity during a day and meteorological conditions.

After entering the data, the software itself starts automatic analysis, develops the model and finds patterns regarding the relation between pollutants and meteorological parameters, and based on these results, several patterns indicating significant relation between air pollution and meteorological parameters were confirmed. These can be used to predict air quality in Banja Luka, through meteorological parameters successfully.

Results of modelling show that under certain meteorological conditions ocuring in winter, the probability of exceeding limit value for NO_2 in Banja Luka area during the testing period was 100%. Statistical analysis confirms this finding.

Mathematical modelling is based on numerous data and results of systematic measurement. The value of calculated coefficient for linear correlation is r = 0.180 for NO, 0.272 for NO_2 and 0.219 for NO_X and it evident that there is an important degree of linear correlation and correlation is significant at the 0.01 level.

Correlations and regression NO, NO_2, NO_X and meteorological parameters (speed and wind direction, average temperature, relative humidity) have been tested. As shown as that a correlation exists between pollutants and meteorological parameters and the high level of linear correlation is evident.

Between NO, NO_2 and temperature is obtained the mathematical model for linear dependence between y, x_1 and x_2, e.g. a dependence $y = a + bx_1 + cx_2$, or $y = a + bx_1 + cx_2 + dx_2,x_3$. Coefficient correlations have high value and shows that a correlation exists.

Correlation between NO_2 and t ^0C has tested and mathematical model (function) was established for linear dependence between NO_2 and t ^0C ($NO_2 = f(t\ ^0C) = 54{,}440 – 0891\ t\ ^0C$) (Fig. 1).

Statistical analysis NO_2 and NO gave out a mathematical model (function) for linear dependence between NO_2 and NO, which is shown as: $NO_2 = f(NO) = 31.590 + 0.429$ NO, and the value for coefficient of correlation r = 0.601 (Fig. 2). For NO_2 and NO_X was established a mathematical model of linear dependence between NO_2 and NO_X, which is shown as $NO_2 = f(NO_X) = 21.006 + 0.263\ NO_X$; the value for coefficient of correlation is r = 0.749 (Fig. 3).

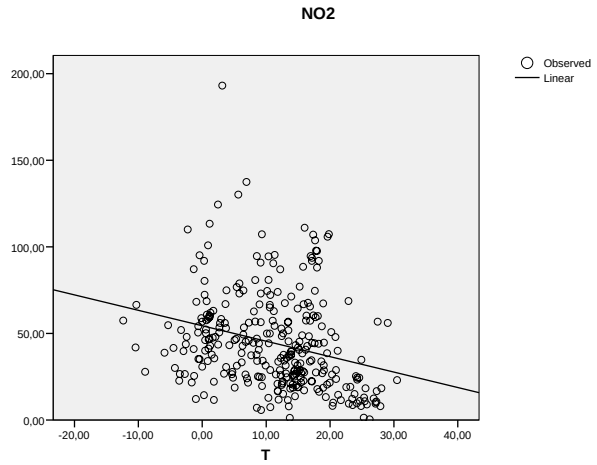

Figure 1. Linear interpolation between NO_2 and t ^0C

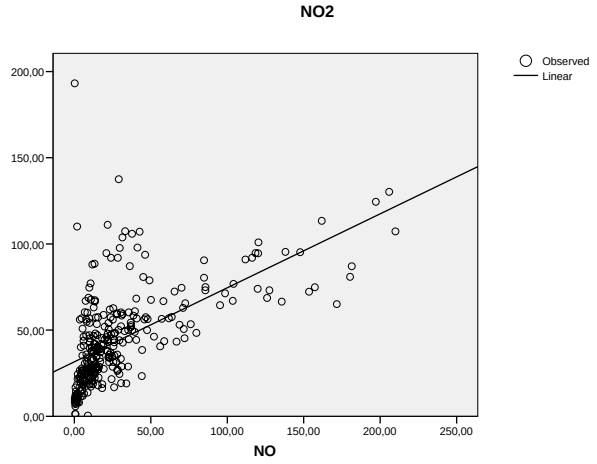

Figure 2. Linear interpolation between NO_2 and NO

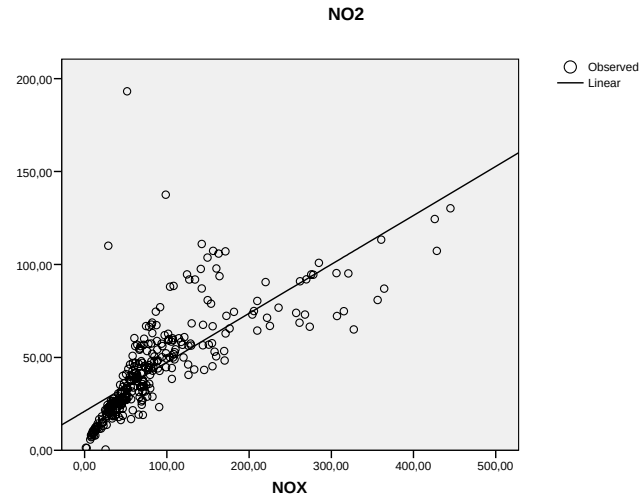

Figure 3. Linear interpolation between NO_2 and NO_X

4. CONCLUSIONS

Mathematical models have been created to describe a functional dependence between some air pollutions parameters and meteorological parameters in Banja Luka.

The dependence between NO_2 and NO has showed as: NO_2 = f (NO) 31,590 + 0,429 NO with the value for coefficient of correlation r = 0,601.

The function between NO_2 and NO_X is: NO_2 = f (NO_X) 21,006 + 0,263 NO_X the value for coefficient of correlation r = 0,749.

The functional dependence for NO, NO_2, NO_X and meteorological parameters. The results have shown that exist high level of linear correlation for some meteorological parameters.

Results suggest the importance of such research, and need for additional research regarding the relation between pollutants in air and meteorological parameters.

5. ACKNOWLEDGEMENT

In this work, we used the equipment belonging to Ministry of Space Planning, Urbanism and Ecology of the Republika Srpska and Institute of Protection, Ecology and Informatics, Banja Luka.

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6.4 Reduced CO_2 emission due to decreased gas consumption in generation plant "CERAK"

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ABSTRACT
The generation plant "Cerak" is a highly attractive location for location of solar collectors. Within the plant area up to 5,000 m^2 exists for placing of solar collectors without significant investments in preparation work for collector field installation. The plant size (under 10 MW) means there is no necessity for pre-feasibility study. The simulation has been performed within software package "Trnsys 16" specialized for various system calculations including solar systems. The simulation is made for a combined system for district heating water production for two collector areas: 5,000 m^2 and 8,000 m^2 during the summer operating mode of the generation plant "Cerak". Three possible operating modes of the combined system have been analysed for the specified heat capacity of 6 MW: the present 62/45 ^oC with flow of 300 m^3/h hot water, a designed 65/22 ^oC system with flow of 120 m^3/h and a future 60/40 ^oC system with flow of 250 m^3/h, that will be achieved after planned reconstruction and modernization of the entire system of the generation plant "Cerak". Gas savings are proportional to collector area, since significant advantages from solar radiation can be obtained during the summer season in the "Cerak"generation plant. In accordance with type of collector and its operating mode, gas savings range from 7.58 % to 17.89 % [8].

1. Solar system in generation plant "Cerak"

The ''Cerak'' Generation plant is an integral part of the Public Utility Company ''Beogradske elektrane'' and it produces and delivers energy for heating and domestic hot water to customers in the Belgrade municipalities of Cukarica and Rakovica. The basic fuel currently used in the plant is natural gas or fuel oil. Total boiler installed capacity is 244.3 MW, the capacity for heating and hot water is 230 MW, while the estimated installed capacity of 16.3 MW produces hot water. The designed level for summer operation mode (15 June - 15 October) is 65/22 °C, with the flux of 120 m^3/h for sanitary hot water production. The present summer operation mode is set up at 62/45 °C for the capacity of 6 MW with flux of 300 m^3/h of hot water. It is expected that in the upcoming period modernisation and new operation mode of district heating substations would be set up at 250 m^3/h flux and temperature mode of 60/40 °C.

Figure 1 presents the technological process of connection between new equipment with the existing plant "Cerak". The area possible for solar collectors placing is approximately 15,000 m^2, including covering of two parking areas. The present route of gas line and main district heating pipeline have been considered in the selected location (calculated 5 m from the gas line route). In consideration of future enlargement of the main plant structure, a location for accompanying structure with the area of 8 x 8 m for equipment storage (pumps, equipment for measuring and regulation, plate heat exchangers, expansion vessel) has been chosen, as well as location of heat accumulator with capacity of 1,000 m^3.

Due to differences in pressure between main pipelines and solar collectors and different fluids used in circulation (during heating plant winter operation mode, working fluid of solar plant would be the mixture of liquid of water and propylene-glycol, while the main pipeline would use chemically adjusted hot water), it would require installing plate heat exchanger. During the design phase, it would be proper to calculate plate heat exchanger area extension for 30% due to the presence of propylene glycol in the working fluid.

2. RESULTS FOR CO_2 REDUCTION OBTAINED BY SIMULATION FOR DIFFERENT TYPES AND COLLECTOR AREAS

Republic of Serbia has ratified the Kyoto protocol, according to which Serbia is not in the group of Annex I countries. Thereby the opportunity for including this type of project in CDM project (Clean Development Mechanism) is opened, as installation and use of thermal receptors of solar energy reduces consumption of fossil fuel and CO_2 emission.

Natural gas combustion releases 50.33 kg CO_2/GJ fuel energy [8]. Based on the results obtained by simulation of different types and different collector areas, reduction in CO_2 emission is calculated for summer operating mode of the "Cerak" generation plant [10]. Two collector types are used for calculation: evacuated tube collectors (manufacture Apricus type AP-30, Australian-British company manufacturing in China) and flat-plate collector (NAU type "Flatline BE Ultra plus and manufacture by GJ Denmark A/S type GJ 140A, Danish company manufacturing in Vietnam). These were chosen as readily available and data on their features necessary for system simulation have been accessible. Tables 1-3 show values for reduction of CO_2 emissions for all simulated cases.

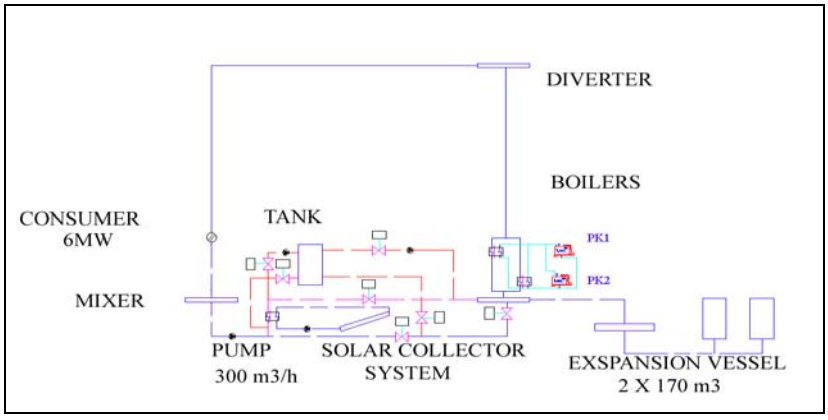

Figure 1. Scheme of technological connection between equipment and existing plant "Cerak" [8]

Table 1. Reduction of CO_2 emissions for mode of operation 62/45 °C, 300 m^3/h [5].

Reduction of CO_2 emissions (t/year)		
Manufacturer of collectors	Collector area 5000 m^2	Collector area 8000 m^2
a) Apricus	453.97	750.39
b) NAU	549.60	885.49
v) GJ	515.07	829.48

Table 2. Reduction of CO_2 emissions for mode of operation 65/22 °C, 120 m^3/h [5].

Reduction of CO_2 emissions (t/year)		
Manufacturer of collectors	Collector area 5000 m^2	Collector area 8000 m^2
a) Apricus	517.83	831.13
b) NAU	699.38	1084.10
v) GJ	665.27	1043.67

Table 3. Reduction of CO_2 emissions for mode of operation 60/40 °C, 250 m^3/h [5].

Reduction of CO_2 emissions (t/year)		
Manufacturer of collectors	Collector area 5,000 m^2	Collector area 8,000 m^2
a) Apricus	471.31	753.47
b) NAU	585.36	935.07
v) GJ	550.47	882.65

Savings in CO_2 emission of 1 t/year is equal to 1 CER value with a market value of 4 to 14 euros. A value of 8 euro/CER has been adopted, as well as the certificate terms of collection 3 x 7 years (total period of 21 years, which is forecasted operation life of collector).

Savings using combined system for water heating due to reduction of CO_2 emission for different operating modes are given in the Tables 4-6.

Table 4. Reduction of CO_2 emissions for operating mode 62/45 °C, 300 m^3/h [5].

	Savings by CDM project for 21 years (euro)	
Manufacturer of collectors	Area 5,000 m^2	Area 8,000 m^2
a) Apricus	76,267	126,066
b) NAU	92,333	148,762
v) GJ	86,532	139,353

Table 5. Reduction of CO_2 emissions for operating mode 65/22 °C, 120 m^3/h [5].

	Savings by CDM project for 21 years (euro)	
Manufacturer of collectors	Area 5,000 m^2	Area 8,000 m^2
a) Apricus	86,995	139,630
b) NAU	117,496	182,129
v) GJ	111,765	175,337

Table 6. Reduction of CO_2 emissions for operating mode 60/40 °C, 250 m^3/h [5].

	Savings by CDM project for 21 years (euro)	
Manufacturer of collectors	Area 5,000 m^2	Area 8,000 m^2
a) Apricus	79,180	126,583
b) NAU	98,340	157,092

v) GJ	92,479	148,285

Costs of validation, monitoring and certification for the entire project amount to 85,000 euros, and based on this information we can say that, in principle, it is not profitable to participate in CDM projects for the total collector area of 5,000 m^2. However, by increasing solar collector's area, the situation changes and additional savings can be achieved by installation of a combined system for water heating when participating in CDM projects. Thereby for improved the operation regime 60/40 °C and 250 m^3/h hot water, the total saving for 8,000 m^2, is approximately 41,000 euros for collector type Apricus, approximately 72,000 euros for collectors of NAU type and approx. 63,000 euros for collectors of GJ type, which is approximately 7 % of investment costs.

3. CONCLUSION

Investment can be paid out in period between 5.2 and 8.8 years depending on collector type and operating mode of combined system [8]. The study uses annual increase in gas price with growth rate of 6 % (present gas price is 0.3 euro/m^3 in 2009 year) and an increase in gas price that favourably influences pay out period, and the best saving is forecasted for the end of operation life of solar collectors. Due to constant yearly decrease in collectors' production price, it was impossible to include collector's price in feasibility calculation.

Installation of solar collectors would reduce hazardous gases emission, especially CO_2, that has a significant effects on environment and health at local level. Additionally, CO_2 emission reduction has been introduced in the EU, and in accordance with Kyoto protocol, its market value and opens the possibility of applying for CDM project. For areas of 8,000 m^2, savings for 21 years are approx. 7 % of total investment costs, and by increasing collector areas, the savings additionally increase due to fixed costs for equipment and monitoring of the CDM project [8].

Simulation shows that the forecasted modernization of substations also reduces pay out period, and enables better usage of solar system in the "Cerak" generation plant. It is important to emphasise that price of collectors produced by NAU manufacturer is given in euros, while the price of other manufactures is given in dollars, which badly reflects on pay out period for collectors produced by NAU, due to the devaluation of the dollar in the last six months in comparison to euro. In the following period, until commencement of solar system installation work in the "Cerak" generation plant, the changes in current values of these two currencies may occur that could lead to change in data on system pay out period depending on collector's manufacturer.

Project "Exploring possibilities and feasibility of substitution of fossil fuels with solar energy in district heating water production in the "Cerak" generation plant in Belgrade, financed by Ministry of Science of Republic of Serbia, and will be ongoing for the following 15 months as a design brief has an optimization of entire combined system for hot water production. Therefore, in the upcoming period, the optimization of individual system parts will be performed. This predominantly means the additional reduction in temperature at the collector field output (due to reduction of boiler transmission lost), whereby there will be no

reduction in efficiency of other system parts such as heat accumulator and heat exchanger.

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6.5 Diurnal and seasonal variation of particulate matter (PM_{10}) in Podgorica background and traffic sites

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In the framework of Annex III to the Memorandum of Understanding signed on the 30th of January 2007 between the Italian Ministry for the Environment, Land and Sea (IMELS) and the Montenegrin Ministry for the Tourism and the Environment, a Work Plan was prepared concerning the technical assistance to the Republic of Montenegro in the field of environment.

In this framework the Institute for Atmospheric Pollution of the Italian National Research Council was entrusted with the technical responsibility of the "Technical Assistance for the activities related to atmospheric pollution in Montenegro". Part of the project, which is for the city of Podgorica is done in co-operation with the Institute for Atmospheric Pollution and the Centre for Ecotoxicological Researches of Montenegro (CETI) in Podgorica. Podgorica is the capital and the biggest city of Montenegro; furthermore it is affected by traffic pollution and is very close to the KAP (Kombinat Aluminijuma Podgorica). Regarding PM_{10}, during the feasibility study it was concluded that a minimum of two sampling sites would be enough to fully characterize Podgorica air quality. These sites were located one in the centre of town close to a very busy street and one in a background location near the Skadar Lake, north-east of Podgorica.

6.6 Recent efforts towards improving the assessment of particulate matter in the Czech Republic

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Ambient air pollution load caused by suspended particles (PM) represents a major problem in Europe. The EU directives and national legislation set air pollution limit value for PM_{10} fraction, and air pollution measurements are mostly carried out with regard to this fraction. The analysis of the measured data shows that these limit values are markedly exceeded in a number of sites in the Czech Republic.

Several types of information are essential in order to manage this problem. In addition to the required compliance monitoring, we need to know what sources contribute to the loads, and this in turn requires detailed chemical and physical characterization of PM, preferably including also smaller fractions such as $PM_{2.5}$ and PM1. Further, in order to comply with the requirements of warnings to the population, the authorities need access to a predictive dispersion model for PM. Concentrations of PM comprise contribution of primary emissions of PM of both anthropogenic and natural origin, as well as particles formed in the atmosphere from the primary emissions of both individual constituents of PM and a large number of gaseous substances of organic and anorganic nature.

In order to address these challenges, the CHMI in collaboration with ICPF and NILU have designed a three-year program that has three research activities: (1) Improved characterization of PM_{10} focused on the contribution of secondary particles to total load in ambient air, (2) formulation of chemical model of secondary particles formation and source identification and (3) application and verification of atmospheric transport and dispersion model.

An extended monitoring and analysis program was implemented on two urban background sites in Prague, located at the outskirts upwind and downwind of the main wind direction. Sampling equipment was installed that allows collection of two fractions of PM and subsequent analysis of ions, metals, and organic compounds (carbon and organic tracer analyses). This is complemented by local meteorological data and routine monitoring results, as both sites are members of the compliance air quality monitoring network. 24-hour samples were collected every 6^{th} day, so that the resulting database now contains speciation based on 80 samples, two fractions, and will be used in an analysis aiming at quantification of source contribution.

At the start of the project, the CHMI has not decided which chemical transport model will be used to upgrade their modeling framework, but during the first year, the CAMx model was selected and is being implemented. The project team has formulated a chemical reaction scheme, based on the EMEP chemical scheme enhanced by own research, looking especially at the secondary organic aerosol formation. During the project, we plan to implement this scheme into the CHMI

modeling framework, and to set up modeling exercises that would lead to model evaluation.

The project period will run until April 2010, at which point we would like to organize a stakeholder workshop making the results available to the appropriate authorities, as well as to research colleagues. The project is supported by a grant from Norway through the Norwegian Financial Mechanism (www.eeagrants.org), project number CZ0049, and by the participating institutions.

6.7 Atmospheric Pollution from Organic Toxicants in Pancevo

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ABSTRACT
Airborne particulates of Pančevo, Serbia, were chemically characterized for their burdens of organic toxicants at five locations over the urban and surrounding areas through in-field measurements conducted from July 2006 to March 2007 (five sites in total). Airborne particulates were collected at low-flow conditions, pooled in monthly groups and processed through soxhlet extraction, column chromatography fractionation and CG-MSD analysis. The atmosphere was found to be contaminated at different degrees according to typology of site and year time. In particular, among polynuclear aromatic hydrocarbons (PAH) benzo(a)pyrene in winter was demonstrated to exceed by far (four to seven times) the European guidelines (1 ng/m3). Nitro-PAH affected the industrial district at much higher extent than the rest of the city and showed a peculiar group profile, since the presence of chemicals associated to direct emission was observed there. *n*-Alkanes were quite abundant in all year and seemed to be overall associated to anthropogenic sources. Other important air contaminants were nicotine and caffeine. The industrial district appeared affected by the residues of plastic manufacture plants, including phthalates, benzenesulfonamides and chlorinated benzofurans. Nevertheless, the principal source of sanitary concern seems to lie in the duty contamination from chlorinated toxicants; in fact, presumably high concentrations of polychlorobenzenes and polychlorotoluenes were found to affect the airborne particulates, and polychlorobiphenyls were also identified, although all these chemicals are semi-volatile and exist overall in the gas phase. Owing to these compounds are banned since long time, their occurrence presumably came out from the Balkan War, which caused the destruction of industrial and power facilities of the city and heavy contamination of waters and soil.

1. INTRODUCTION

The industrial complex of Pančevo (80,000 inhabitants, 20 km NE of Belgrade, Serbia) was seriously compromised during the Balkan War [1]. The OTAN bombardments destroyed plants; consequently toxicants and chemicals were poured into the river waters and soil [2], which worsened the environment already compromised. In fact, air, soil and water were heavily affected by emissions and wastes, which was recognized to cause the insurgence of tumours including the so-called *Pančevo's cancer* [3]. At the end of the war a big plan of mitigation was launched with the participation of International Community (United Nations, OTAN, Russia, European Union), together with programs aimed at promoting the development of the region [4]. Moreover in the last decade new pollution sources have gained importance, including house heating plants and motor vehicles exhausts. In the context of the renewed co-operation of International Community with the Republic of Serbia, extensive studies have been conducted to characterize environmental pollution in the Pančevo city. Our study was focussed on airborne particulates and on their organic burden. Measurements were made in July and October 2006, and in January and March 2007.

2. METHODOLOGY

Airborne particulates were collected at five locations, namely: *i)* at the top of the Public Health Institute, located inside a park in the Pančevo centre (site A); *ii)* at the Fire Brigade side, close to the new road to Belgrade (site B); *iii)* in a dwelling area hosting coal-stove heated houses (site C, residential quarter); *iv)* inside the fertilizer plant (site D, industrial district); and *v)* in the rural outskirts (site E, urban background). Sampling was made at low-flow and particles (PM_{10}) was collected on Teflon filters. Aerosols were collected daily and stored at 4°C, then they were pooled in monthly samples to characterize *n*-alkanes, PAH and polar compounds. For nitro-PAH and chlorinated toxicants the monthly extracts were further combined to obtain one sample per site per season. According to the method adopted [5] and to air volumes sampled (namely ≈150 m^3), the LOQ, corresponding to signal-to-noise ratios equal to ten, were better than ~0.02 ng m^{-3} for all *n*-alkanes, ~0.01 ng m^{-3} for PAH, ~0.01 for nicotine, and ~0.02 for caffeine. The LOQs of Nitro-PAH up to nitropyrenes ranged from 0.005 to 0.020 ng m^{-3}. The overall uncertainty associated to the analytical procedure was calculated better than 16 ± 7 % for all compounds.

The protocol characterization of particulates included identification and quantification of "usual" air contaminants. It was performed according to the following procedure: after fortification with a set of perdeuterated reference compounds, the samples were extracted in soxhlet with dichloromethane/acetone, reduced close to dryness and fractioned by alumina column chromatography. Non-polar, low-polar and highly-polar compounds were eluted, in the sequence, by means of isooctane, isooctane/dichloromethane (3:2) and dichloromethane/acetone (1:1). The compounds were identified and quantified by GC-MSD (EI, *SIM* mode). Sample aliquots were injected in split-less mode and the compounds were separated by a RTX-type capillary column (30 m, 0.25 mm, 0.25 μm) operated in temperature gradient (60°C to 190°C at +15°C min^{-1}, then up to 290°C at +4°C min^{-1}) [5].

Non-polar and low-polar fractions contained the aliphatic (*n*-alkanes) and polyaromatic (PAH, Nitro-PAH) hydrocarbons, respectively. The highly-polar fraction comprised oxygen (OPAC) and nitrogen (NPAC) heterocyclic compounds, plus nicotine and caffeine.

n-Alkanes are among the principal components of organic particulates and their percent profile allows to draw insights about the nature of sources [6]. On the other hand, PAH are less abundant but subject of regulations due to their well known carcinogenic properties [7-8]; several Nitro-PAH are strong mutagens [9] and source-specific [10]. Among the OPAC and NPAC, 9H-fluorenone, anthrone, 9,10-anthraquinone, benzanthrone, acridine, carbazole and benz(c)acridine are considered toxicants. OPAC have been associated with direct emission and PAH decomposition, while NPAC are anthropogenic, coming out from burning of organic matter burning. Nicotine and caffeine can be considered as tracers of the tobacco smoking and food cooking respectively.

After the protocol analyses, the samples were again processed to draw further insights about the aerosol composition, without any quantitative purposes but in the perspective of recognizing important contaminants. First, the main

components in the highly-polar fraction were tentatively identified by means of GC-MSD operated in *scan* mode, by comparing the corresponding mass spectra to the NIST and WILEY libraries and to authentic standards. Second, the polarity fractions corresponding to each site were gathered together and eluted through a SiO_2/H_2SO_4 column with *n*-hexane; organic compounds prone to decomposition were cut-off, and the solution was eluted again on silica with *n*-hexane/chloroform (80:20). By processing again the extracts through GC-MSD both in *scan* and *selected-ion-monitoring* modes several chlorinated organics, including polychlorinated benzenes (PCBz), toluenes (PCTo), biphenyls (PCB), naphthalenes (PCN), pesticides (OCP), styrenes, cyclohexanes and cyclopentanes, were identified.

3. RESULTS AND DISCUSSION

The concentrations reached by *n*-alkanes, OPAC, NPAC and Nitro-PAH in the five sites are reported in Table 1.

Total *n*-Alkanes were equal to 90±15 ng m^{-3}, independently of the site, and peaked in July. Also the percent distribution within the group was fairly constant, peaking in the correspondence of C_{29} and presenting a pattern typical of anthropogenic emission with a small contribution of natural sources. Much wider variations site to site and along the year were shown by the other groups. Nicotine reached its maximum in October (28±15 ng m^{-3}), peaking in B (~42 ng m^{-3}); caffeine peaked in March (10±9 ng m^{-3}), in C (23 ng m^{-3}). Both OPAC and NPAC touched their maximum in January (23±13 ng $m^{-3}$and 7±3 ng m^{-3}, respectively), with concentrations surprisingly high at the suburban site (OPAC, 43 ng m^{-3}; NPAC, 4.5 ng m^{-3}). Nitro-PAH were quite high in C (1.8 ng m^{-3}) and D (3.6 ng m^{-3}), and low elsewhere (0.35±0.1 ng m^{-3}), however the percent profiles at the two main sites were very different, C being affected by secondary pollution (Nitro-PAH coming from oxidation of PAH), D undergoing the influence of direct emission.

Looking to PAH, airborne particulates collected in January, they were three to seven times richer than in July, October and March (Table 2). On the average, benzo(a)pyrene was close to 1 ng m^{-3} at the five sites in the "clean" months and reached 5.5 ng m^{-3} in January. Total PAH were 16±2 ng m^{-3} in July, October and March and 74±26 ng m^{-3} January, when exceeded 42 ng m^{-3} even in the background. As concerns the PAH percent composition, A and B sites were characterized by benzofluoranthene and benzo(e)pyrene, each accounting for more than 13% of the total, while indenopyrene and benzo(ghi)perylene were the major components in C and E. Benzofluoranthenes and benzo(e)pyrenes were fairly equal in D (each ~12% of total), except in October, when benzo(b)fluoranthene alone accounted for 23%.

Table 1. Particulate n-alkanes, OPAC, NPAC and Nitro-PAH (ng n^{-3}) detected in Pančevo.

site	A		B		C		D		E	
	ave.	st.dev.	ave.	st.dev.	ave.	st.dev.	ave.	st.dev.	ave.	st.dev.
n-C18	1.3	0.4	1.1	0.7	0.8	0.2	3.0	3.4	1.5	0.4
n-C19	1.1	0.3	0.9	0.4	0.8	0.2	1.0	0.4	1.3	0.3
n-C20	1.1	0.4	0.9	0.4	0.8	0.2	0.9	0.5	1.2	0.3
n-C21	1.1	0.4	1.1	0.4	0.8	0.2	1.4	1.1	1.2	0.4
n-C22	0.8	0.0	1.1	0.2	1.0	0.2	1.5	0.8	0.9	0.1
n-C23	1.1	0.2	1.3	0.2	1.4	0.5	1.7	0.6	1.2	0.2
n-C24	1.8	0.5	1.9	0.5	2.4	0.9	2.1	0.4	2.0	0.4
n-C25	2.8	1.0	2.8	0.8	3.8	1.6	3.1	0.7	2.9	0.8
n-C26	3.5	1.0	3.6	0.9	4.8	1.8	3.7	1.4	3.6	1.1
n-C27	4.4	1.0	4.7	1.1	6.0	2.2	5.7	1.3	4.4	1.2
n-C28	10.1	2.9	8.8	1.2	12.9	6.2	11.3	4.5	8.8	2.3
n-C29	13.9	2.6	13.4	2.0	19.0	7.2	18.5	2.1	14.8	4.5
n-C30	8.0	2.8	7.7	2.5	12.1	7.3	10.8	4.4	8.4	3.4
n-C31	13.0	3.0	10.8	3.0	18.6	7.3	15.6	1.2	13.8	5.3
n-C32	4.9	2.4	4.6	1.8	8.0	5.2	6.8	2.7	6.0	3.1
n-C33	4.9	1.5	4.1	1.3	7.6	3.4	5.9	0.7	5.8	2.4
n-C34	1.9	1.1	1.6	0.6	3.5	2.5	2.3	0.6	2.6	1.5
n-C35	1.6	0.6	1.4	0.5	2.8	1.5	1.8	0.4	2.4	1.0
nicotine	27	15	8.8	4.9	25	14	19	14	8.4	2.6
caffeine	3.6	2.8	7.6	8.2	11.1	8.5	3.6	2.0	1.1	0.9
fluorenone	0.12	0.16	0.09	0.10	0.09	0.04	0.20	0.27	0.04	0.02
anthrone	0.70	0.51	0.79	0.67	1.43	1.00	1.38	1.76	0.32	0.22
anthraquinone	0.27	0.42	0.10	0.08	0.09	0.06	0.32	0.52	0.04	0.04
benzanthrone	0.35	0.40	0.38	0.63	0.22	0.29	1.81	3.39	0.99	1.70
acridine	0.30	0.30	0.49	0.40	0.59	0.48	0.33	0.52	0.14	0.16
carbazole	0.10	0.12	0.06	0.04	0.04	0.03	0.17	0.20	0.03	0.03
benzoacridine	0.06	0.07	0.02	0.02	0.03	0.02	0.16	0.25	0.01	0.00
2-NFln	n.d.	--	n.d.	--	0.02	--	1.70	--	0.00	--
9-NAn	0.02	--	0.04	--	0.16	--	n.d.	--	0.02	--
9-NPh	0.01	--	0.04	--	0.10	--	n.d.	--	0.02	--
3-NPh	0.02	--	0.02	--	0.08	--	1.33	--	0.02	--
2-NAn	n.d.	--	n.d.	--	0.21	--	0.20	--	0.03	--
2-NFa	0.15	--	0.09	--	0.44	--	0.08	--	0.10	--
4-NPy	0.09	--	0.08	--	0.25	--	0.15	--	0.01	--
1-NPy	n.d.	--	n.d.	--	n.d.	--	0.04	--	n.d.	--
2-NPy	0.14	--	0.12	--	0.49	--	0.06	--	0.05	--

Table 2. Average PAH concentrations (ng m^{-3}) recorded in Pančevo at the five sites investigated.

site	A		B		C		D		E	
	J.O.M.	Jan.	J.O.M.	Jan.	J.O.M.	Jan.	J.O.M.	Jan.	J.O.M.	Jan.
Fa	0.4	0.4	0.3	0.6	0.3	0.6	0.7	2.4	0.3	0.5
Py	0.3	0.5	0.2	0.5	0.3	0.8	0.3	0.8	0.2	0.4
BaAn	0.1	2.2	0.1	0.9	0.2	2.2	0.2	1.3	0.1	0.6
Ch	0.4	3.9	0.4	3.1	0.5	4.0	0.8	2.6	0.4	1.4
BbFa	1.5	21	2.4	8.2	1.1	6.1	2.4	10.3	0.8	3.7
BkjFa	1.9	26	3.1	15.6	1.2	6.5	1.9	10.7	1.0	4.0
BePy	1.4	20	1.9	7.6	1.1	5.3	1.9	9.0	0.9	3.4
BaPy	1.0	7.1	1.0	3.6	1.0	7.2	1.2	4.9	0.7	4.0
Pe	0.2	1.5	0.3	0.8	0.2	1.4	0.2	1.0	0.2	0.7
IPy	2.2	9.1	2.4	7.4	2.3	10.9	2.2	7.1	2.0	6.7
DBAn	0.2	1.1	0.2	0.9	0.2	1.4	0.2	0.8	0.2	0.7
BPe	2.1	8.4	2.1	6.4	2.1	8.8	1.9	5.9	1.8	5.7

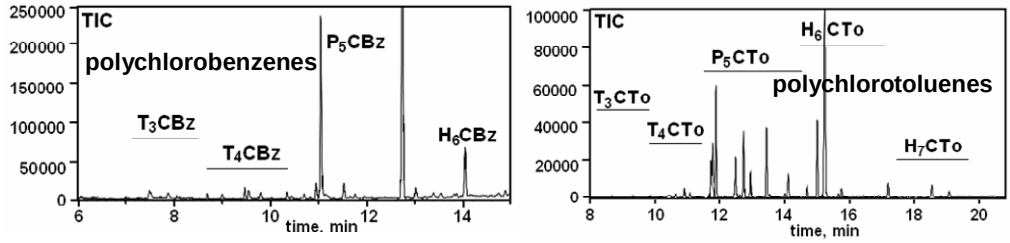
Symbols: Fln: fluorene; An: anthracene; Ph: phenanthrene; Fa: fluoranthene; Py: pyrene; BaAn: benzo(a)anthracene; Ch: chrysene; BbFa: benzo(b)fluoranthene; Bk/jFa:

benzo(j)fluoranthene/benzo(k)fluoranthene; BePy: benzo(e)pyrene; BaPy: benzo(a)pyrene; PE: perylene; IPy: indeno(1,2,3-cd)pyrene; DBAn: dibenz(a,h)anthracene; BPe: benzo(ghi)perylene; J.O.M.: average of July, October and March.

Further compounds detected

All particulate samples revealed the presence of plastic residues (phthalate esters and benzensulfonamide) as well as the imprint of biomass burning (C_{16}~C_{32} alkanols, sitosterols) and meat cooking (cholesterol). Nevertheless, the most important finding lied in the large presence of chlorinated organic compounds. In fact, the industrial district was affected by two major chlorinated chemicals and numerous other chlorine-containing groups. In particular, polychlorinated benzenes (PCBz) and toluenes (PCTo) were suspected to occur in noticeable amounts, while polychlorinated biphenyls, styrenes and cyclo-alkanes were present at lesser extents. Since it is well known that big PCB-oil containers were bombed during the Balkan War and caused their spilling into the surface waters and soil, the doubt exists that remediation actions subsequent to war end failed, or that toxic wastes have been poured out in the land. In fact, PCBz and PCTo were found only in the industrial district. Since these substances are semi-volatile and exist overall as vapours in the atmosphere, their presence in the airborne particulates suggests that they reach concentration levels enough high to represent a risk for the health of Pančevo inhabitants (See Figure 1).

Figure 1. GC-MSD profile of chlorinated benzenes and toluenes detected in the industrial district



4. CONCLUSIONS

The organic airborne particulates collected in Pančevo presented, on the average, the typical features of mid-to-highly polluted areas of Europe. Their composition revealed the predominance of anthropogenic emissions, with benzo(a)pyrene exceeding 1 ng m^{-3} on annual average also in the rural outskirts, and 5 ng m^{-3} in winter. A special pollution form was observed, associated to polychlorinated organic compounds. In particular, the occurrence of chlorobenzenes, chlorotoluenes and chlorobiphenyls was ascertained.

5. ACKNOWLEDGEMENTS

The research was conducted by the Institute for Atmospheric Pollution of the Italian National Research Council (CNR-IIA) within the "Industrial Air Pollution Management System in Pančevo" Project, financed by the Italian Ministry for the Environment Land and Sea – Department for Environmental Research and Development. We would also to thank the following Institutions and Companies for the support provided to carry out this study:

- the Italian Ministry for the Environment Land and Sea (IMELS) and in particular its Task Force for Central and Eastern Europe;
- the Serbian Ministry of Science and Environmental Protection;
- the Municipality of Pančevo;
- the Institute for Public Health in Pančevo;
- HIP Azotara, HIP Petrohemija and NIS Refinery Companies.

As for our CNR-IIA colleagues, we want to thank P. Romagnoli, M. Biscotto, Z. Radetic and L. Paciucci for their personal contributions to the in-field experiments, literature acquisition and manuscript edition.

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6.8 Particulate Matter Assessment in the context of Health Impact Study in Abu Dhabi (United Arab Emirates)

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ABSTRACT

A project dealing with the quantitative assessment and chemical characterisation of particulate matter (PM) in Abu Dhabi started in early 2009. By measuring PM in two size categories, respirable and fine particles, an estimation of the natural background fraction and the anthropogenic contribution shall be made. Ten monitoring stations with PM_{10} measurements, which are distributed over the Abu Dhabi Emirate, are the basis for the AD air quality monitoring programme. At three of the stations $PM_{2.5}$ is monitored in parallel. There are indications for a large regional contribution for both PM_{10} and $PM_{2.5}$ at all three stations. In a preliminary evaluation, more than 50% of the PM_{10} mass was found to be in the coarse fraction. The objectives and fundamentals of the project and first results are presented in this study.

1. INTRODUCTION

Abu Dhabi is the biggest of the United Arab Emirates and located on the Arabian Peninsula. The emirate experienced a rapid economic growth during the last 40 years. As the GDP and revenues from oil increased, large-scale projects were initiated, including building modern infrastructures and industries. This has induced a rapid shift of population from nomadic communities to urban centres as well as large-scale flow of workers to Abu Dhabi. The resulting growth of the population and the high living standard, based on oil extraction, involved a tremendous growth in road traffic in the city area and a high demand of energy. Consequently, the transportation, power and industrial sectors have to be seen as major sources for pollutant emissions to air in Abu Dhabi, where the importance of each of the sources may vary among different areas of the emirate. In the oil and gas industry, emissions are generated in all production steps; exploration, production, refining, gas processing and petrochemical industries. Road traffic should be regarded as the main air pollution source in the urbanised area where more than 85% of the emirate's population lives. Due to its location in the desert, the Abu Dhabi Emirate also has a relatively high, naturally occurring, level of particulate matter in the ambient air.

The adverse health effects of particulate matter (PM) are undoubted today. However, which particles pose the greatest threat to health is subject of discussion. Even though PM_{10} mass is the internationally recognised parameter to legislatively control the particulate matter content in ambient air, from the health effect point of view, $PM_{2.5}$ mass concentrations are considered to be more relevant (e.g. Pope and Dockery, 2006). Particles indicated by $PM_{2.5}$, also referred to as alveolar particles, can be breathed more deeply into the lungs and remain suspended in air for longer periods of time than larger particles. Apart from the size, the chemical composition of a particle is crucial for its health impact.

The large number of studies that have shown strong associations between particulate matter levels and a variety of health outcomes, led to changes in air quality standards in many regions, especially Europe and the United States. The very high natural particle background in the Middle East countries, surrounding the Persian Gulf and other desert countries (e.g. Brown et al., 2008; Ozer et al., 2006) is the reason for somewhat higher air quality standards (see Table 1) in these areas.

Table 1. Air quality standards (AQS) for particulate matter in Europe, USA and the Abu Dhabi Emirate (24 h / annual limits, in µg/m^3).

	WHO AQG[a]	**EU AQS**	**USA NAAQS**	**AD AQS**
PM_{10} (µg/m^3)	50 / 20	50 / 40[b]	150 / ~~50~~[d]	150 / -
$PM_{2.5}$ (µg/m^3)	25 / 10	- / 25[c]	35 / 15	- / -

[a] Air Quality Guideline (WHO, 2006)
[b] EC-Directive 99/30/EC, annual limit changes as from 2010: 50 / 20
[c] EU target value, CAFE-directive; limit value coming into force in 2015
[d] 2006 revision of US National Ambient Air Quality Standards revoked annual PM_{10} standard

Whether the high PM levels in Abu Dhabi are reason for serious concern depends both on the fraction of fine particles, which may be of combustion related origin, and on the composition of the particles. The aim of this study is to identify the anthropogenic and natural sources and to examine the occurrence of hazardous compounds.

2. METHODOLOGY

Ten measurement stations are operative in the Abu Dhabi Emirate, monitoring PM_{10}, as well as various gaseous compounds and meteorological parameters. At all stations, the measurements are performed on an hourly basis using beta gauge ambient suspended particulates monitors (MP 101 M, Environnement S.A., France). At three of the sites, $PM_{2.5}$ is monitored in addition, also using beta-attenuation mass monitors (BAM 1020, Met One Instruments Inc., USA). One sequential sampler (SEQ47/50, Sven Leckel Ingenieurbüro GmbH, Germany), accumulating particulate matter on filters, has been installed at one site to collect daily samples of airborne particles with aerodynamic diameter less than 2.5 µm ($PM_{2.5}$) over a four-week period, before it will be moved to the next site. During the first two weeks, the samples are taken on PTFE-filters for later analysis of heavy metals and inorganic ions. In the second half of each sampling period, quartz fibre filters are used for later analysis of elemental carbon (EC) and organic carbon (OC). It is planned to take filter samples from seven to ten sites in the emirate. The results from the quantitative laboratory analysis of the filters will give indications for the pollution sources influencing the different sites and provide a basis for an assessment of health impacts.

The city of Abu Dhabi is located on an island. This study focuses on the three monitoring sites with intensive particle measurements, two of which (H,K) are located on the island and one (B) on the mainland, close to the city. The first site (H) is a street site in downtown Abu Dhabi, which is located a few metres from a busy intersection, surrounded by high-rise buildings. Local sources influencing this site are mainly traffic sources. The second island site (K) is located on the premises of a school in a residential area. Low two to three storey buildings form the townscape and the site is a bit apart from the major traffic routes in the city, so

that only residential traffic is present. The third site is located on the mainland in a residential area, surrounded by low, wider spread buildings. It has a more desert-like character.

From earlier measurements in Abu Dhabi it is known that the PM_{10} air quality standard is occasionally exceeded at several monitoring stations and frequently at others. To figure out the significance of the exceedances, it is necessary to know the origin of the particles, their size class and composition. Information about this is expected from the mass ratio method. The mass ratio $PM_{2.5}/PM_{10}$ gives an indication of the relative importance of natural and anthropogenic sources to particulate matter. A low $PM_{2.5}/PM_{10}$ mass ratio indicates a relatively large contribution from natural sources, since they tend to dominate in the particle size range 2.5-10 µm. The additional chemical speciation of the $PM_{2.5}$ filter samples will give more insight into possible health impacts of particulate matter at Abu Dhabi sites. PTFE-filters will be analysed for inorganic ions (ion-chromatography) and elemental composition (ICP-MS), whereas the analysis of quartz filters by thermal optical reflectance will give information about the carbonaceous species. The elements can be interpreted as source specific markers, e.g. Zn (tyre wear), Cu, Fe, Sb, Sn (brake wear), V (fuel combustion), Ni (heavy oil combustion), whereas Al, Si, Ca, Ti, Mn, Fe, Sr, K, Mg are crustal elements. The air mass origin and meteorological conditions have to be considered as well in the analysis.

3. RESULTS AND DISCUSSION

The $PM_{2.5}$ measurements were added to the existing PM_{10} measurements during the first half of 2009, filter sampling began in June 2009. Before the onset of continuous monitoring, test and intercomparison measurements were carried out to assure a high data quality. The evaluation of first monitoring data is in progress and filter samples have not been processed yet. The amount of results is therefore very limited to date and only preliminary, exemplary results can be shown here.

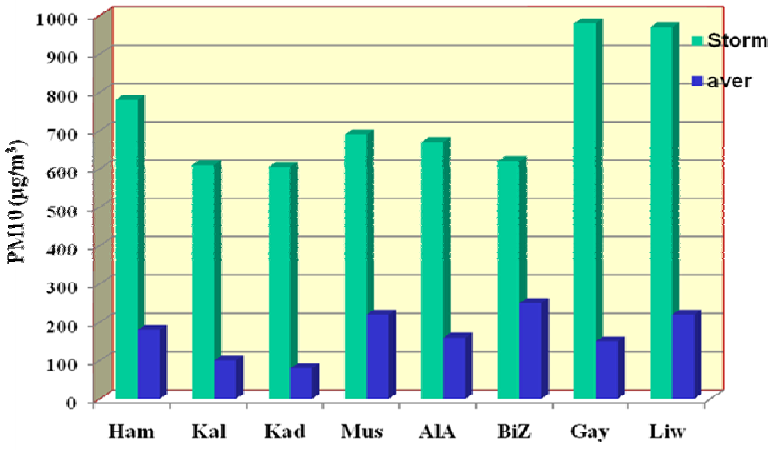

Figure 1: Dust storm 3 March 2009 concentrations compared to average PM_{10} concentration levels at 8 Abu Dhabi stations.

Average PM_{10} concentrations at Abu Dhabi sites exhibit rather high values as shown by the blue bars in Figure 1. The variation of concentrations among the stations may mirror the different area types and locations of the stations. The regional background station (Liw) shows as high values as the industrial site

(Mus) and an urban site (BiZ) in the western part of the emirate. This may be explained by their location in the desert. At the road side (Ham, Ala) and some downtown (Kad, Gay) and urban residential (Kal) stations, lower PM_{10} concentrations are found. PM_{10} concentrations during a dust storm episode in comparison to average PM_{10} concentrations at several sites in the Abu Dhabi Emirate are shown in Figure 1 as well. The first two stations correspond to stations H and K of this study. At all sites, particle levels during the dust storm are several times over the usual PM_{10} concentrations and levels of more than 1000 $\mu g/m^3$ can be reached. The last two stations with the highest PM_{10} concentrations during the storm are located in western part of the emirate, in the desert. Dust storms occur with a frequency of 20-50 days per year on the Arabian Peninsula, deteriorating the air quality and visibility significantly. The health impact of windblown desert dust, however, is regarded as lower than the effect of the smaller combustion particles.

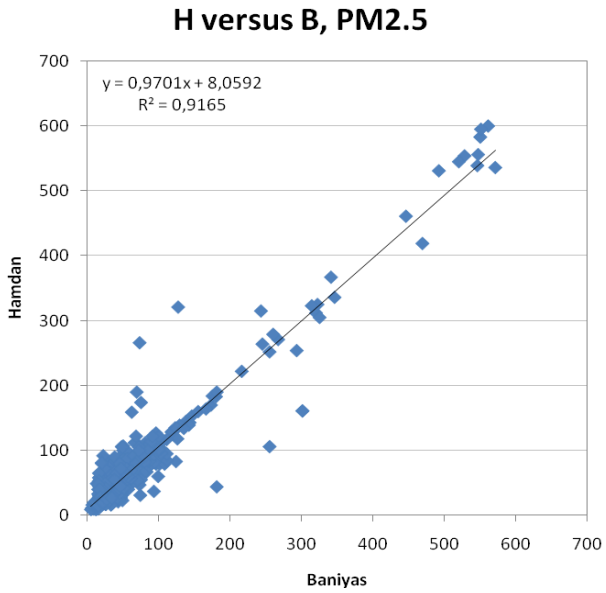

Figure 2: Scatter plot of $PM_{2.5}$ mass concentrations ($\mu g/m^3$) from the street site (H) and a suburban site (B).

The hourly $PM_{2.5}$ concentrations from all three stations were compared with each other. As an example, the scatter plot comparing the street site (H) in the city centre and the suburban site (B) on the mainland, is shown in Figure 2. A very high correlation for the entire observation period was found, although the sites were assumed to be influenced by different local sources. Especially for the street site (H), a higher contribution from traffic and therefore higher $PM_{2.5}$ was expected. The comparison of both data sets with the data from the third station (K) gave a very similar result. Regression slopes of ~1.0 make the covariation of the $PM_{2.5}$ concentrations at the three sites even more clear. This observation, on the basis of the first month of $PM_{2.5}$ data available, indicates that not only PM_{10}, but also $PM_{2.5}$ poses a regional problem. The relatively uniformly distributed $PM_{2.5}$ concentrations beyond the city limits suggest that also in the fine particle fraction, a significant portion is due to windblown dust. However, the speciation analysis of the filter samples will help identifying the origin of the particulate

matter and finding out whether the individual sites are influenced by different sources.

$PM_{2.5}$ measurements close to roadways in downtown Abu Dhabi during rush hour showed peak $PM_{2.5}$ hourly average concentrations of over 50 µg/m^3. During dust storm episodes, $PM_{2.5}$ levels of up to 600 µg/m^3 were found. Preliminary analysis of $PM_{2.5}/PM_{10}$ mass ratios at the urban traffic site (H) during usual conditions in February 2009 suggests that 50-60% of the PM_{10} mass observed was in the 2.5-10 µm size range. The high levels of PM_{10} and large fraction of coarse particles comprising PM_{10} may partially be explained by the resuspension of dust and soil from the desert crust. A longer time series is needed to obtain significant results on the mass ratio.

4. CONCLUSIONS

The focus of this article was on presenting the project and its objectives, since the evaluation is in an early stage. Present day PM_{10} levels at Abu Dhabi sites are high and frequently exceed the 24 hour air quality standard of 150 µg/m^3. Most of these particles are assumed to be of natural origin. A high natural background seems to be present for both PM_{10} and $PM_{2.5}$. The variation of $PM_{2.5}$ concentrations between different sites seems to be very low. These indications suggest that also in the fine particle fraction a considerable amount is regional. A chemical analysis of the fine particle fraction and combination with meteorological analysis will give more insight into the origin of the particles.

Since particle exposure in the United Arab Emirates has been identified as a source of concern, the outcome of the study will be valuable for taking actions on the improvement air quality in the future.

5. ACKNOWLEDGEMENTS

The authors gratefully acknowledge Leif Marsteen from NILU and the colleagues from the NILU office in Abu Dhabi.

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6.9 Formation of secondary organic aerosol from isoprene oxidation over Europe

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The role of isoprene as a precursor to secondary organic aerosol (SOA) in the atmosphere over Europe was studied using the two-way nested global chemistry transport model TM5 with a horizontal resolution of 1x1 degrees. We analysed results from three scenarios: 1) reference scenario: similar to the study by Tsigaridis and Kanakidou (Atmos. Chem. Phys., 3, 1849–1869, 2003) but including SOA formed from isoprene oxidation (SOA-I), 2) best guess scenario: considers several updates in parameterisations and uses the recent MEGAN isoprene emission inventory, and 3) zero SOA-I scenario: SOA formation from isoprene oxidation is ignored. The predicted tropospheric production of SOA-I over Europe using the best guess scenario is 0.10 Tg yr^{-1}. Total tropospheric SOA production in this scenario is 0.70 Tg yr^{-1}, roughly 40% higher than in the zero SOA-I scenario. Summertime measurements of particulate organic matter (POM) during the extensive EMEP OC/EC campaign 2002/2003 are better reproduced when SOA formation from isoprene is taken into account, reflecting also the strong seasonality of isoprene and other biogenic volatile organic compounds (BVOC) emissions from vegetation. However, during winter, our model strongly underestimates POM, likely caused by missing wood burning in the emission inventories. Uncertainties in the parameterisation of isoprene SOA formation have been investigated based on our reference scenario. The sensitivity of our model results to different European isoprene emissions inventories, different representations of the isoprene SOA formation route, and assumptions regarding the effectiveness of wet removal of isoprene oxidation products were investigated. Maximum SOA production is found for irreversible sticking (non-equilibrium partitioning) of condensable vapours on particles, with tropospheric SOA production over Europe increased by a factor of 4 in summer compared to the reference case. The amount and the nature of the absorbing matter are shown to be another key uncertainty when predicting SOA levels. Tropospheric isoprene SOA production over Europe in summer more than doubles when, in addition to pre-existing carbonaceous aerosols, condensation of semi volatile vapours on ammonium and sulphate aerosols is considered.

6.10 Chemical Composition of PM_{10} in Bor

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Twenty five elements were quantified by GF AAS and ICP AES in particulate matter PM_{10} collected in Bor during the seven days at the end of March and beginning of April 2009. The objective of this study was to assess the level of selected elements in PM_{10} with the emphasis on those elements which exceed the limits established by National Ambient Air Quality Standards of Serbia. The results of the PM_{10} analysis have shown that the concentration of arsenic exceed the permitted limit even in four of seven case. The concentration of nickel and cadmium exceeds the permitted limit in one and two cases, while the concentration of copper exceeds the permitted limit in three cases. There are no other ambient air quality standards to compare the concentrations of the other measured elements.

ACKNOWLEDGEMENTS
This work was supported by the Serbian Ministry of Science and Technological Development, project No. 21009.

6.11 Pollutants emitted by cement kilns – case study: co-incineration of tyres in Serbia

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ABSTRACT
Particulate matter and gaseous chemicals emitted from a source into the environment could be directly transmitted to humans through air inhalation. Therefore, for accurate health risk estimation, the emission of each of these pollutants must be determined. In this work, an analysis is made of the emission of different pollutants when partially replacing the fuel type used in a cement kiln. Dioxins and furans (PCDD/Fs), polycyclic aromatic hydrocarbons (PAHs), PM, PM_{10}, heavy metals, HCl, HF and volatile organic compounds (VOCs) are analysed, according to standard methods of sampling and determination. The sampling and analysis methods are standard ones suggested by the EU regulations for stack analysis. Experimental results have shown encouraging results: in particular clinker characteristics were unmodified, and stack emissions (NOx, SO_2 and CO mainly) were in the case of tyres, slightly incremented, but remaining almost always below legal limits, and in some cases were even decreased.

1. INTRODUCTION
Cement is an important binding agent for construction industry and is produced world-wide in large amounts (app. 300-400 million tons in Europe). A central process step during the manufacturing of cement is the production of the intermediate product clinker. For this production, inorganic raw materials are calcined at temperatures in the range of 1000–1500^{o}C (2). In order to reduce the costs of this energy-intensive process, regular fuels like coal and petroleum coke are increasingly substituted by different types of waste. In the last 10 years, use of alternative fuels is continuously increasing. The share of secondary fuels in the total use of fuels in cement plants is expected to increase further. On the other hand, accumulation of millions of worn automotive tyres poses a considerable environmental problem. On average, approximately one scrap tyre per person per year accumulates in industrialized countries. The use of solid wastes as a supplementary fuel or raw material substitutes in cement kilns is one of the best technologies for complete and safe destruction of these wastes, due to the fact that there is a simultaneous benefit of destroying wastes and obtaining energy (3) Nevertheless, some wastes, such as those containing significant amounts of mercury (Hg), should be carefully treated in the kiln. At the same time, substituting primary fossil fuels has environmental and economic advantages. In an incineration process, some chemicals are emitted as a consequence of the combustion process, and these chemicals could be directly transmitted to humans through air inhalation.

The present work has the main purpose of checking the amounts of pollutants emitted by a cement kiln in different situations. Tyres were used as alternative fuels in clinker kilns of two different cement plants (A and B).

2. METHODOLOGY

Because combustion processes generate gaseous pollutants and solid waste materials, which must be disposed of or re-used as secondary raw materials, it is important to characterize these combustion products in order to assess the environmental impacts of energy recovery from whole tyres.

The cement factories (Plant A and B) are located in Serbia with the current production of 2000 and 4000 t cement clinker per day, respectively. Plants are equipped with state-of-art bag filters (4).

Our tests in the cement kilns were performed over more than five years. Several series of runs were carried out, with different mass flows of coal, petrol coke and tyres. The present work has the main purpose of checking the amounts of pollutants emitted by a cement kiln in different situations. Characterization of the coals, petrol cokes and tyres was carried out (Table 1).

The methods used for sampling and analysis are the standard methods suggested by the EU and national regulations for stack analysis: PCDDs/Fs: EN 1948-1 to 3 (HRGC/HRMS with labelled congeners), PAHs: ISO 11338, EPA, UNICHEM i UNI 10169, ISO 16362-modified, VOCs analysis: EN 12619 and 13526, BTX: EN 13649, Heavy metals: EPA, UNICHEM and UNI 10169; EN 14385, HCl/HF: EN 1911-1 to 3 VDI 2470, Bl.1, PM: ISO 9096, EPA, UNICHEM and UNI 10169, NO/NO_2: EN 14792, SO_2: ISO 10396 and ISO 7935, CO: EN 15058, CO_2 and O_2: ISO 12039. Almost all these methods have in common the necessity to employ an isokinetic regime for gas sampling. The isokinetic sampling equipment was a ZAMBELLI 6000 Isoplus, according to ISO 9096:2003.

In addition, in all the samplings, some parameters were continuously monitored with equipment for continuously monitoring in both plants: O_2, SO_2, NO_2, NO, CO_2, CO, PM and gas temperature.

***Table 1**. Characteristics of the fuels used in the experiments (analytical mass, mean values)*

Property	Plant A – coal + petrol coke	Plant B - coal	Plant B – Petrol coke	Tyre without metal
W, %	1,24	0.74	0.45	0,32
Combustible, %	81,91	80.06	92.36	98,07
A, %	16,85	19.20	7.19	1,61
Volatile, %	21,00	18.57	13.19	61,55
Coke residue, %	77,76	80.69	86.36	38,13
Cfix, %	60,91	61.49	79.17	36,52
Hg, kJ/kg	28440	27181	33767	44528
Hd, kJ/kg	27741	26293	32979	43112
C, %	70,81	65.11	81.86	88,14
H, %	2.97	4.23	3.77	6,26
N+O, %	5,01	10.59	4.16	1,42
S, %	3,12	0.13	2.57	2,25

3. RESULTS AND DISCUSSION

Tables 2 and 3 present the results on the emission of emitted gaseous from both cement kilns (all results are presented at 273K, 101,3kPa and 10% O_2 in dry gas).

Table 2. Characteristics of gaseous and emissions (without and with tyres content -Plant A – Direct mode)

Property	Plant A – coal + petrol coke	Plant B - coal	Plant B – Petrol coke	Tyre without metal
W, %	1,24	0.74	0.45	0,32
Combustible, %	81,91	80.06	92.36	98,07
A, %	16,85	19.20	7.19	1,61
Volatile, %	21,00	18.57	13.19	61,55
Coke residue, %	77,76	80.69	86.36	38,13
Cfix, %	60,91	61.49	79.17	36,52
Hg, kJ/kg	28440	27181	33767	44528
Hd, kJ/kg	27741	26293	32979	43112
C, %	70,81	65.11	81.86	88,14
H, %	2.97	4.23	3.77	6,26
N+O, %	5,01	10.59	4.16	1,42
S, %	3,12	0.13	2.57	2,25

Other results on this plant are: PM_{10} 34 mg/m_N^3, Phenol 0,024 mg/m_N^3, Formaldehyde 2,99 mg/m_N^3, NMVOC 28,7mg/m_N^3, N_2O 4,6 mg/m_N^3, Benzo(a)pyrene, Benzo(ghi)perylene, Benzo(k)fluoranthene, Benzo(b)fluoranthene and Fluoranthene 0,0038 $\mu g/m_N^3$ each, Indeno(1,2,3-cd)pyrene 0,0075$\mu g/m_N^3$, and Sum PAH, 0,0264 $\mu g/m_N^3$.

Figures 1 (a and b) and 2 (a and b) present a comparison of the emissions of heavy metals and each of 17 congeners of PCDD/F and also of the total amount of dioxins (I-TEQ units).

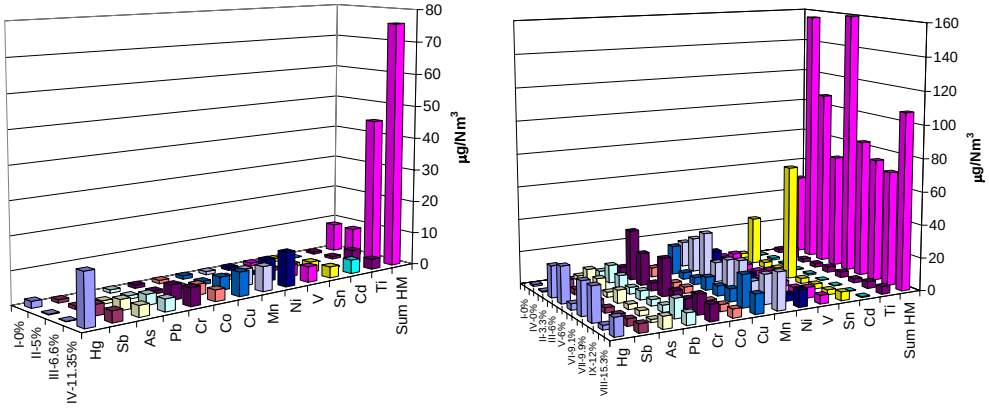
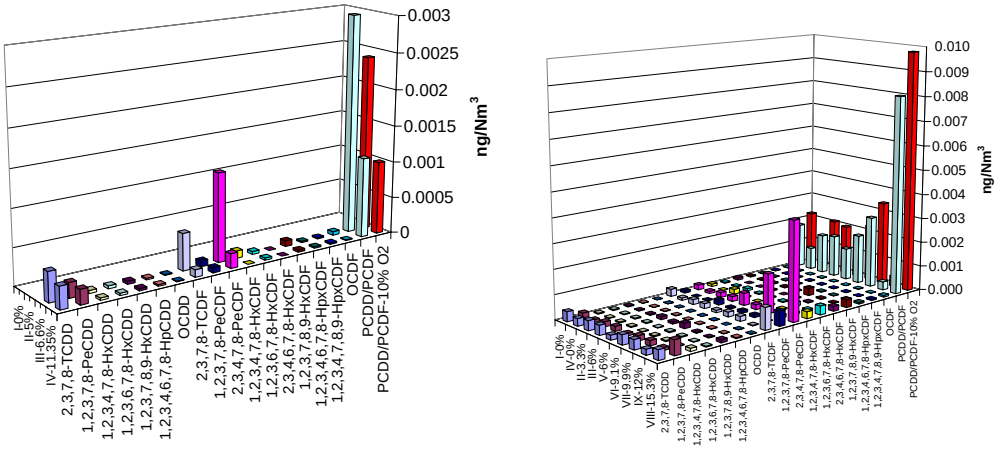


Figure 1. Emissions of heavy metals.. Left panel – plant A, right panel – plant B.

Table 3. Characteristics of gaseous emissions (without and with tyres content -Plant B)

No of measurement/tyres content, % of heat	**I- 0%**	**IV- 0%**	**II- 3.3%**	**III- 6%**	**V- 6%**	**VI- 9.1%**	**VII- 9.9%**	**IX- 12%**	**VIII- 15.3%**
O_2, % vol.	11.88	13.51	12.53	11.6	12.5	11.66	11.65	12.6	11.92
CO_2, % vol.	14.64	11.4	12.72	14.89	12.7	14.17	14.04	15.3	13.84
Flue gas flow, m_N^3/h	438773	507247	436938	427450	465807	424402	429923	487716	446205
Temperature, ^OC	140	134	166	140	136	138	146	148	140
PM, mg/m_N^3	7	10.1	7.8	7.4	5.1	8.1	7.9	1.4	7.9
NO_2, mg/m_N^3	511	699	385	387	779	383	418	892	566
SO_2, mg/m_N^3	300	441	170	379	351	330	244	179	297
CO, mg/m_N^3	1508	977	1133	1143	968	1128	1233	736	1673
HCl, mg/m_N^3	2.99	3.38	2.31	3.68	5.76	3.36	3.6	1.92	3.57
HF, mg/m_N^3	0.32	0.75	0.95	0.26	0.64	0.33	0.34	0.45	0.32
Benzene, mg/m_N^3	1.86	2.93	4.76	4.33	4.76	3.13	4.9	3.59	4.87
Toluene, mg/m_N^3	7.23	n.d.	2.65	1.99	n.d.	0.98	1.95	0.85	1.63
Xylene, mg/m_N^3	4.4	0.49	1.87	1.45	0.39	1.4	1.91	0.85	1.2
TOC, mg/m_N^3	157.7	50.3	39.8	21.6	41.5	25.8	25	32	17.8



Figures 2. Emissions of PCDD/Fs. Left panel – plant A, right panel – plant B.

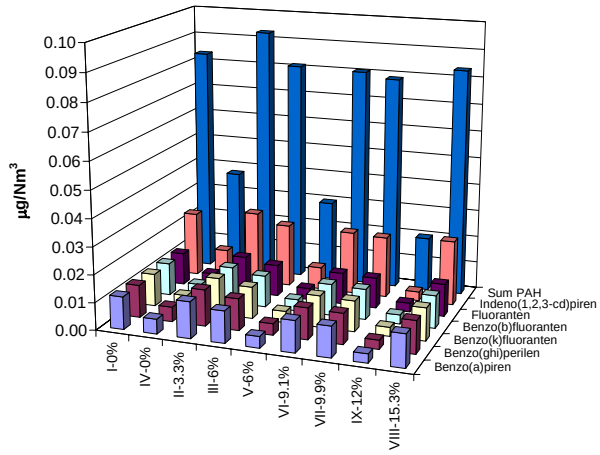


Figure 3. Emissions of PAHs from Plant B.

4. CONCLUSIONS

National legislation does not consider ELV for co-incineration of waste (7). For this reason we recommend EU directive 2000/76/EC (1) and very strong national ELV for incineration of waste (7).

Experimental results have been encouraging: in particular clinker characteristics were unmodified, and stack emissions (NO_x, SO_2 and CO mainly) were in the case of tyres, slightly incremented, but remaining almost always below the law imposed limits, and in some cases were even decreased.

The data shown on Figure 1a apparently indicate that the emission of some metals increased when using increasing amounts of waste tyres, but all results are under ELV.

Also, emission of all 17 congeners and also the total of PCDD are low and under ELV. The data shown on Figure 2b indicate that the total emission of dioxins is increased when using increasing amounts of waste tyres (especially with 15,3% of tyres). Karstensen (5) indicate that the material used as a fuel in industrial furnaces is not responsible for the emission of dioxins. The conditions of the furnace (very high temperature, good mixing and excess of oxygen) make the cement kiln factory an ideal place to get very good combustion. Some sources reported that the amount of organic matter in the cement raw material seems to be responsible for the possible changes in emission of organic compounds (6, 8).

In general terms, it can be concluded that the incremental risk due to the emissions of the cement plant is comparatively very small, not only with respect to human health effects due to emission of criteria contaminants, but also in relation to toxicological and cancer risks produced by exposure to pollutants such as metals and PCDD/Fs emitted by the facility. Further investigations should also include other waste and also long-range transport and detailed evaluation of health risks.

5. ACKNOWLEDGEMENTS

The authors are grateful to people from Lafarge BFC a.d. and Fabrika Cementa Novi Popovac a.d., Holcim Company for help and information provided both during and after the experimental and regular test burns.

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Appendix A

Author Index

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Name	Institution	Contribution
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Adjanski-Spasić, Lj.	Public Health Institute of Belgrade, Vinča Institute of Nuclear Sciences, Faculty for Applied Ecology "Fututa", Serbia	5.2, 5.7
Alavantić, D.	Vinča Institute of Nuclear Sciences, Laboratory for radiobiology and molecular genetics, Serbia	4.4
Amorim, J.H.	CESAM, Department of Environment and Planing, University of Averia, Portugal	4.2
Balducci, C.	Italian National Research Institute for Atmospheric Pollution, Italy	6.7
Bartonova, A.	Norwegian Institute for Air Research, NILU, Norway	1.1, 1.3, 2.3, 3.3, 4.6, 5.6, 6.6
Borrego, C.	CESAM, Department of Environment and Planing, University of Averia, Portugal	4.2
Bulajić, B.	Institute for lung Diseases, Clinical center of Serbia, Belgrad, Serbia	4.7
Cascão, P.	CESAM, Department of Environment and Planing, University of Averia, Portugal	4.2
Cecinato, A.	Italian National Research Institute for Atmospheric Pollution, Italy	6.7
Costa, A.M.	CESAM, Department of Environment and Planing, University of Averia, Portugal	4.2
Csobod, E.	The Regional Environmental Center, Country Office Hungary	4.1
Cvetković, A.	Public Health Institute of Belgrade, Municipality of Smederevo, Serbia, Vinča Institute of Nuclear Sciences and Faculty for Applied Ecology "Fututa", Serbia	2.3, 3.3, 5.6, 5.7

Name	Institution	Contribution
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P.O. Box 100, N-2027 Kjeller, Norway
Associated with CIENS and the Environmental Research Alliance of Norway
ISO certified according to NS-EN ISO 9001

REPORT SERIES SCIENTIFIC REPORT	REPORT NO. OR 37/2009	ISBN: 978-82-425-2130-9 (printed) 978-82-425-2131-6 (electronic) ISSN: 0807-7207	
DATE	SIGN.	NO. OF PAGES 153	PRICE NOK 150.-

TITLE	PROJECT LEADER
Particulate Matter: Research and Management Proceedings from the 2nd WeBIOPATR Workshop, Mokra Gora, Serbia 31.8.-2.9.2009	Alena Bartonova NILU PROJECT NO. N-106088
AUTHOR(S) Alena Bartonova and Milena Jovašević-Stojanović, eds.	CLASSIFICATION * A CONTRACT REF. NFR Project ID: 174817

REPORT PREPARED FOR
Norges Forskningsråd, West Balkan Program
Postboks 2700, St. Hanshaugen
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ABSTRACT
The aim of the workshop was to provide a forum for discussion of new research results regarding particulate matter (PM), and atmospheric PM monitoring and management. Participants came from Serbia, Montenegro, Bosnia Herzegovina, Croatia, Turkey, Portugal, Hungary and Norway, representing research, managers and authorities. The workshop had four sessions: PM sources and source apportionment, Pollution trends and levels, Exposure and health, Air Quality Management. In all, over 40 participants presented papers and posters from authors from 16 countries. A special number of the Serbian journal Chemical Industry and Chemical Engineering is being prepared. The workshop was supported from the WeBIOPATR project (Research Council of Norway), and from the grant of the Ministry of Science and Technological Development of the Republic of Serbia.

NORWEGIAN TITLE

Partikler: forskning og forvaltning

KEYWORDS		
Particulate matter	Determination and source identification	Management strategies

ABSTRACT (in Norwegian)
Møte tok sikte på å skape et forum for diskusjon av nyere forskningsresultater om partikler, og måter hvordan forvaltningen kan takle utfordringer med målinger og tiltak for partikkelreduksjon som kreves av lovgivningen. Deltakere fra Serbia, Montenegro, Bosnia Herzegovina, Kroatia, Tyrkia, Portugal, Ungarn og Norge kom fra forskningsmiljøer og forvaltningen. Resultater var presentert både som foredrag og postere, med nesten 40 presentasjoner med medforfattere fra 16 land, i fire sessjoner: partikkelkilder og kildebestemmelse, Nivåer og trender i forurensningen, Eksponering og helse, og Forvaltning av luftkvalitet. Som resultat av møte blir det utgitt spesialnummer av serbisk tidskrift "Chemical Industry and Chemical Engineering". Møte var et ledd i prosjektet WeBIOPATR, med bidrag fra serbiske departementer for forskning samt miljø og arealplanlegging.

** Classification*
A Unclassified (can be ordered from NILU)
B Restricted distribution
C Classified (not to be distributed)

REFERENCE: OR 37/2009
DATE: FEBRUARY 2010
ISBN: 978-82-425-2130-9 (print)
978-82-425-2131-6 (electronic)

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