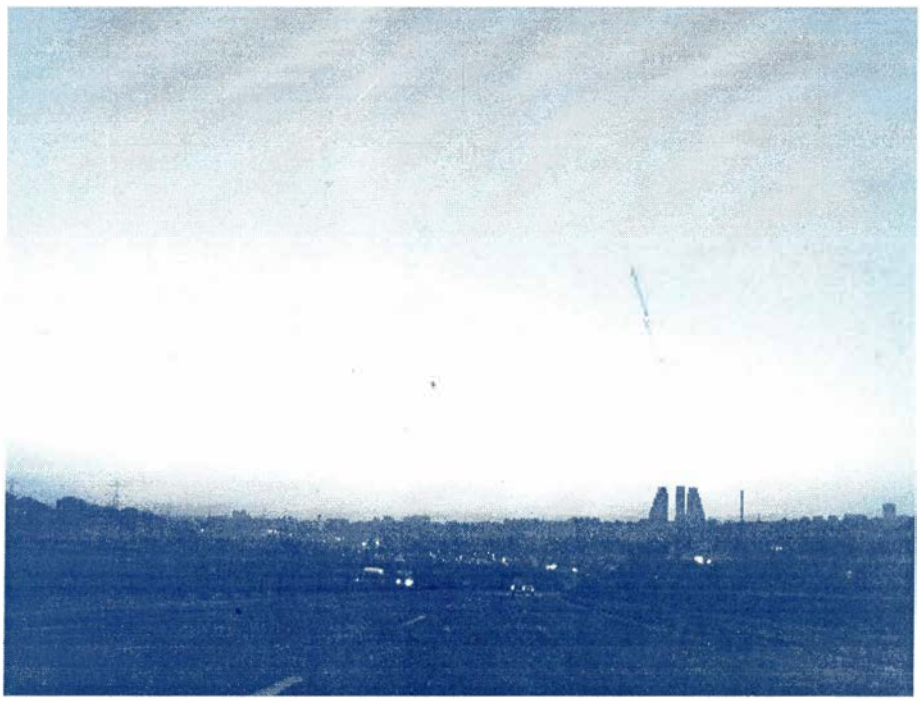
THE FIRST INTERNATIONAL WeBIOPATR WORKSHOP

PARTICULATE MATTER: RESEARCH AND MANAGEMENT

BOOK OF EXTENDED ABSTRACTS



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INFORMATION ABOUT WEBIOPATR PROJECT AND WORKSHOP

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Ongoing project "Outdoor concentration, size distribution and composition of respirable particles in WB urban areas, WeBIOPATR", (www.vin.bg.ac.yu/webiopatr) has been funded, in period from October 2006 to October 2009, by the Reseach Council of Norway through Norwegian Cooperation Programme on Research and Higher Education with countries in the Western Balkans in 2006-2009., http://siu.no/en/programoversikt/vest_balkan_2006_2009. Participants in project from Norwegian side are Norwegian Institute for Air research (NILU) and from Serbian side Institute Vinca (IV) and Institute of Public Health of Belgrade (IPH).

Exposure to respirable Particulate Matter in outdoor and indoor environment was neglected in the past, in comparison to exposure to Particulate Matter at workplace. Today there are many research projects that investigate heath effects of respirable, fine and ultrafine as well as nanoparticles from anthropogenic and natural sources. Different 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 particulate matter in outdoor and indoor environment. It is of great importance for air quality management aiming to reduce risks to human health, to provide evidence and assess characteristic of PM at local and at regional level as well as in different indoor environments typical for Western Balkan Countries.

The need for a modern updated air quality programmed is based on the modern air pollution related legislation, and on urgent need for better planning processes leading to improvement of local air quality. Air quality monitoring data, appropriately linked to statistical and numerical models, will enable the authorities to identify needs and monitor the improvement of air quality. Most importantly, the authorities have to ensure professional implementation and running of the systems and adherence to stringent quality assurance and control protocols. For such program to exist in everyone country, including Republic of Serbia, it needs to be underpinned by research activities, because it is the best way to ensure up-to-date quality.

Continuous pollution measurements are performed in small number of towns in Serbia as part of local monitoring perform at level of local, municipal, authorities. First continuous monitoring network in Serbia has been established in Belgrade. Such measurements provide information that is more than it is necessary according to current national legislation. Institute of Public Health of Belgrade which performs such measurements transfers data to EEA. But, these measurements although they are the most complete in Republic of Serbia have only limited value in terms of contributing to up-to-date identification of specific sources and their contributions.

Institute Vinca and Institute of Public Heath of Belgrade operates several advanced analytical instruments, that are capable of gravimetric analyses of fractionated particulate matter (PM10, PM2.5 and PM1) as well as to measure on-line number and particle size distribution in range of 10 nm to 800 nm. NILU has recently been in forefront in development and application of methods for identification of tracers for specific particulate matter sources. and to speed up the analytical process in laboratories of partner from Serbian side where they are human and analytical resources.

WeBIOAPATR project participant beside others plan to perform next activities in period of project duration:

To organize two international workshops in the aim of dissemination up-to-date information both to scientific community in Serbia and to the authorities about PM research and management

To support training of MS and PhDs students in Serbia

To organize six measuring campaign in the field, in duration of 21 day every, of collection PM10, PM2.5 and PM1 as well as meteorological data at chosen site that belong to municipal monitoring network

To establish monitoring methods and procedure for appropriate gravimetric measurements of PM10, PM2.5 according to relevant international standards (EN, EPA) as well as appropriate gravimetric measurements of PM1.

To establish elemental analysis by AAS, ISP-EOS and ICP-MS and analysis cations and anions with ion chromatography.

To collect data of particle number and particle size distribution in range less than 1 μm with DMPS and CPC and to collect data about continual measurements of PM10 form same site even that is not collecting routinely at selected sampling site

To perform gravimetric measurements, elemental analysis and analysis of cations and anions of collected PM10, PM2.5 and PM1

To generate data about organic and elemental carbon and up to two selected tracers such as a levoglucosan (tracer for wood burning and combustion)

To make databases about all performed measurements and other measurement at same sampling site like meteorological data, data about continual measuring SO_2, NO_2, ozone

To try to collect more data of analytical measurements if it would be possible due to restricted financial, human and analytical resources

To attempt statistical analyses for sources identification and attribution, source apportionment, based on these data

Part of activities of WeBIOPATR project is organization of two workshops. The 1st WeBIOPATR Workshop at the beginning of project before first measuring campaign will be perform. The 2st WeBIOPATR is plan after last, the sixth, measuring campaign will be finished. The workshops should enable exchange of scientific information about Particulate Matter and field work experiences on the PM issue in next topics:

The state of the art

Characteristic of anthropogenic and natural sources of PM

Emissions of air pollutants and particularly PM

Exposure to PM from different sources

Assessment of exposure to different content of PM and its influence to health effects

Modelling of air pollution and health effect modelling

Technical aspects of PM, monitoring and management, are covered with next topics

about field work experience:

Monitoring objectives

Characteristics of particular monitoring design

Reference laboratory

Abetment strategy in the case of accidence limits and target values

Out of many ideas regarding "The First WeBIOPATR Workshop", one was through informing each other on our research activities, to initiate more collaborative research and field measurements in Western Balkan area and region of Southeastern Europe. To link data of PM to exposure and health effects and to express that partner from Serbia are ready to participate in EU and other international project in the field of to PM as well as gaseous air pollution and health effects. In particular to initialize sample and analyzing of respirable PM with different equipment, and to make field and laboratory intercomparisons of equipment and methods and cohort epidemiological studies.

SELECTED STUDIES OF INTEGRATED ASSESSMENT OF PM

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According to Rotmans and van Asselt (2006)[1], Integrated Assessment has two main characteristics: it should contain added value compared to insights derived from disciplinary research, and it should provide decision-makers with useful information. IA can primarily provide insights that inform policy (and the public) and the disciplinary sciences: IA can help to put a problem in the broader perspective of other problems or developments.

Several recent or current international collaborative research projects contribute to the current knowledge regarding impact pathway approach to particulate matter, especially in the framework of health impact assessment related to the Environment and Health Action Plan of the EU (COM(2004) 416).

The integrated assessment framework developed in the FP6 INTARESE[2] project, and what makes use of an impact pathway approach. This implies the ability to be able to track hazards or agents (such as PM) from their source through their various releases into the environment, and then via various media to the point where exposure occurs in whatever setting this might be. This again implies considerable knowledge and interdisciplinary integration. A schematic example of such impact pathway, in this case for one of the main PM sources, traffic, can be seen in the following diagram.

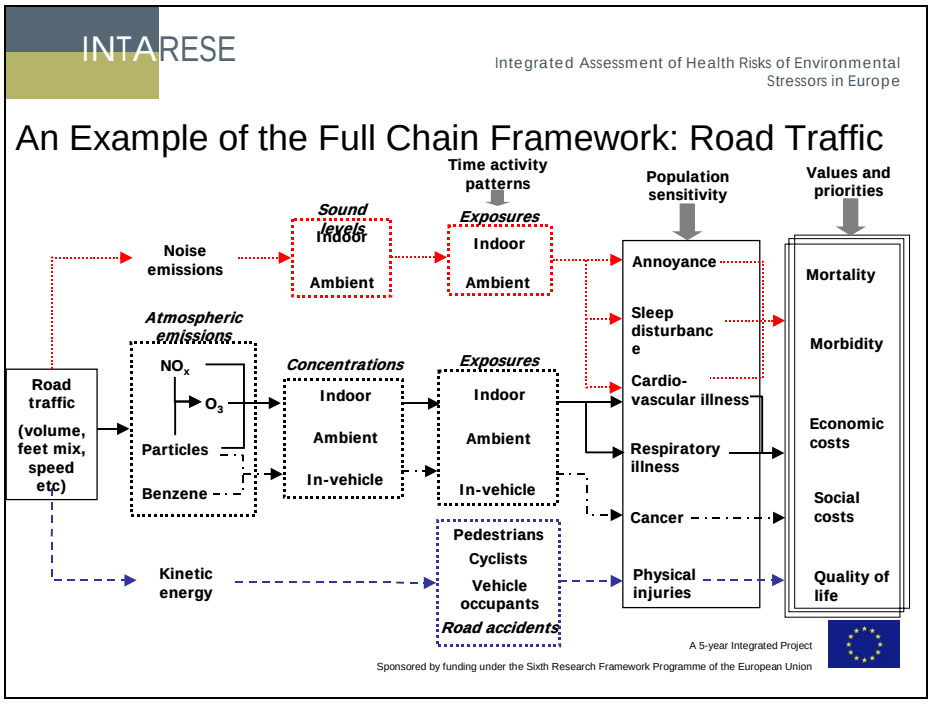
Other projects looking at PM in the framework of integrated assessment include a newly completed network of stakeholders in children's environmental health PINCHE[3] , reviewing for policy advice children's environmental health relative to problem areas such as air pollution and noise, cancer, or neurodevelopmental disorders. The project DROPS[4] looks at health effects of selected persistent pollutants (often carried on particles) in relation to man-made emissions that are followed through the "impact pathway" towards their health effects and associated macroeconomic impacts. The recently started Integrated project HEIMTSA (Health and environment integrated methodology and toolbox for scenario assessment) looks at particulate matter from the point of view of how will different societal development scenarios translate to health impacts, also related to particulate matter.

[1] Rotmans, J and M. van Asselt (1996) Integrated assessment: a growing child on its way to maturity. An editorial essay. Climatic Change 34, 327-336-

[2] www.intarese.org

[3] http://www.pinche.hvdgm.nl/

[4] www.nilu.no/DROPS



These projects are all taking their starting point in health effects. On the other hand, there is a number of collaborative projects or networks that are targeting physical and chemical properties of particulate matter: these include the Network of Excellence Accent[5], the Integrated Project EUSAAR[6], and the COST 633 action[7] "Particulate matter: Properties related to health effects". A smaller completed FP5 project Urban Exposure[8] put emphasis on individual exposure assessment for PM of a general population, taking into account both outdoor and indoor sources of PM and studying their contribution to PM inhaled dose. These projects are all enhancing our theoretical knowledge, but more importantly, provide for a dialogue among scientists and between scientists and other important societal actors including industries and central decision makers, and thus enhance chances for informed decision-making on all levels.

In Norway, we are contributing to the scientific knowledge regarding integrated assessment of particulate matter in many ways. Measurements and advanced analyses of particulate matter are being performed on one background site and on a number of urban sites, both as a part of routine monitoring or compliance monitoring, and in specific studies. Contribution of different sources, physical and chemical characteristics, and exposure to PM are studied. We have also initiated several health-related studies of particulate matter.

[5] http://www.accent-network.org/
[6] www.eusaar.net
[7] http://cost633.dmu.dk
[8] www.nilu.no/urban_exposure

Here, being able to model exposure to particulate matter using advanced air dispersion models supported by air quality monitoring of air pollutants and meteorological parameters were critical elements. These research projects provided scientific knowledge on the particle composition, formation and on contribution of primary and secondary particles to particle load They were further able to contribute to an assessment of impacts of implemented traffic measures on respiratory health and well being, they gave authorities an overview of air pollution loads on population in the capital Oslo, or they provided an assessment of the effectiveness of measures towards reduction of particulate matter related to studded tyres to the overall pollution by PM in Oslo, where the winter load of PM from this very Nordic source is considerable.

Based on the research, we have also been able do develop an integrated air quality management tool for the use both by authorities and in research. This tool, integrating most of our knowledge on air pollutants, their sources, monitoring methods, meteorological processes, and individual and population exposure issues, reflects the main characteristics of integrated assessment: it contains added value compared to insights derived from disciplinary research, and it provides the decision-makers with useful information.

CARBONACEOUS PARTICULATE MATTER - A GREAT CHALLENGE

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1. Introduction

Particulate matter (PM) is currently the most severe air contaminant, causing approximately 300 000 pre mature deaths in Europe on an annual basis. PM also affects the Earth's radiative balance through scattering of solar radiation and through absorption of solar and terrestrial radiation. Whether the aerosol scatter or absorb, they will prevent solar radiation from reaching the Earth's surface, leading to a cooling of the surface. In addition, aerosols influence the radiative balance indirectly by affecting the microphysical properties, frequencies and lifetimes of clouds.

Of particular importance with respect to these topics is the carbonaceous fraction, consisting of organic material (OM) and elemental carbon (EC), which frequently dominates the mass of PM. Despite this, we know very little about its origin, fate, and chemical character. Obtaining a solid understanding of the sources of non-anthropogenic OM and EC, and what are their relative contributions to PM, is particularly important in order to sort out the policy of controlling man-made emissions.

Attempting to apportion the carbonaceous fraction of the ambient aerosols to various sources is highly challenging due to the diversity and complexity of the sources. Further, common sampling methodologies and analytical methods are susceptible to severe artefacts when it comes to collecting and quantifying the carbonaceous content. Here we present the output of various analytical approaches, which combined effort will provide a better understanding of the sources contributing to the carbonaceous fraction of the ambient aerosol.

2. Methodology:

Thermal-optical analysis (TOA) is commonly used to quantify the aerosols total content of OC and EC. Unfortunately, this methodology is prone to severe artefacts with respect to separating between EC and OC and it fails to provide such useful information, which could be obtained from analysis of highly source specific organic compounds using GC- and LC technology. On the other hand, analysis on the molecular level fails to account for more than ~30% of the organic carbon content of PM. Hence, TOA and GC- and LC technology should be regarded as complementary approaches.

Recent development within radiocarbon analysis has made it possible to distinguish between modern carbon and carbon originating from combustion of fossil fuel in the OC and EC fractions obtained by TOA analysis, even for very low concentrations. By combining radiocarbon analysis with GC- and LC analysis of source specific compounds, it is currently possible to separate between anthropogenic and biogenic sources contributing to EC and OC.

3. Discussion:

PM emissions from wood burning have a high carbon content. For Europe, the relative importance of this source is likely to increase, as the Gothenburg protocol will lead to decreased concentrations of SIA, as it regulates anthropogenic emissions of SO_2, NO_x and NH_3. Further, emissions from biomass is regarded as CO_2 neutral, hence an increased focus on biomass as fuel is likely. Finally, increased ambient temperatures and drought, following from climate change, could increase the frequency of forest fires.

Levoglucosan is currently the most recognized organic molecular marker for tracing emissions of particulate matter from biomass burning:

- It is emitted in high concentrations from the combustion of wood
- It is not present in the vapour phase
- It is associated with fine aerosols only
- It is not selectively removed from the atmosphere

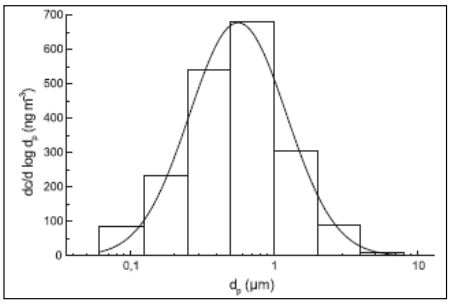

Figure 1: Size distribution of levoglucosan measured in ambient air in Elverum (Norway), using a Berner cascade impactor. The unimodal size distribution has a maximum at 561 nm. Eighty percent of the levoglucosan is associated with particles <1 µm [1].

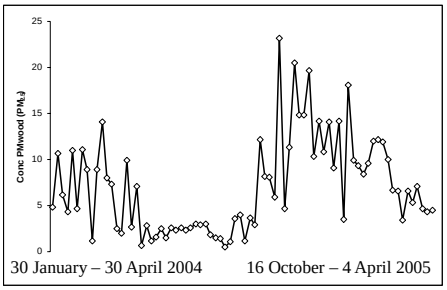

Figure 2: Concentrations of $PM_{2.5}$ from wood burning during winter in Oslo, as predicted by Positive Matrix Factorization (PMF2). The source profile of wood burning is found to rely on levoglucosan

By simple means, levoglucosan could be used to study the size distribution and the temporal variation of PM_{Wood}. Levoglucosan could also be used to quantify PM_{Wood}.

Primary emissions and secondary formation of carbonaceous aerosols from biogenic sources are not well understood and difficult to quantify, hence their relative contribution to ambient PM remains speculative. Further, the suggested feedback mechanisms, following from climate change are suggested to increase the concentrations of biogenic aerosols.

Examples on how to address size distribution and seasonal variation of Primary Biological

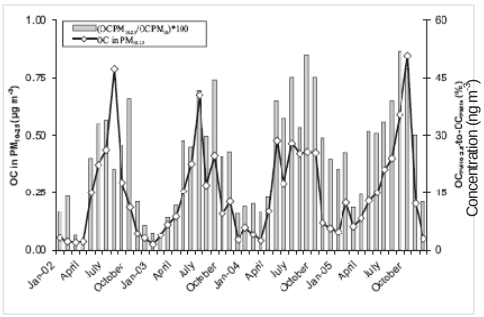

Figure 3A: Annual variation of the sum of sugars (fructose, glucose, sucrose and trehalose) and sugar-alcohols (arabitol, inositol and mannitol) in PM_{10} and $PM_{2.5}$ along with concentrations of levoglucosan in PM_{10} at the rural site Birkenes for the year 2002 [2].

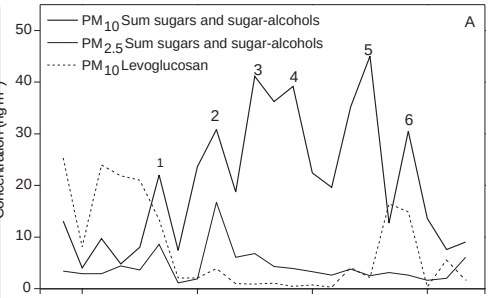

Figure 4: Monthly mean concentration of OC in $PM_{10-2.5}$ at the Norwegian site Birkenes for the period 2002–2005, illustrating the characteristic seasonal variation (left axis) and the relative contribution of $OC_{PM10-2.5}$-to-OC_{PM10} increasing considerably during the vegetative season, most likely attributed to PBAP [3].

Aerosol Particles (PBAP) by quantifying the aerosols content of sugars and sugar-alcohols is shown in Figure 3.

4. References:

[1] Yttri, K.E., et al. Quantification of monosaccharide anhydrides by negative electrospray HPLC/HRMS-TOF – Application to aerosol samples from an urban and a suburban site influenced by small scale wood burning. J. Air & Waste Manage. Assoc. 55, (2005) 1169-1177.

[2] Yttri, K.E. et al. Ambient aerosol concentrations of sugars and sugar alcohols at four different sites in Norway. Atmos. Chem. Phys. Discuss., 7, 5769-5803, 2007

[3] Yttri, K.E et al (2007). Elemental and organic carbon in PM_{10}: a one year measurement campaign within the European Monitoring and Evaluation Programme EMEP. Atmos. Chem. Phys. Discuss. 7, 3859-3899.

SOME ISSUES OF RISK FROM EXPOSURE TO NANOPARTICLES FROM DIFERENT SOURCES

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1. Respirable particulate classification

Particulate matter (PM) is a mixture of different particle types regarding to particles size, source of emission and its content as well. Regarding to size, PM are defined as inhalable (for human) 10-20 μm; respirable (for human) < 5 μm; respirable (for rat) < 3 μm; fine 0.1-3 μm; ultrafine and nanoparticles <100 nm. In many publications ultrafine particles (UFP) and nanoparticles (NP) are considered the same, particulate matter less than 100 nm. Some authors consider that UFP as particles less than 100 nm and NP particles less than 50 nm. It seems that it would be more precise to define NP as primary particles with at least one dimension <100 nm and UPF as particles < 100 nm in all dimensions [1].

Particulate matters consist of three size modes formed by different processes:

- Nucleation mode: particles in this mode are in the order of nanometers, formed by nucleation of atmospheric gases in a supersaturated atmosphere
- Accumulation mode: origin of particles in this mode are from primary emissions as well as through gas to particles conversion, chemical reactions, processes condensation and coagulation
- Coarse mode: particles are generated by mechanical processes

Figure 1. shows the typical relationship between different size range of ambient particulate matter that is typically found in urban atmosphere.

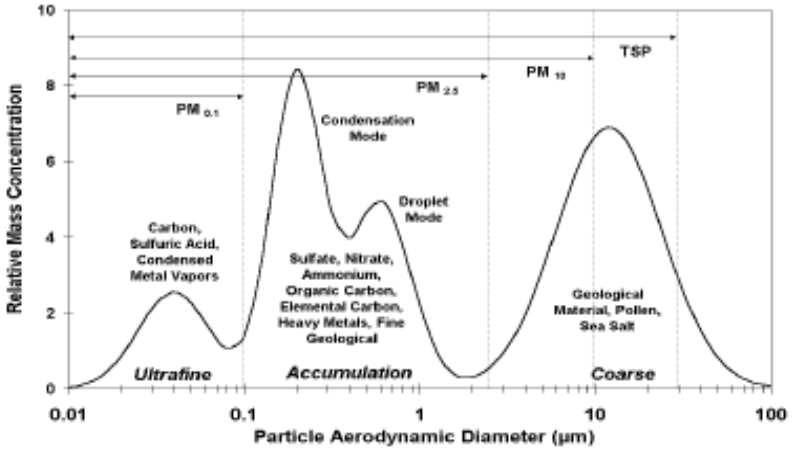

Figure 1. Typical relationship between different size ranges of particulate matter in urban environment

2. Nanoparticle sources

Sources of NP are numerous, and they can be natural or anthropogenic. Anthropogenic NP may be formed and emitted by unintentional and intentional way. There are several anthropogenic sources of NP in environment, such as stationary industrial sources [2,3], as there are coal fired combustion systems and incinerators, mobile sources, cars and diesel power vehicles [4,5,6] as well as number of occupational environments including welding processes and processes of engineering nanoparticles synthesis. There is evidence that nanoscaled dimensions particles may be generated in explosions and fires. Natural sources of NP may be of biological origin pollen fragments, viruses that cause highly infectious diseases like AIDS, SARS, Hepatitis B and others are dominantly of nanoscaled dimension particles. Figure 2. shows an example of sources of ambient particulate matter, from which it may be recognized that on-road traffic and stationary fuel are dominant sources of NP in ambient.

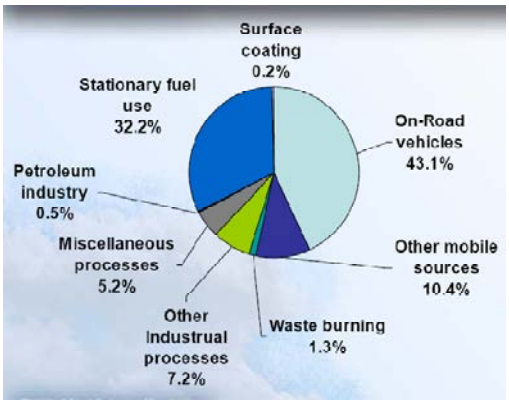

Figure 2. An example of sources of ambient ultrafine particles in the South Coast Basin, USUS [7]

Diesel engines are example where major source of NP is dominate by number concentration, whereas the mass distribution is dominated by accumulation mode, range of particles between 50 nm and 1 μm, as it is shown at Figure 3. [8] It may be underlined that exposure to ultrafine particles is very different on road where diesel trucks dominate, light-duty vehicles and in the residential area. Season as well as diurnal variation of ultrafine particles in residential area can be significant, in period of emissions from wood and coal burning. In-vehicle spend time significantly contribute to exposure to NP.

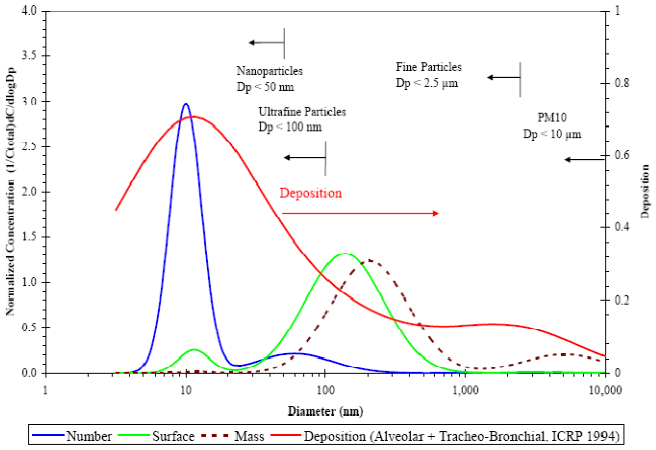

Figure 3. Typical engine exhaust particle size distribution by mass, number and surface area

3. Particle size deposition in lungs

Inhalation is major route of exposure for NP, although ingestion and dermal exposure also need to be taken in account. When particles are inhaled, depending on their size, they may deposit in different regions of the respiratory tract including: nasal, tracheobronchial and alveolar (gas-exchange). At Figure 5. modeled regional deposition of particle deposition it is shown. Deposition has been modeled assuming breathing through the nose at light exercise (25 l/pm) and exposed to spherical particles with density of 1000 kg/m^3 [9]. Particles deposition modeling indicates that up to 90% or more of the inhaled mass fraction of particles smaller than 100 nm would deposit in human respiratory tract, with up to 50% in alveolar region and up to 99% of particles deposition within the respiratory tract at 1 nm. Nanoparticles are deposed on the deep lung regions more efficiently than fine particles. The fraction of depositing particles is higher with exercise

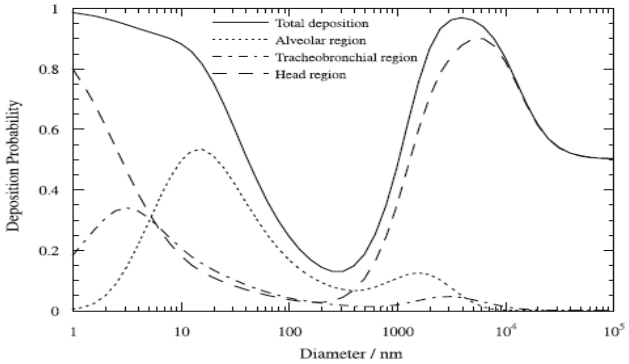

Figure 5. Modeled total particle probability in respiratory tract, and deposition probability in alveolar region [10]

4. Particle number and particle surface area

Table 1. shows particle number and particle surface area for particle diameters between 5 and 5000 nm for concentration of 10 $\mu g \times m^{-3}$. Higher penetration is represented by the particle number rather than by the particle mass for NP. When particles size decreased <100 nm, percent of molecules at surface increased exponentially, which reflects the increase of chemical and biological activity of nanosized particle. The majority of published studies indicate that toxicity of insoluble particles of similar composition increase with decreasing particle diameter and increasing surface area, thus challenging current mass-based risk evaluation approach.

Table 1. Particle number and particle surface area per 10 $\mu g \times m^{-3}$ [9]

Particle diameter	Particle number	Particle surafce area
nm	cm^{-3}	$\mu m^2\ cm^{-3}$
5	153 000 000	12 000
20	2 400 000	3016
250	1200	240
5 000	0.15	12

5. References

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[9.] Oberdorster G., Oberdorster E.,, Oberdorster J., Nanotoxicology: An Emerging Discipline from Studies of Ultrafine Particles, Environmental Health Perspectives, 113(2005)823-839
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POTENTIAL PATHOPHYSIOLOGICAL MECHANISMS OF ULTRAFINE PARTICLES EFFECTS IN HUMANS

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Over last decade, numerous epidemiological and clinical studies suggested association of ambient air pollution and increased morbidity and mortality, mainly from respiratory and cardiovascular diseases. Some air pollutants, like carbon monoxide, sulfur dioxide, nitrogen oxides, ozone and lead, are well known toxic agents, but there is a growing interest on particular matter deleterious effects. Except the chemical structure, the size of particle has great influence on their toxicity. The strongest connections are seen for the respiratory and cardiac disorders.

Ultrafine particles (UFP) are defined as those particles with diameters < 100 nm (1). General hypothesis proposed by Seaton et al. (2) suggested that exposure to inhaled particles induces alveolar inflammation as a basic pathophysiological event. Inflammation is complex defense reaction of the organism, and some characteristic cellular and humoral markers of body response could be used as the measure of its occurrence and intensity. Thus, exposure to inhaled particles produces increase in blood concentration of C-reactive protein (CRP), fibrinogen, and proinflammatory cytokines, like IL-6 and IL-1 beta. UFP cause more inflammation when inhaled and deposited in the lung than larger particles of the same material. They possess more ability to produce reactive oxygen species (3). In vitro studies also have shown that UFP can stimulate the expression of proinflammatory genes in epithelial cells and alveolar macrophages. It is probably caused by their ability to increase intracellular calcium levels and this way to inhibit phagocytosis (4). There are theories that are trying to explain the mechanisms behind the increased toxicity of ultrafine particles. The most well established theory is that it has to do with the increased surface area and/or combination with the increased number of particles. However, biological effects of UFP are also determined by their shape and chemical composition, so it is not possible to estimate their toxicity in general way. Some low toxic UFP may absorb substances with higher toxicity, like metals and gases, or may facilitate transition of adenoviral infection. On the other hand, inhibition of phagocytosis may be connected with increased susceptibility to bigger particles or to bacterial infection. Air pollution research on bigger particles has established clear links with the increase of particular matters in the air and lung diseases. Increase in particle concentration in the air may overload the lung and the phagocytes that are responsible for the eliminating those particles. This overloading of the lungs causes inflammation of the surrounding tissue, also known as the oxidative stress. In case of chronic exposure to UFP, persistence of high inflammatory response may damage the lung tissue with clinical consequence manifested as the exacerbation of preexisting lung disease and/or development of asthma, chronic bronchitis, lung fibrosis or cancer (5, 6). The degree to which UFP contribute to these diseases is not yet established.

Inhaled UFP are also able to translocate trough the circulation from the point of intake in the lung to secondary organs (7), and there is a possibility of many different interactions with biological systems of the body. If the size of the foreign substances entering the bloodstream is great enough, they are removed by phagocytes, but being smaller than

particles phagocytes could recognize, UFP can freely move trough the circulation. They can pass blood-brain barrier, entering central nervous system (8), as well as other organs. The effects ultrafine particles cause in the secondary organs are not known yet.

The linkage between airway inflammation with cytokine/chemokine release and autonomic stress response caused by inhalation of UFP and cardiovascular disorders has not been directly demonstrated in humans. Some links between pulmonary and cardiovascular response to UFP are suggested. There is a growing evidence from animal models that airway inflammatory reaction may trigger systemic inflammation and hypercoagulability (9). Effect of inflammation, with increased ROS, proinflammatory cytokines, CRP and fibrinogen in bloodstream is one of the proposed pathophysiological mechanisms of UFP deleterious effects on the cardiovascular system. Subsequently, a cascade of physiological responses may follow, including disturbances in blood rheology facilitating thrombosis and the development of atherosclerotic plaques. Increasing in blood coagulability is connected with higher risk of cardiovascular disorders. Chronic inflammation is very important underlying mechanism in the genesis of atherosclerosis. Atherosclerosis is characterized by formation of plaques within blood vessels, which may cause their narrowing or obstruction, with consequent tissue hypoxia or necrosis. Clinically, it may be manifested by ECG changes of myocardial ischemia, like ST segment depression, or like more serious disorders, including angina pectoris, myocardial infarction, and even cardiac arrest and death. Alterations in the autonomic nervous system induced by pulmonary reflexes may in some extent influence vascular tonus and cardiac impulse conduction, which may be manifested as fluctuations in blood pressure and heart rate including occurrence of arrhythmias. The results of studies investigating disturbances of cardiac autonomic nervous system are controversial but there are findings supporting the notation that air pollution is capable of altering autonomic balance in a manner that significant tachyarrhytmias. The underlying responsible mechanisms remain unclear, but may involve activation of pulmonary neural reflex arcs, direct effect of pollutants on cardiac ion channels, or consequences of the heightened systemic inflamatory state (10). However, clinical significance of those comparing with other well recognized risk factors for cardiovascular diseases, like age, hypertension, hyperlipidemia and diabetes is probably much lower.

Current knowledge base of the risks of ultrafine particles to human health is primarily based on epidemiological studies of air pollution, indicating increased morbidity and mortality, mainly from respiratory and cardiovascular diseases. Some basic biological mechanisms of ultrafine particles effects are suggested upon experimental studies in vitro and in vivo on animal models and human volunteers, but their pathophysiological relevance for the development of disease needs to be proved by further research. From the clinical toxicology point of view, more studies on recognizing of toxicological endpoints of UFP are needed. Determination of various UFP toxicity, and estimation of their internal and biologically active dose, as well as better understanding of their pathophysiological pathways is necessary for evidence based conclusions connecting air pollution by UFP and humans diseases.

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ULTRAFINE PARTICLE NUMBER CONCENTRATION AND SIZE DISTRIBUTION MEASUREMENTS DURING A WINTER CAMPAING IN BELGRADE

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1. Introduction

Sampling site in Despot Stefan Boulevard has been part of municipal air quality monitoring network located just below the site and operated by Institute of Public Health of Belgrade. It is situated near business center of Belgrade in a dense populated area at one ot the most frequent traffic squares. Since 2004, at that sampling site in the framework of municipal monitoring network continual, automatic, monitoring of PM_{10}, SO_2, NO_2, CO has been performed, as well as monitoring of benzene, toluene, xylene and ethylbenzene since 2006. Basic meteorological parameters has been collected by the automatic meteorological station. Time resolution of the measurements has been 10 min, but the data has been recorded as half an hour average concentrations. General public is provided by information through web www.beoeko.com with hourly average data about air pollution.

Bus station for several lines, dense traffic with cars and heavy-duty diesel vehicles as well as number of available data about air pollution monitoring, was criteria for selection that sampling site for first measurements of traffic related nanoparticles in Belgrade city center. Measurements of particle size distribution for range between 10.7 and 487 nanometer was performed in period of December 25, 2006-March 25, 2007.

2. Methods

The number concentration and particle size distribution of particulate matter in the size range of 10.7-486 nm are measured continuously using scanning mobility particle sizer SMPS, TSI Model 3936, with time resolution of measurement 3 min (i.e., up-scan 150s and retrace 30s).The SMSP consist of an electrostatic classifier, TSI Model 3080, and a condensation particles counter, TSI Model 3025, that counts particles in 64 channels. SMSP was set to run at 0.5 sample flow rate with a sheath flow rate of 5 l/min. The inlet height was about 8 m, at second floor above the street level, by 2 m of rubber sampling tube. Analysis of the SMSP data was carried out by the Aerosol Instrument Manager (version 5, TSI Inc.)

3. Results

There are 30 min-averaged meteorological parameters summarized for period of recent winter campaign (temperature, pressure, relative humidity, wind speed and solar radiation flux) throughout period in Figure 1. Wind direction was also measured. In this presentation we defined particles in the size range of 10.7-100 nm as ultrafine and 10.7-487 nm as submicron particles. Figure 2. show diurnal variation of $PM_{10.7\text{-}487nm}$ number concentration during January and March 2007**,** respectively. Variations of $PM_{10.7\text{-}100\ nm}$ were similar in

same period. Figure 3. show average monthly diurnal variation of $PM_{10.7\text{-}487nm}$ and $PM_{10.7\text{-}100\ nm}$ number concentration in January and March. From Figure 4. it may be recognized differences in diurnal variations of 30 min concentrations of gaseous pollutants collected at the same period and site. Table 1. shown correlations between 30-min sampling data of SO_2, CO, NO_2, C_6H_6, PM_{10} and $PM_{10.7\text{-}100}$ with $PM_{10.7\text{-}487\ nm}$.

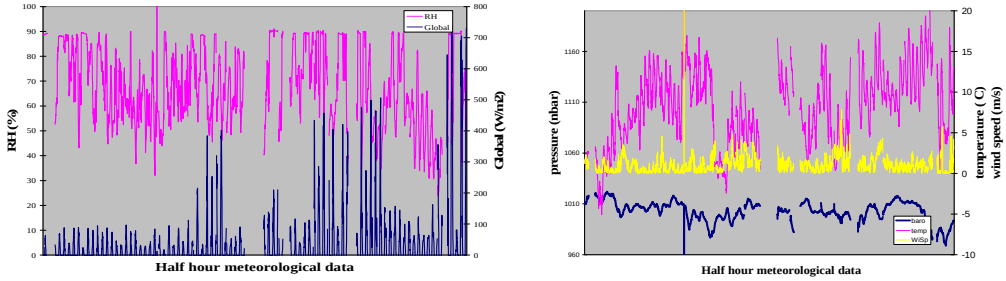

Figure 1. Variation of meteorological parameters during winter 2006/2007

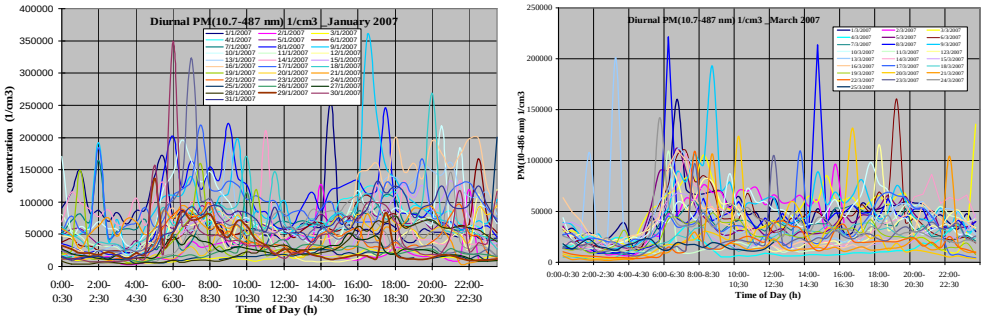

Figure 2. Diurnal variation of $PM_{(10.7\text{-}487\ nm}$ concentration in January and March 2007

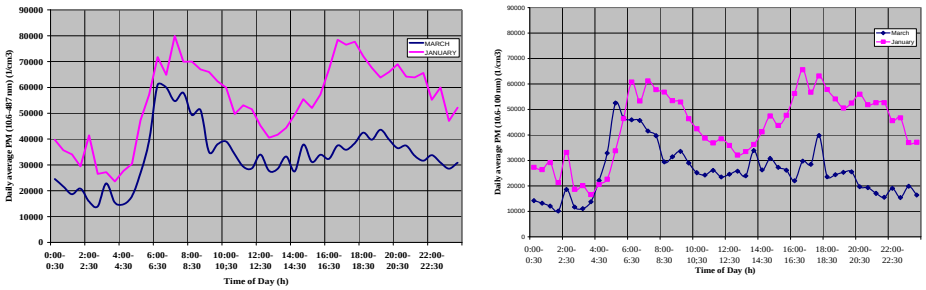

Figure 3. Monthly average diurnal variation of $PM_{10.7\text{-}487\ nm}$ and $PM_{10.7\text{-}100\ nm}$ concentration, during January and March 2007

Table 1. Correlation between 30-min number concentration $P_{10.6\text{-}487nm}$ and SO_2, C_6H_6, NO_2, CO, PM_{10}, number concentration of $PM_{10\text{-}100nm}$

Air pollutants		Fitting of experimental data				
X	Y	Curve	a	b	r	r^2
$PM_{10.7\text{-}487nm}$	SO_2	Y=a+b log X	-537.23082	138.61003	0.65965	0.4351
	C_6H_6	Y=a+b log X	-73.66855	19.57949	0.57243	0.3276
	NO_2	Y=a+b log X	117.12310	33.81756	0.64076	0.4106
	CO	Y=a + b×X	0.38801	3.50975E-5	0.60097	0.3611
	PM_{10}	Y=a+b log X	-291.34639	77.66631	0.49849	0.2485
	$PM_{10\text{-}100nm}$	Y=a+b×X	8354.94285	1.01119	0.85025	0.7229

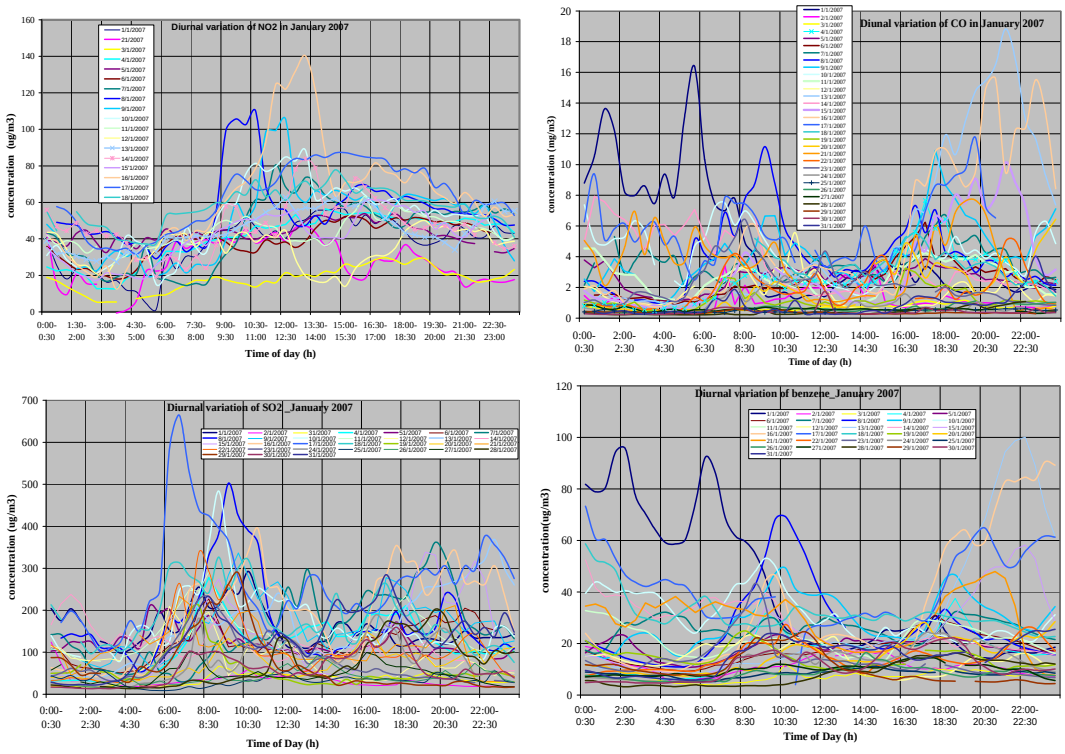

Figure 4 Diurnal variation of SO_2, CO, NO_2, and C_6H_6 during January 2007

4. Discussion and conclusion

Meteorological parameter and basic air pollutant collected at measuring site that is part of municipal monitoring network was compared with collected data of ultrafine particle number concentration and size distribution, at 3 min intervals, in the period of 90 days of winter 2006/2007.

Number of events related to particle number concentration and size distribution described in recently published literature [1] may be recognized in collected samples

during measuring campaign. Particles generated by exhaust have been reported in the size range of 20-130 nm for diesel engines [2] and 20-60 nm gasoline engine [3]. That means that difference between successive samples are due to changes in traffic situation in vicinity of monitoring site. Analyzing data of number size distribution of particulate matter in range of 10.7-487 nm showed that particle mode diameter were found to be less than 100 nm in more than 99%. samples.

It is known that days with peaks and without peaks occurred [4], from Figures 2. and 3. it may be recognized two dominant ultrafine number concentration peaks in January and March 2007. The first one occurred in the morning, and second in the afternoon hours. The morning ultrafine particle peak occurred between 6 and 10 a.m. Peak in the afternoon hours showed less significant level. Peak concentration occurs in the same time of day in January and March, although both peaks of number concentrations were higher during January than during March 2007. During this first measuring campaign evening maxima was detected during January, but in March no clear evening maximum is detected.

Some recently published data [5] about measurement of aerosol particle number less than 1 μm in five EU cites show that maximum of monthly average in winter period in Scandinavian towns is between 10000-20000 cm-^{3}, while in Meditation towns like Rome and Barcelona aerosols particle number is closed to 100000 cm^{-3}. In Belgrade during winter 2007, monthly average diurnal variation was between 25000-80000 cm^{-3} in January and 25000 cm^{-3} and 15000-60000 depending of hour of day, taking in account particles less than 0.5 μm. In EU cities maximum particle number concentration in the morning hours occurred between 7 and 10 a.m. Future measuring campaigns should be performed to consider data for concentration and size distribution for different seasons in Western Balkan region, particulary summer and winter, that expected to be higher during winter than during summer season usually by factor more than 3 [5,6].

At Figure 4. there are diurnal variation of SO_2, NO_2, CO and C_6H_6 during January 2007 are shown. In Table 1. there are coefficient correlation of 30-min $PM_{10.7\text{-}487\ nm}$ and data of air pollutants collected at same location for whole 90 days of study. There is highest correlation coefficient for particle collected in range 10.7-100 nm and particles from wider range 10.7-487nm, and weakest correlation is found between $PM_{10.6\text{-}487nm}$ and PM_{10}. Emission from traffic, stationary sources as well as photochemically driven reactions might contribute to ultrafine particles concentration. In upcoming period of WeBIOATR project we plan to identify sources of ultrafine particles at receptor site through measuring both number concentration, size distribution, gas pollutant, as well as analysing chemical content of coarse (PM_{10}), fine ($PM_{2.5}$) and particles of submicron range (PM_1) and OC/EC. In further analysis of recently obtained data, as well as data form upcoming measuring campaign of particle size distribution of submicron and ultrafine particles, positive matrix factorization method will be applied[7].

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COORDINATED EUROPEAN PARTICULATE MATTER EMISSION INVENTORY PROGRAM (CEPMEIP)

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1. Introduction

The "Coordinated European Particulate Matter Emission Inventory Program" (CEPMEIP) was initiated within the EMEP working programme and supported by the European Environment Agency (EEA) to develop default methods and emission factors for the use of national experts when submitting primary particulate matter (PM) emission inventories within the CRLTAP/EMEP framework. CEPMEIP started in 2000, it was attempted to include all available information on primary PM emissions thus far. The emission factors developed within CEPMEIP can, upon combination with activity data, be used to generate national (source and technology-specific) primary PM emissions.

2. Methodology

The intention of CEPMEIP was to compile a general and consistent methodology to estimate the emission of all known anthropogenic sources of primary PM in Europe. CEPMEIP started with collecting and re-organizing all PM emission-related information within TNO that was available from relevant previous projects (e.g. within UNECE context). This information included among others results of stack concentration measurement and size distribution data from European countries and sources. A 'library' of PM related reports (e.g., from UBA, BUWAL, MSC-East, TNO, US-EPA) was compiled and incorporated in the emission factor database. NILU (a co-executive of CEPMEIP) provided additional stack measurement data for Central European countries. Subsequently, a literature survey was made to identify other important information that was not yet accounted for. Finally, a questionnaire was sent out to national experts asking for any information underlying the existing national PM emission inventories. Twenty European countries responded to the questionnaire and provided additional data.

The above mentioned information was used to list about 200 source categories covering nearly all known anthropogenic emission sources: production and combustion of fossil fuels, combustion of biofuels, industrial activities, the use of products, transport, waste disposal and agriculture. For each source category TSP, PM10 and PM2.5 emission factors have been derived. Since many source contributions depend heavily on the effectiveness of emission abatement, CEPMEIP has paid considerable attention to differences in control technologies used in Europe.

3. Results

Emission factors

Where appropriate, emission factors were specified according to 3 to 4 levels of technological "sophistication" to account for different degrees of emission abatement. CEPMEIP contains ultimately over 800 emission factors for TSP, PM10 and PM2.5 that can be used by national experts in preparing primary PM emission inventories by selecting the most appropriate emission level reflecting the local/national situation. Fuel consumption in industry has been corrected downwards to avoid double counting since combustion emissions are partly accounted in the emission factors for 'processes with contact' (as defined by UNECE).

An overview of the emission factors used in CEPMEIP is presented at http://www.air.sk/tno/cepmeip/. Although CEPMEIP is extensive in source coverage, improvements are still needed as emission factors for some anthropogenic sources of primary particulate matter are still lacking or only partly covered (e.g., resuspension, drying equipment in the food industry and (some) fugitive emissions from industry and agriculture).

Table 1. Distinguished emission levels due to technological sophistication

Emission level	Description
Low	Modern advanced facility, as in use in a small number of countries; strict enforcement of stringent emission standards
Medium	Average age, well maintained; as in-use in a large number of European countries; no BAT though, and might not meet latest European emission standards yet
Medium high	Older equipment and technology, reasonably maintained but not meeting current EU/UNECE emission standards
High	Old facility with limited emission control and often obsolete technology; currently not meeting EU/UNECE emission standards

Emissions for 1995

The CEPMEIP emission factors have been applied in a PM inventory for the year 1995 using activity data obtained from national and international statistical information sources (e.g., FAO, Eurostat, UN) and TNO estimates. Through the collaboration with country experts, information on the sophistication level installed for each sector in most countries was available, enabling us to select the appropriate emission level for each activity in each country. The inventory provides a better understanding of the extent of PM emissions in Europe and regional differences in source contributions (Figures 1 and 2).

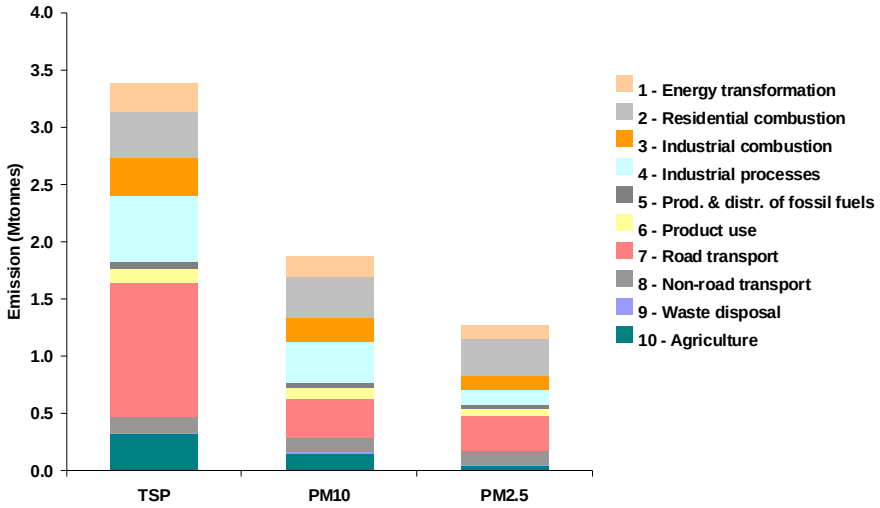

Figure 1. Anthropogenic TSP, PM10 and PM2.5 emissions from old EU-15 countries, Iceland, Norway and Switzerland in 1995

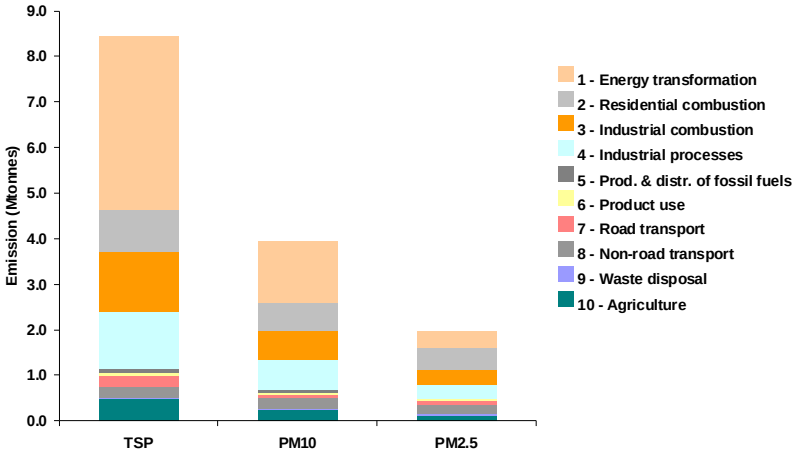

Figure 2. Anthropogenic TSP, PM10 and PM2.5 emissions for other European countries in 1995

Gridded emission data

Spatially distributed 1995 emission data maps have been prepared for air quality modelling (Figure 3 and 4). In the emission maps area and point sources are distinguished. Area sources for which the spatial patterns follow population density have been gridded using the CIESIN-NOAA high resolution rural and urban population density data. Agricultural emissions are distributed according to animal populations by NUTS 3 regions from Eurostat (2003a) and the distribution of arable land and pastures. Large point sources (LPS) are distributed according to their exact location and characteristics (e.g., fuel types, capacities). Point sources include large combustion plants, large industrial activities (e.g., steel, non-ferrous, cement, chemical), waste combustors, refineries and off shore oil production platforms.

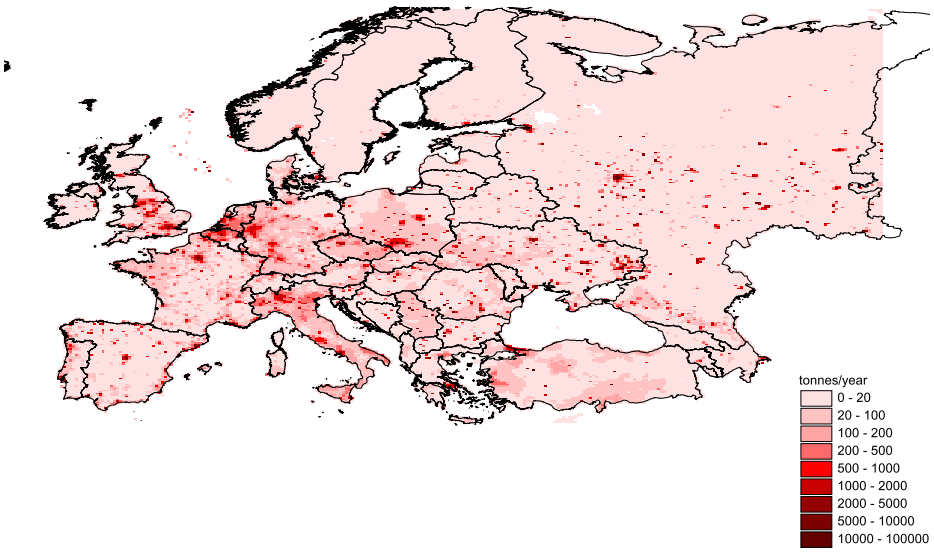

Figure 3. Pan-European primary PM10 emissions

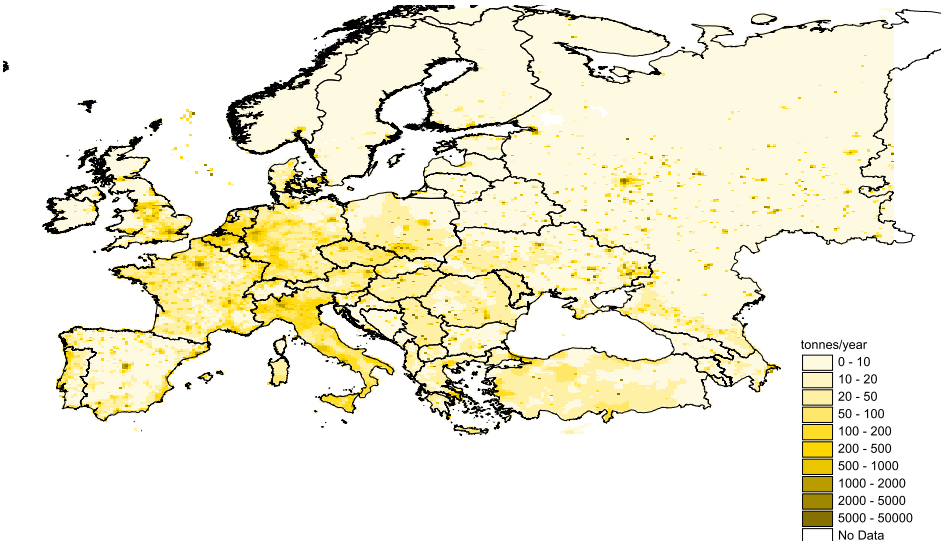

Figure 4. Pan-European primary PM2.5 emissions

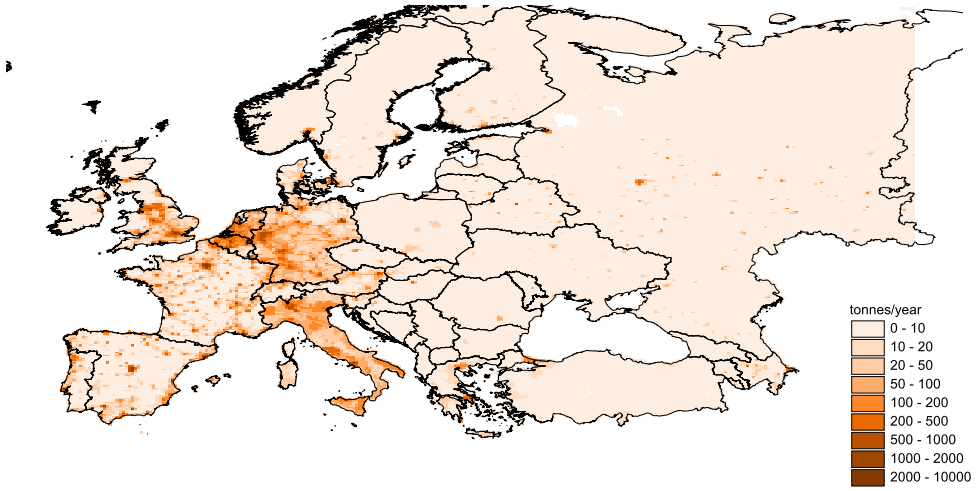

Figure 5. Pan-European primary PM10 emissions due to road transport

4. Recent developments

International shipping emissions were not included in the original CEPMEIP project but have been estimated using detailed data for the North Sea area and scaling to EMEP SOx data for other seas. The original CEPMEIP data are further improved by making a better spatial distribution of the traffic data through the use of traffic density data and road location (Eurostat, 2003b) (Figure 5). In should be noticed that the results do not represent official emission estimates for the countries, as they are calculated with the CEPMEIP proposed emission factors. However, the advantage of this approach is transparent and comparable national emission estimates.

The CEPMEIP data have been expanded with size distribution and uncertainty estimates (Visschedijk, 2002). Size distribution of a particular emission source is dependent on technology level and each technology is characterised by a unique size distribution. This implies that changes in size distribution over time (e.g. 1990-1995-2000) cannot be generalised and accurate information on in-use technologies is crucial. CEPMEIP now covers nearly all of the relevant sources of primary anthropogenic TSP, PM10, PM4, PM2.5 and PM0.95 emissions. The need for such a data base (and a possible update) is illustrated by the frequent use of the CEPMEIP data by the modelling communities. Furthermore, the CEPMEIP data have successfully been used to derive a European Black Carbon inventory (Schaap et al. 2004; Denier van der Gon et al., 2004).

5. Conclusions

The results show that in the Western European countries the fraction of PM2.5 in PM10 is considerably larger than in the Eastern European countries (Figure 1 and 2). Furthermore, the source contributions differ between West and Eastern Europe: the Western European countries have a relatively low contribution of stationary combustion (~ 27 % of TSP emission) to the emissions of particulates as compared to the Eastern European countries (~ 70 % of the TSP emissions). Mobile sources contribute in Western Europe ~25 % and in Eastern Europe ~8 % to PM10 emissions.

High emission densities are observed in some parts of Western Europe in spite of rather stringent emission standards (Figures 3-5). The results thus suggest that current legislation and “business as usual” will not be enough to meet desired air quality standards.

6. Acknowledgement.

The CEPMEIP project was financed via EMEP by the Swiss and Dutch governments, the European Environment Agency and TNO.

7. Data accessibility.

Activity rates, emission factors, emissions and some references are accessible through the URL http://www.air.sk/tno/cepmeip/.

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SOURCE APPORTIONMENT OF PARTICULATE MATTER ($PM_{2.5}$) USING DISPERSION AND RECEPTOR MODELLING - A CASE STUDY FOR OSLO

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1. Introduction

As a part of the EU-funded project Air4EU, a source apportionment study has been performed on PM data from a traffic hot-spot monitoring station in Oslo [1]. In this study, the quality of the emission inventory for particulates ($PM_{2.5}$) was assessed. This assessment was performed by comparing source contribution estimates from a dispersion model, using the official emission inventory, with source apportionment estimates from a receptor model. The chemical composition of $PM_{2.5}$ filter samples from a measurement campaign performed from January 2004 to April 2005 was analysed. With these data as input, Positive Matrix Factorization (PMF) was applied to detect and quantify the various source contributions. For the same observational period and site, we performed emission and dispersion model calculations using the Air Quality Management system AirQUIS. Based on comparison of the two methodologies, the emission inventory was adjusted for individual source categories and the $PM_{2.5}$ concentrations were recalculated. These updated $PM_{2.5}$ concentrations were compared with measurements at three other independent stations to evaluate the improvements of the updated inventory.

2. Methodology

From January 2004 to April 2004 and from October 2004 to April 2005, a PM measurement campaign was carried out at the same site as one of the street stations, identified as Rv4. 12 hour filter samples of $PM_{2.5}$ were collected using a Kleinfiltergerat (KFG) instrument [2].

78 $PM_{2.5}$ filter samples were selected for chemical analysis (Hagen et al., 2005). The components and elements analysed were selected to provide as much information as possible for the source identification. Based on the chemical analysis, receptor modelling was performed to detect and quantify the various source contributions. Positive Matrix Factorization (PMF) [3,4, 5] was used in the present study.

The AirQUIS modelling system [6] was applied in this study to calculate ambient concentrations of $PM_{2.5}$. AirQUIS is a GIS based integrated management system that includes a user interface, comprehensive measurement and emission inventory databases, and a suite of models for simulating ambient air concentrations and exposure. To carry out the source apportionment using the dispersion model, calculations of hourly concentrations from single source categories, or a suite of categories, were performed. The classification of the sources was made according to the sources indicated by the receptor modelling.

3. Results and Discussion

The results identified differences between the dispersion and the receptor model results (Figure 1). Particularly for contributions from wood burning and traffic, there were significant differences. For domestic wood burning, the dispersion model estimated an average $PM_{2.5}$ concentration twice the concentration estimated by the receptor model. On the other hand, the receptor model estimated a contribution from traffic-induced suspension that was 7 times higher than the dispersion model estimate. For the other sources, i.e., long range transport and sum of vehicle exhaust and other combustion sources (sources in bars 4, 5, and 6 in Figure 1), the models agreed fairly well. In spite of the deviation for individual sources, the average $PM_{2.5}$ deviation between the dispersion model (20.9 µg/m^3) and filter samples (23.9 µg/m^3) was only 13%.

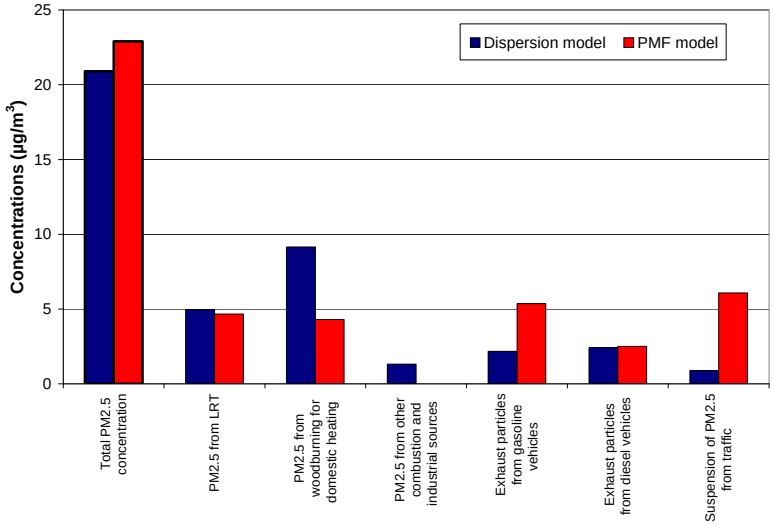

Figure 1. Estimated average concentrations of $PM_{2.5}$ (µg/m^3) from different source categories using the dispersion (blue) and receptor models (red) at Rv4. The comparison was performed for the period where filter samples were collected during winter/spring 2004.

To assess if the differences between dispersion and receptor model calculations, found at the one site, were generally applicable throughout Oslo, we adjusted the emission inventory for individual source categories by a simple rescaling of the emission rates and recalculated PM2.5 concentrations using the dispersion model. Based on the above results, the emission inventory was updated for the wood burning and traffic induced suspension. New PM2.5 estimates were calculated using the dispersion model. The newly estimated PM2.5 concentrations were compared with measurements at three other independent stations, Kirkeveien, Løren, Aker hospital, to evaluate the improvements of the updated inventory. New statistics were calculated for all the four stations. The statistical analysis

showed a general improvement in the estimated concentrations for PM2.5 at all sites.

4. Conclusions

Comparison of source apportionment estimates of $PM_{2.5}$ using receptor modelling and dispersion modelling, provides a good basis for independent assessments of emission inventories. Even though both dispersion and receptor modelling have weaknesses, comparison of source apportionment estimates can reveal both differences and conformities and is a good basis for a detailed analysis of the results. Although the measured and modelled $PM_{2.5}$ concentrations on the average are in good agreement at all sites in Oslo, the analysis has shown large deviations for individual sources. Largest deviations were revealed for wood burning and traffic induced suspension. This study has shown how updated emission estimates for single sources may have significant impact on the spatial concentration distribution estimates and the associated exposure estimates and abatement measures.

5. Acknowledgements

The Air4EU project (Air Quality Assessment for Europe: from local to continental scale) was funded by the European Commission under contract 503596. The authors are grateful for the active involvement and help from colleagues at NILU.

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MODEL CALCULATIONS TO ESTIMATE URBAN LEVELS OF PARTICULATE MATTER IN OSLO

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1. Introduction

During the winter and spring seasons, Norwegian cities are susceptible to poor air quality events that can lead to concentrations in exceedence of limit values, as defined in the Council Directive 1999/30/EC (EC, 1999). Such events typically take place during periods with strong temperature inversions, weak winds and little vertical mixing. For particulate matter, these episodes are enhanced during cold and dry conditions when emission of PM from domestic wood burning and from traffic- induced resuspension are at their highest. In recent years air quality limit values has been exceeded at several measurement sites in Oslo.

The problem of PM emission by traffic resuspension is compounded in Scandinavian cities by the use of studded tyres, which produce a large reservoir of dust particles during their wintertime use as well as enhanced emission from impact with road surfaces. This reservoir is made available for resuspension when road surfaces become snow and water free. This problem has been reduced in Norwegian cities by introducing a tariff for the use of studded tyres

Since PM is considered to be an important contributor to human health the Norwegian Pollution Control Authority have examined the consequences for Norwegian cities of the various recommendations made in connection with Revision 1 of the EC Daughter Directives. The current study, which looks at the results of modelling studies for 2003 of PM_{10} and $PM_{2.5}$, is part of a larger study intended to assess the impact of these recommendations by performing model simulations of ambient PM_{10} and $PM_{2.5}$ concentrations, as well as population exposure, in 2010 and 2015 for Oslo.

The problem of resuspension of particulates from road surfaces is well known but the ability to model this form of emission is not. Recently improvements have been made to the resuspension model used in the AirQUIS modelling system (Tønnesen, 2005). This is the system currently applied in Oslo, and several other Norwegian cities, to assess strategies for improving air quality. This paper deals with the evaluation of model simulations for PM_{10} in Oslo for the year 2003. An improved emission model for traffic induced resuspension is tested and the model concept is validated against available PM_{10} measurements.

2. Methodology

Modelling

The modelling system applied to simulate concentrations of particulates in this study is the AirQUIS modelling system, developed at NILU (AirQUIS, 2004). AirQUIS is a PC based integrated management system that includes a user interface, an extensive database solution, a comprehensive emission module, a suite of models for use in simulations, exposure models and a GIS based system for presentation and analysis.

The models used in the calculations are the MATHEW diagnostic wind field model (Sherman, 1978; Foster et al., 1995) and the EPISODE dispersion model (Slørdal et al.,

2003). This dispersion model contains a standard Eulerian type model for calculating concentrations from area emissions as well as the line source model HIWAY-2 (Petersen, 1980) which is used to calculate traffic related contributions at receptor points close to roads.

Emission from traffic is introduced into the model as area or as line source emissions, dependent on the average daily traffic intensity. The Eulerian model is applied to calculate the concentrations levels in the model grid system and in individual receptor points. At receptor points close to main roads, the HIWAY-2 line source model is applied to estimate the contribution from the nearest roads. The contribution of road related sources greater then 500 m from the receptor points is calculated solely through the Eulerian model.

Emissions of PM from wood burning are introduced into the model as area sources into the three lowest levels of the Eulerian model (71 m). These emissions are based on factors derived from wood consumption, fireplace type e.g. (Finnstad et al., 2004).

Measurements

Measurements of PM_{10} and $PM_{2.5}$ are carried out at 7 stations in Oslo using TEOM instruments. Hourly averages are available from two of theses stations for the entire 2003 period. These stationsare analysed in this study and are representative of traffic/wood burning and traffic stations respectively. In 2003 the number of days when the daily average concentration of PM_{10} exceeded 50µg/m^3 was 37 and 60 respectively at these two stations.

3. Results and discussion

Results of the model calculations have been compared to observed levels of PM_{10} at the two stations Kirkeveien and Løren for the year 2003. PM_{10} results are presented as a time series for the month of March in Figure 1 for the traffic station at Løren. During this period the road surface and road shoulder became dry, 13.03.2003, leading to the availability of a large amount of accumulated dust. In addition, during this period, wind speeds were low with strongly stable conditions prevalent in the period 13 – 20 March. As a result high concentrations of PM_{10} were observed, up to 300 µg/m^3 as hourly means, with daily averages exceeding 148 µg/m^3. As seen in the figure these extreme PM_{10} levels are well reflected in the model.

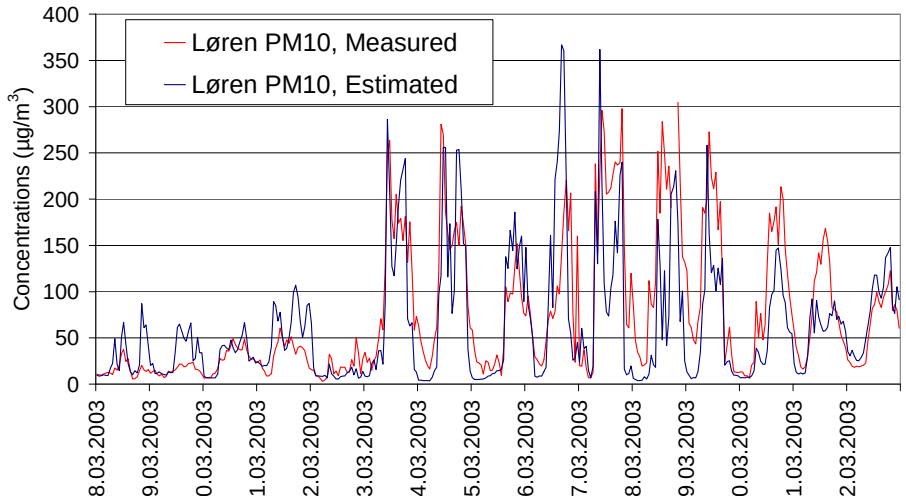

Figure 1: Observed and calculated PM10 levels during March 2003 at Løren.

For the year 2003, the calculated daily average concentrations of PM_{10} are shown, in order of descending concentration, in Figure 2 for both observations and model calculations. For the station at Løren there is good agreement between model and measurements though not all peak values are captured and the lower concentration levels, corresponding mostly to summer time periods, are also underestimated. However the number of exceedences is well modelled. At Kirkeveien the daily concentrations are slightly underestimated.

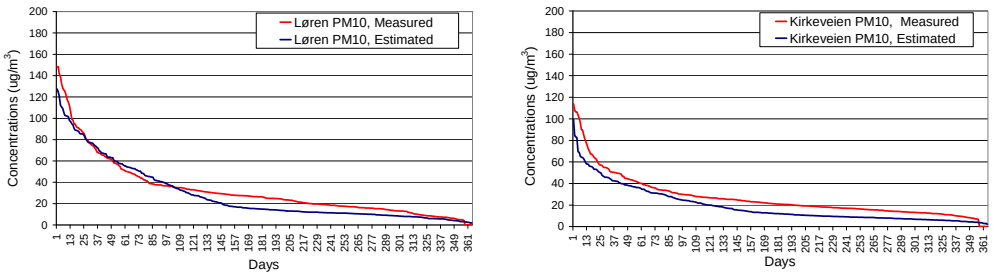

Figure 1: Unpaired daily average concentrations of PM_{10} ordered in descending concentration for the stations Løren (left) and Kirkeveien (right).

The ability of the model to correctly simulate particulate concentrations is dependent on many factors but these can be essentially split into 3 aspects; the models description of meteorology, of emissions and of transport processes. For traffic related stations the correlation between observed and calculated concentrations is to a large extent dependent

on the timing of traffic. Meteorological information, used in the model, also influences correlation. The station Løren, which is situated closest to the meteorological mast used as meteorological input, shows the best correlation of all the stations in Oslo, for all pollutants.

The emission model for resuspension of particles is currently empirically adjusted emission intensity in order to reflect road surface conditions. This is necessary because the data required for establishing road wetness is not available. Even though near surface humidity stations could be established near roads, the complexity of the surface coverage, e.g. snow on curbs, and its small-scale spatial variability may make such objective determinations unreliable. However, it is clear that much can be gained by improvements in the resuspension model. This will in the future require active field campaigns and committed sensors for detection of road surface conditions.

The model used to determine near road concentrations is an open line source model. In reality most stations are only partially 'open' and many are significantly influenced by nearby buildings and other obstacles. The largest deviations between calculated and observed values often occur when wind directions are not properly defined for the line source model.

4. Conclusion

The model evaluation presented in this study shows that the applied AirQUIS system is able to reproduce observed PM_{10} concentrations rather well. The system is consequently well suited for studies of air quality exceedences of the proposed limit values of the EC Daughter directives. On request, by the Norwegian **Pollution Control Authority, NILU** has examined the consequences for Norwegian cities of the various recommendations made in connection with the first revision of these directives.

One of the main challenges in modelling the high percentiles of PM_{10} in Norwegian cities is linked to the process of traffic-induced resuspension. It is therefore of high importance to estimate the particle emission well during these episodes. One of the main problems is to define the state of the road surface (ice coverage/wetness), which to a large extent determine the source strength of the resuspension. The emission model for resuspension of particles is currently empirically adjusted in order to reflect road surface conditions. This is necessary because information about the reservoir of dust particles is lacking and data required for establishing road wetness is not available. It is clear that much can be gained by improvements in the resuspension model. Knowledge about the emission intensity from these reservoirs over time together with information about surface condition is critical. This will in the future require active field campaigns and committed sensors for detection of road surface conditions.

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SOURCE IDENTIFICATION OF TRACE ELEMENTS IN URBAN PARTICULATE MATTER

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1. Introduction

Trace elements are released into the atmosphere by natural emissions and human activities. The combustion of fossil fuels constitutes the principal anthropogenic source for Be, Co, Hg, Mo, Ni, Sb, Se, Sn and V, and high percentages of As, Cd, Cu, Ni and Zn are emitted from industrial metallurgical processes. Exhaust emissions from gasoline contain variable quantities of Pb, Cu, Zn, Ni and Cd [1,2]. Trace metals are found in almost all aerosol size fractions. This has a great effect on the toxicity of metals as, when inhaled, the degree of respiratory penetration is dependent on particle size [3]. The aim of this study was to evaluate, for the first time, the trace metal concentration in PM_{10} and $PM_{2.5}$ in the Belgrade urban air and to identify the main sources by Principal Component and Cluster Analysis.

2. Experimental

Particulate matter with aerodynamic diameter <10 μm (PM_{10}) and <2.5 μm ($PM_{2.5}$) was collected at two sites in urban area, from June 2003 through July 2005. Suspended particles were sampled on Pure Teflon filters (Whatman, 47 mm) using two MiniVol air samplers (Airmetrics Co. Inc., 5 l min^{-1} flow rate) provided with PM_{10} and $PM_{2.5}$ cutoff inlets. A total of 273 (209 PM_{10} and 64 $PM_{2.5}$) valid daily samples were taken during the 2-year period. Detailed description of sampling sites and methodology was given formerly [4]. After gravimetric analysis, PM samples were digested in 0.1 mol dm^{-3} HNO_3 on an ultrasonic bath [5] and analyzed for a set of trace elements by graphite furnace atomic absorption spectrometry (GFAAS) using the transversely-heated graphite atomizer (THGA; Perkin Elmer AA 600). For quality assurance, NIST Standard Reference material 2783 was used.

3. Results and discussion

Descriptive statistics for daily mass (μg m^{-3}) and trace element (ng m^{-3}) concentrations in PM_{10} and $PM_{2.5}$ (Table 1) were calculated showing the high mean and maximum levels. The PM_{10} mean mass concentration (68.4 μg m^{-3}) exceeded the proposed annual limit of 40 μg m^{-3} (EU Directive 1999/30 EC) and the average $PM_{2.5}$ concentration of 61.4 μg m^{-3} was three times higher than the annual limit of 20 μg m^{-3} (EU Standard 14907). As to the concentrations of individual metals, Fe was the most abundant metal (1462.9 ng m^{-3}) in the PM_{10} and Zn and Al concentrations were very high (1389.2 ng m^{-3} and 873.8 ng m^{-3}). The highest mean concentration in $PM_{2.5}$ was for Zn. Concerning Cu, a very toxic heavy metal, relatively high mean values of 71.3 ng m^{-3} in PM_{10} and 20.8 ng m^{-3} in $PM_{2.5}$ were obtained. The mean Ni concentration of 28.4 ng m^{-3} in the $PM_{2.5}$ fraction was above the critical value

of 20 ng m^{-3} for PM_{10} (Directive 2004/107/EC).

Table 1. Statistical parameters of daily mass (μg m^{-3}) and trace element (ng m^{-3}) concentrations in $PM_{2.5}$ in Belgrade urban area from June 2003 to July 2005

	$PM_{2.5}$	Pb	Cu	Zn	Mn	Fe	Cd	Ni	V	Al	Cr
N	64	64	64	64	64	64	64	64	64	64	64
Mean	61.4	21.0	20.8	1998.0	15.2	1081.2	0.9	28.4	59.8	1180.3	6.2
S.D.	52.5	27.0	19.2	1846.4	13.7	1360.3	1.2	43.1	56.3	1657.4	3.8
Max.	286.6	193.9	99.6	6642.4	50.7	5996.5	4.8	315.0	248.5	7875.0	26.0
Min.	8.8	0.5	0.2	115.2	2.1	49.7	0.0	0.4	5.2	159.1	1.6
Median	51.9	13.5	17.4	1153.3	10.1	488.4	0.4	17.3	50.2	500.7	5.9
98^{th} perc	237.3	66.8	80.6	6101.7	47.9	5380.6	4.1	107.9	208.7	7307.3	13.2

N- Number of samples; S.D. - Standard arithmetic deviation

Principal component analysis (PCA) was applied to indentify pollutant sources. Factor loadings, with a VARIMAX rotation for PM were calculated. Four factors were obtained for PM_{10}, accounting for 73% of the total variance. Factor 1 (26%) ascribed to road dust resuspension, factor 2 (17%) is highly loaded with the fuel oil markers V and Ni; factor 3 (17%) with Cu, Cd and Pb,is related to traffic and local source. Factor 4 (13%) with Cr and Pb is due to traffic exhausts. For $PM_{2.5}$ data (**Table 2**), four groups explain 88.5% of the total variance. Factor 1 reflects resuspended road dust, Factor 2 (Cr, Pb) emissions from traffic and oil refineries; Factor 3 is related to oil combustion and the fourth to vehicles diesel emissions and local industry (Cu and Cd).

Table 2. PCA Factor loadings after Varimax rotation for the elements in $PM_{2.5}$

Element	Factor 1	Factor 2	Factor 3	Factor 4
Pb	0.27	**0.85**	-0.05	0.06
Cu	-0.1	0.14	0.46	**0.78**
Zn	**0.85**	0.17	0.25	-0.24
Mn	**0.8**	0.22	0.27	0.03
Fe	**0.78**	0.16	-0.09	0.16
Cd	0.1	-0.25	-0.36	**0.79**
Ni	0.06	0.1	**0.88**	0.08
V	0.3	-0.15	0.71	-0.11
Al	0.84	0.09	0.08	-0.01
Cr	0.16	0.91	0.05	-0.15
Var.(%)	29	17.8	17.7	13.5

The results of Cluster analysis for the trace elements in PM_{10}, were obtained as dendograms displaying four main clusters. In the dendogram for PM_{10} the first group containing the variables Pb and Cu with Cd, is associated with traffic emissions; the second group includes Zn and Fe mostly originating from abrasion of mechanical parts of road vehicles. The third cluster containing Ni and V, is associated with oil burning and the fourth group includes Mn, Al and Cr with a soil origin.

PCA loadings >0.5 are marked in bold

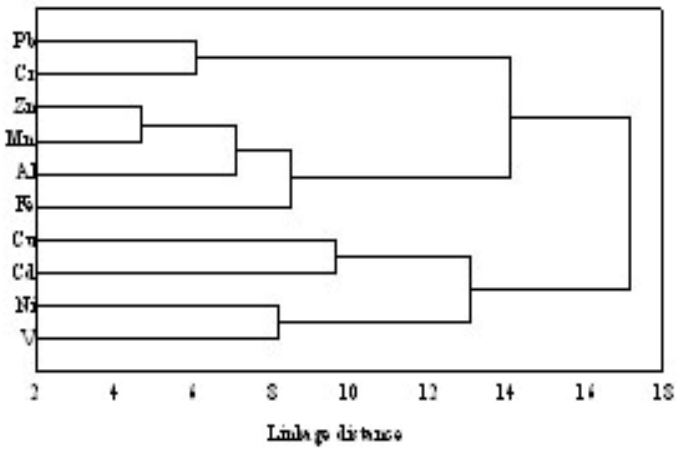

Figure 1. Dendogram for trace elements in $PM_{2.5}$

The dendogram for trace elements in PM2.5 (Figure 1) points to several groups. The first group contains only Pb and Cr, from leaded gasoline vehicular exhaust and possible from the oil refinery. The second group containing Zn and Mn, closely connected with Al and Fe, represents road dust. The third group includes Cu and Cd and as connected with the fourth group (V and Ni) at a higher level suggest a common source for these groups.

4. Conclusion

We demonstrated how to identify the sources of ambient trace metals in PM using multivariate receptor modelling. The higher trace element concentrations were associated with calm conditions suggesting a great influence of local sources. The PCA and CA showed that the main sources of trace metals in PM are combustion processes, e.g. emissions from mobile and stationary units, with the major contribution from traffic and road dust. The results could be used as the baseline data for analysis of health risks due to inhalation of suspended aerosols, and to provide scientific evidence for setting up an air pollution control strategy.

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EXPOSURE MODELLING RELATED TO OUTDOOR AIR

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Releases of contaminants, or their precursors into the atmospheric environment form just the first step in the process that leads to exposure. The process controls the dilution, dispersion, transport and transformation of the released molecules from source via environment to exposure, or contact with a human, and then from intake into a human body all the way to target tissue, and consequently the dose and potential adverse health impacts. Exposure sciences study the first half of this process, from source to exposure. is split into two parts: The first aims at understanding and modelling the environmental fate of the released molecules via air, water and soil, into various microenvironments, where they may contact people, or enter into food items or other products intended for human use. The second brings in the human behaviour, time allocations for various microenvironments and activities, mobility, consumption patterns etc., which create the contact between the contaminants in microenvironments, media, products and articles, and thereby convert environmental contamination into exposure. Exposure is defined by WHO/IPCS Exposure Terminology subcommittee[9] as "Contact between an agent and a target", characterised by contact area and time. Exposure pathway describes "the course an agent takes from the source to the target"(e.g., via air, water, soil, food, consumer products, etc.), exposure route the "way an agent enters a target after contact (e.g., by ingestion, inhalation, or dermal absorption)", and exposure scenario the "facts, assumptions, and inferences that define a discrete situation where potential exposures may occur. These may include the sources, the exposed population, the timeframe of exposure, microenvironment(s), and activities. Scenarios are often created to aid exposure assessors in estimating exposure".

The so-called micro-environmental exposure models are mechanistic (usually stochastic) modelling techniques, which split each individual's day into time allocations in different microenvironments (e.g., home, commuting, street, garden, restaurant with smokers, …) and activities (e.g., cooking, riding in a bus, bathing, …), assigns an exposure distribution to each, and intercorrelation matrix for all microenvironment-activity combinations, and models the daily exposure as a time weighed sum of the exposures in each microenvironment-activity encountered during the day. Real or modelled time-microenvironment-activity and respective exposure data and Monte-Carlo or similar computing techniques are used in the modelling. Pollution levels in the microenvironments are often drawn from actual monitoring data, but when the impacts of exposure reduction policies are evaluated, microenvironment concentrations must usually be modelled. For contaminants from indoor sources, ventilation-dilution models are used. For contaminants from outdoor sources, ambient air dispersion models for each source and source category are used to map ambient concentrations attributed to each respective source. Indoor

[9]) Harmonisation Project Report N:o 1. Harmonization of Approaches to the Assessment Of Risk from Exposure to Chemicals: Exposure Terminology. Exposure Assessment Planning Workgroup, Terminology Subcommittee, WHO/IPCS 2004

EXPOSURE MODELLING RELATED TO OUTDOOR AIR

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Releases of contaminants, or their precursors into the atmospheric environment form just the first step in the process that leads to exposure. The process controls the dilution, dispersion, transport and transformation of the released molecules from source via environment to exposure, or contact with a human, and then from intake into a human body all the way to target tissue, and consequently the dose and potential adverse health impacts. Exposure sciences study the first half of this process, from source to exposure. is split into two parts: The first aims at understanding and modelling the environmental fate of the released molecules via air, water and soil, into various microenvironments, where they may contact people, or enter into food items or other products intended for human use. The second brings in the human behaviour, time allocations for various microenvironments and activities, mobility, consumption patterns etc., which create the contact between the contaminants in microenvironments, media, products and articles, and thereby convert environmental contamination into exposure. *Exposure* is defined by WHO/IPCS Exposure Terminology subcommittee[9] as "Contact between an agent and a target", characterised by contact area and time. *Exposure pathway* describes "the course an agent takes from the source to the target"(e.g., via air, water, soil, food, consumer products, etc.), *exposure route* the "way an agent enters a target after contact (e.g., by ingestion, inhalation, or dermal absorption)", and *exposure scenario* the "facts, assumptions, and inferences that define a discrete situation where potential exposures may occur. These may include the sources, the exposed population, the timeframe of exposure, microenvironment(s), and activities. Scenarios are often created to aid exposure assessors in estimating exposure".

The so-called *micro-environmental exposure models* are mechanistic (usually stochastic) modelling techniques, which split each individual's day into time allocations in different microenvironments (e.g., home, commuting, street, garden, restaurant with smokers, …) and activities (e.g., cooking, riding in a bus, bathing, …), assigns an exposure distribution to each, and intercorrelation matrix for all microenvironment-activity combinations, and models the daily exposure as a time weighed sum of the exposures in each microenvironment-activity encountered during the day. Real or modelled time-microenvironment-activity and respective exposure data and Monte-Carlo or similar computing techniques are used in the modelling. Pollution levels in the microenvironments are often drawn from actual monitoring data, but when the impacts of exposure reduction policies are evaluated, microenvironment concentrations must usually be modelled. For contaminants from indoor sources, ventilation-dilution models are used. For contaminants from outdoor sources, ambient air dispersion models for each source and source category are used to map ambient concentrations attributed to each respective source. Indoor

[9]) Harmonisation Project Report N:o 1. Harmonization of Approaches to the Assessment Of Risk from Exposure to Chemicals: Exposure Terminology. Exposure Assessment Planning Workgroup, Terminology Subcommittee, WHO/IPCS 2004

microenvironment concentrations from outdoor sources are modelled using outdoor to indoor transfer functions. Microenvironmental exposure modelling is particularly useful for spatio-temporal phenomena such as air pollution, noise, radiation and heat.

Some of the routes linking emissions to changes in the exposures experienced by the populations of Europe are relatively simple (though reliable modelling of the associated exposures may still involve substantial complexity). In the case of particulate matter or ozone air pollution, for example, the processes by which emissions to air translate into exposures by inhalation are relatively well known (if we do not consider in full the processes leading to PM or ozone formation to the atmosphere). Yet, modelling of the incremental exposures of individuals is complex.

Exposure assessment/modelling for risk assessment, risk management and risk communication have different goals. For *risk assessment* exposure assessment must provide data at the level of aggregation (people, averaging time), which allows effective association of the health impacts with exposure. Environmental health *risk management* relies almost always entirely on exposure management. For risk management exposures, therefore, need to be attributed to sources as well as those characteristics of human microenvironments and activities, which significantly modify the exposure. *Risk management options evaluation* depends on exposure modelling, and to be able to compare the health benefits of alternative options, exposure models must correctly predict their respective exposure differences. *Policy implementation*, on the other hand, would most benefit from models, which are capable of identifying the trends in exposure from the earliest signals created by the implementation of the new policy. Finally, *risk communication* needs exposure models, which describe the phenomena conceptually to and are easy to comprehend by lay people. Quantitative predictive capabilities are less essential for such models.

In air quality management, exposure assessment is related mostly to the risk management options identification. However, most often only measures on outdoor sources of pollutants are considered, disregarding the fact that exposures – unlike outdoor concentrations – can be mitigated by altered behavior. In order to achieve the goal of limiting public health impacts of air pollution, neglecting the impact of individual or collective behavior on exposures may severely limit the available options.

In Oslo, population-level exposure assessment is implemented in an air quality management tool. Number of persons exposed to pollution levels above limit values in Oslo and other larger Norwegian cities is one of indicators used by the Norwegian Pollution Control Authority to assess the environmental status. This indicator is based on dispersion-modeling generated city maps indicating areas where the pollution levels are above the limit values (on hourly, daily or annual basis), and on identifying the number of residents in those areas.

Using air quality management tools, it is also possible to estimate individual-level exposures. This can be done by coupling of atmospheric dispersion modeling of high temporal and spatial resolution with time-activity-microenvironment information for individuals, or in theory, for populations. In this way, it is possible to identify and analyse the contributions to the exposure from different microenvironments, and to identify sources that contribute most to the exposures.

TOTAL DEPOSITION OF MAJOR INORGANIC IONS AT NON-URBAN SITES IN CHINA, 2001-2003

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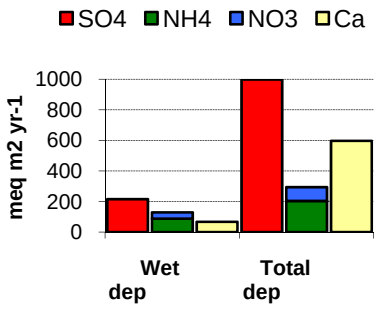
1. Introduction

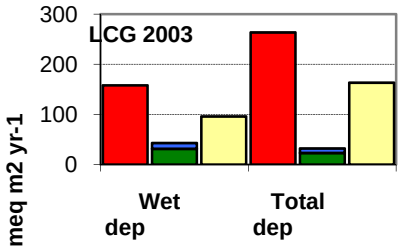
The IMPACTS sites are located in Tie Shan Ping (TSP) in Chongqing, Cai Jia Tang (CJT) in Hunan, Lei Gong Shan (LGS) and Liu Chong Guan (LCG) in Guizhou and Li Xi He (LXH) in Guangdong province. The total deposition was estimated using the ground vegetation through fall measurements. These results were in TSP, LGS and CJT compared with an inferential method, based on the measured air and aerosol concentration and deposition velocities taken from literature. A canopy budget model was used to analyse the influences of canopy exchange process at TSP.

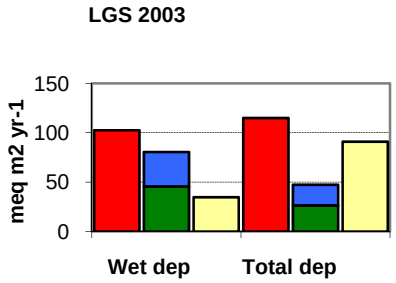
2. Results

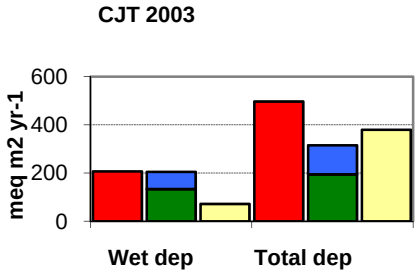
The sulphur deposition was considerable at all sites, and at TSP it was even much higher than observed at any sites in e.g Europe. In 2003 the total deposition of sulphur at these five sites ranged from 2-16 gSm^{-2} depending on the site characteristic and distance to emission sources. The total inorganic nitrogen depositions were comparable with the levels measured in other countries, it ranges from 0.6 to 4.4 gNm^{-2} in 2003. The calcium deposition is also very high and it shows similar site variations as sulphur with a total deposition in 2003 ranging from 2-12 gm^{-2}. The contribution of dry deposition to the total deposition was significant at all the sites. For sulphur the dry deposition was up to 3 times higher than the wet deposition. For calcium it was similar, while for nitrogen the contributions from wet and dry deposition were roughly equal. However, for nitrogen the total deposition might be somewhat underestimated using the throughfall method due to uptake of nitrogen in the crown. The canopy budget model indicates that the canopy is retaining nitrogen as well as it is leaching calcium. The comparison between the throughfall and inferential method show large variations, and it illustrates the difficulty in using

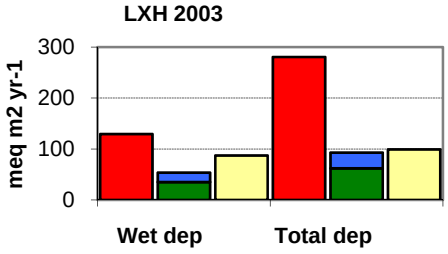
deposition velocities calculated on European forest to estimate the deposition on Chinese forest. In addition, it is probably not correct to use the same deposition velocities at all the sites.











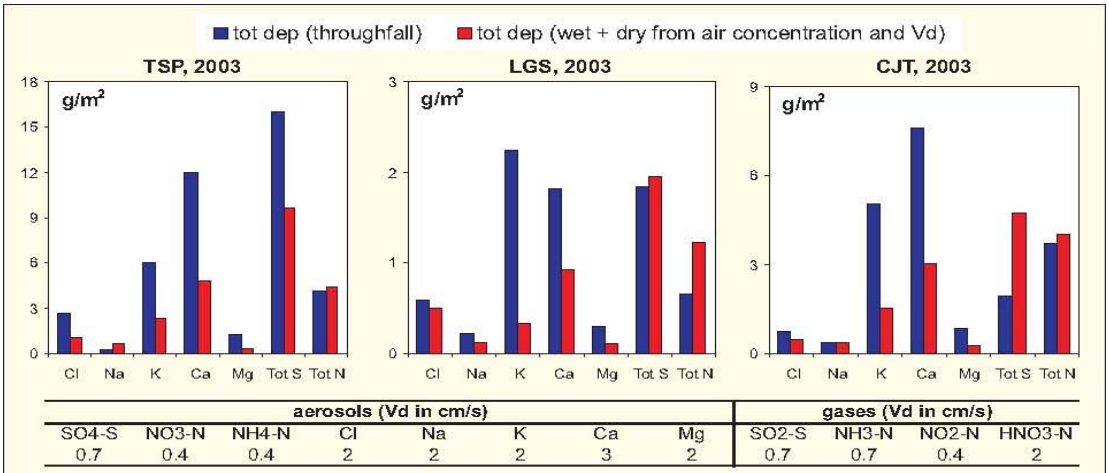


Figure 2. *Total deposition in 2003 estimated by two methods, and the deposition velocities used.*

Figure 1 Wet- and total deposition (throughfall) in 2003.

3. Conclusions

These results clearly show that it is important to include the contribution of alkaline dust as well as inorganic nitrogen in mitigating the effect of acid rain. It is not sufficient to only consider pH and sulphate as is commonly done in China. The contribution of dry deposition is of great importance to the total budget and it is necessary to get better estimates of the dry deposition processes, i.e. using flux methods. The particle size is critical when determining the deposition velocities, and measurements of size distribution of the different ions are needed.

4. Acknowledgments

IMPACTS has been supported by The Norwegian Agency for Development Cooperation

(NORAD), The Chinese State Environmental Protection Administration (SEPA) and the Chinese Ministry of Science and Technology (MOST).

PARTICULATE MATTER MEASUREMENTS AT THE AKROTIRI RESEARCH STATION

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1. Introduction

- Many studies suggest association between exposure to particulate matter and the resulting health effects.

- Mediterranean Sea constitutes an area where atmospheric particles originating from continental natural and anthropogenic sources (for example forest fires),
marine sources and gas-to-particle conversion simultaneously exist.

- Transport of Sahara dust occurs mostly during the spring and summer and causes non-continuous crustal aerosol pulses to the Mediterranean area.

- The meteorological conditions in the Mediterranean area are also quite influential for the Central and Southern European weather.

- Most of the studies on the chemical composition on Mediterranean particulate aerosol have been conducted in the western and north-west region. However relatively few studies have been undertaken in the southern part of eastern Mediterranean and Greece.

- On this basis continuous aerosol measurements are started during 2003 at the Akrotiri research monitoring station on the island of Crete (Greece).

Objective

In this work we study the PM10 and PM2.5 ambient levels and the influence of African dust outbreaks on the particulate matter concentration.

2. Methodology

Location:

- The place of the measurements (Akrotiri station) of particulate matter (PM10 and PM2.5) is at a rural station on the island of Crete, Greece, mid-distance between Athens and the northern African coast (*Figure 1*).

- The Akrotiri station (35° 31’ N, 24° 03’ E) is a coastal site eastward of Chania at an

elevation of 180 m.

- The region of interest includes parts of the southern Greece which is consistent mainly from marine environments and islands. The main urban and industrial areas are located along the coastal of the Greek mainland. The region is characterized from a complicated topography combined with strong winds, long sunny and humid periods.

Figure 1: Geographical location of the Akrotiri research station on the island of Crete.

Measured parameters and Measurement periods

Measured parameters	***PM_{10}***	***$PM_{2.5}$***
Measurement periods	***15/04/2003-10/03/2004***	***10/03/2004-31/05/2005***

Instrumentation:

Automatic beta radiation attenuation monitor (FH 62 I-R)

3. Results

- Daily average PM10 concentrations.
- The average value for the whole period is 35.1 μg/m^3.
- There is a large variability of the PM10 values mainly during the summer period with concentrations up to 80- 90 μg/m^3.
- During the winter period the PM10 concentrations are in general lower and the variability smaller (*Figure 2*).

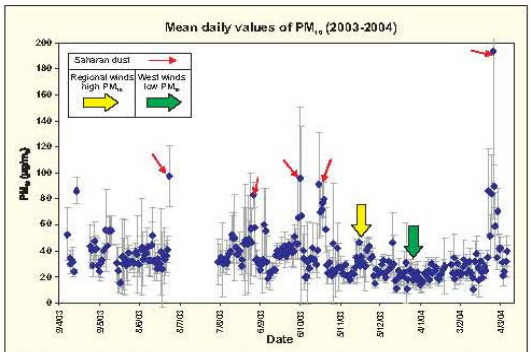

Figure 2: Daily average PM_{10} concentrations at the Akrotiri research station (The July and August 2003 data are missing due to technical problem in the station).

4. Some considerable days

- Although during the winter period the PM10 concentrations are in general lower, on the 27/02/2004 a major Sahara dust events leads to an average PM10 level of 193.2 μg/m^3.

- The lowest observed PM10 value during the measurement period was on 13/02/2004 (10 μg/m^3) during a storm event.

- High PM10 concentrations were also associated with elevated O_3 levels at the station during regional transport from Central Europe (for example the period from 15/11/2003 until 05/12/2003).

5. Mean monthly values of PM10

- High aerosol concentrations were observed during the whole measurement period with an average concentration for October 2003 equal to 45.8 μg/m^3 (*Figure 3*).

- The reason for the elevated concentrations during some months as for example October 2003 is the outbreak of a number of Sahara dust episodes in the area of the station.

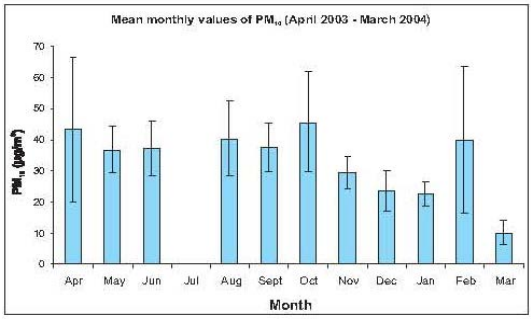

Figure 3: Mean monthly PM_{10} concentrations during April 2003 – March 2004 at the Akrotiri research station.

6. Daily average PM2.5 concentrations

- The average PM 2.5 concentration during the measurement period is 27.23 μg/m^3.
- There are some days where the PM2.5 concentration reached high values which correspond to Sahara dust episodes in the area (*Figure 4*).

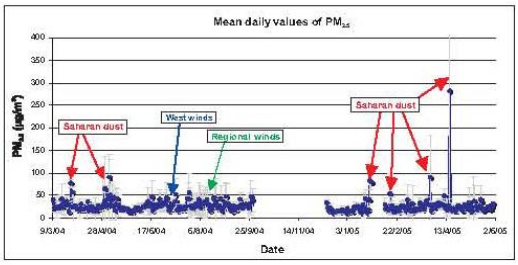

Figure 4: Daily average $PM_{2.5}$ concentrations between 10/03/2004 – 31/5/2005.

- The last Sahara dust episode was very intense with a considerable reduction in the visibility. At 17:45h on 17/4/2005 the PM2.5 concentration reached the 780 μg/m^3.
- In general, PM2.5 concentrations are lower during the winter period (*Figure 5*).

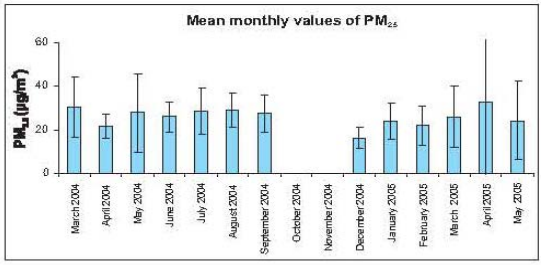

Figure 5: Mean monthly $PM_{2.5}$ concentrations during March 2004 – May 2005 at the Akrotiri research station (Crete).

7. Conclusions

- The ambient PM10 and PM2.5 concentrations at the Akrotiri research station on Crete (Greece) show a large variability.
- It is observed elevated concentrations during Sahara dust episodes whereas low PM10 and PM2.5 concentrations events occur during in winter storm episodes and transport originating from the west Mediterranean sea and the Atlantic region.
- Sahara dust episodes are observed during all the year.

MODELLING OF SECONDARY BIOGENIC AEROSOLS

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1. Introduction

An important problem in atmospheric chemistry is to improve our understanding of secondary organic aerosol (SOA) formation. In the current work we present recent advances in the development of an efficient and realistic model for SOA formation, which is tested against several gas chamber experiments. The work is based on the MAPS model, extracted from the 3D-air quality model UAM-AERO (Kumar et al.,1995), and the SAPRC-97 mechanism.

In this work we focus on two groups of VOC's (terpenes and aromatics) which produce aerosols through oxidation processes. Comparisons between model simulations and experimental data from smog chambers reveal that the existing yield functions in MAPS need modifications.

2. The model

The SAPRC-97 mechanism in MAPS (Model for Aerosol Process Studies) includes eight groups of VOC's that can form secondary organic aerosols through reactions with OH, O3, NO3, or O:

SOA1: CRES + OH	(cresols)
SOA2: ALK1 + OH	(less reactive alkanes)
SOA3: ALK2 + OH	(more reactive alkanes)
SOA4: ARO1 + OH	(less reactive aromatics)
SOA5: ARO2 + OH	(more reactive aromatics)
SOA6: OLE1 + OH, O_3, NO_3, O	(less reactive alkenes)
SOA7: OLE2 + OH, O_3, NO_3, O	(more reactive alkenes)
SOA8: OLE3 + OH, O_3, NO_3, O	(monoterpenes)

3. Yield

Secondary organic aerosols (SOA) are formed when VOC's are oxidized in the atmosphere, creating semi volatile products that partition from the gas to the aerosol phase. The aerosol yield Y is defined as:

$$Y = \frac{SOA(formed)}{VOC(consumed)}$$

The aerosol yield in the original MAPS model is a constant. Several recent studies have demonstrated that Y depends on temperature and the amount of organic matter present (M_O):

$$Y = M_0 \sum_i \frac{\alpha_i K_i}{1 + K_i M_0}$$

Here α_i is the individual formation yield for oxidation product *i* and K_i is the corresponding absorption equilibrium constant.

The temperature dependence of K_i can be expressed as:

$$K_i(T) = K_i \cdot \frac{T}{T_{ref}} \cdot EXP\left[\frac{H}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right]$$

where T_{ref} is a reference temperature (e.g. 303K), R is the ideal gas constant (0.0019872 kcal/mol K) and H is the enthalpy of vaporization.

4. Results

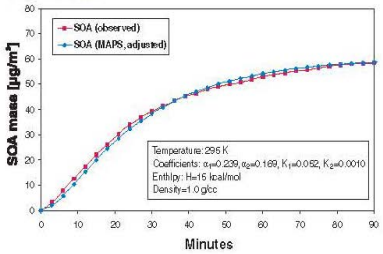

Figure 1: Gas chamber experiment from Stanier and Pandis (2002) at 295 K, where 400 ppb ozone is mixed with 73 ppb α-pinene (with 2-butanol as OH scavenger). The aerosol mass formed during the experiment is compared to SOA concentrations calculated from MAPS with inclusion of new partition coefficients.

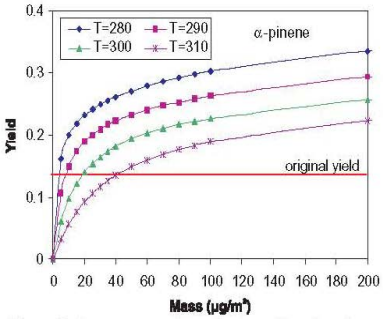

Figure 2: Temperature dependent partition functions for α-pinene reactions with O_3. The following coefficients are used: α_1=0.239, α_2=0.169, K_1=0.052, K_2=0.0010, H=15 kcal/mol, and T_{ref}=303K.

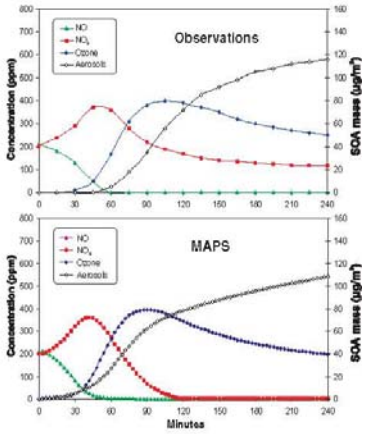

Figure 3: Gas chamber experiment from Takekawa et al. (2003) where 4.33 ppm toluene, 0.211 ppm NO, 0.202 ppm NO_2, and 0.9 ppm propene are mixed and irradiated by black lights. The upper panel represent observed values, whereas the lower panel is modelled gas and aerosol concentrations with inclusion of the partition function shown in Figure 4.

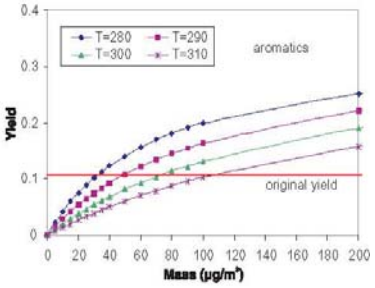

Figure 4: Temperature dependent partition function for toluene reactions with OH (based on experiments from Takekawa et al., 2003). Partition coefficients: α_1=0.340, K_1=0.0057, H=7.4 kcal/mol, and T_{ref}=303K.

5. Conclusion

SOA concentrations measured from the gas chamber experiments seem to agree fairly well with aerosol formations calculated from MAPS with adoption of the new partition functions. However, most experiments are performed at high temperatures and more model testing needs to be done for lower temperatures.

6. References

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HEAVY METAL PHASES IN FLY ASHES: AN INVESTIGATION BY SCANNING ELECTRON MICROSCOPY

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1. Introduction

In extended urban areas, the large amount of particulate matter in the air is a matter for concern; especially heavy metals associated with them have high toxicological potential, able to cause serious effects on the environment and on man health. It is well known that heavy metals are always present contaminants in fuel oils. They are not destroyed by incineration but are simply concentrated in the remaining ashes mostly like oxide phases located into the cenosphere hollow. Their concentration in the carbonaceous ashes is highly dependent on the amounts of heavy metals in the oils being incinerated, which vary with the geographic origin of the oils, while oxide phases in which they appear in fly ash depend on the chemistry of the combustion process.

The goal of this study was to examine the presence of heavy metals (Fe, V, Ni, Ti, Cr, Zn), that are emitted in solid form, associated with the fly ash particles coming from fuel oil combustion process in power plants, and to obtain chemical and compositional data of the major metallic phases. Obtained data are used as information for the control strategy and the study of urban atmospheric pollution in the area near Rome.

Scanning electron microscopy (SEM) coupled with EDX (Energy Dispersive X-ray Detector) system enables the analysis of particles size and composition, while statistical methods are used to classify the particles into groups with similar chemical composition. On the basis of the obtained compositional and morphological data the categories of the major metallic oxide phases are determined.

2. Experimental – materials and methods

Fly ashes from heavy fuel oil combustion were collected from electrostatic precipitator of two ENEL electrical power plants burning fuel oil. The granulometric fraction not lower than 1.5 μm, was used for the experiment. Two samples obtained in different combustion conditions were studied: one, named “sample A” came from the power plant that used old-fashion production method while the other – “sample B” came from the plant with modern production line. For each fly ash three kind of samples were prepared with following techniques: a) to examine the morphology of fly ash particles – cenospheres, the ash is dispersed in the ethanol and agglomerates are separated after being exposed half an hour to ultrasonic vibrations, and this solution is used for standard SEM preparation of powder samples; b) fly ashes were crushed using pestle and mortar, with few drops of ethanol, in order to make visible heavy metal particles that mainly reside inside the cenospheres, and the procedure from a) was applied; c) fly ashes were embedded in ordinary epoxy resin, grounded and polished for SEM examination using standard metallographic procedures. In order to avoid charging effects conducting coating with

carbon was applied for all samples.

The experiments are performed on SEM CAMBRIDGE 250MK3 equipped with an ultra thin-window detector for X-ray microanalysis by energy dispersion spectrometry. We mainly used backscattered electrons for imaging, as particle brightness in this mode is governed by the effective atomic number (Z) of the particle. Particles with high Z (e.g. Fe-rich) have a high backscattered electron yield and appear brighter on the SEM images, while particles with low Z (carbon, sulphates) appear dim, resulting in excellent discrimination between metallic particles and organic embedding medium. For each particle that was brighter than matrix (matrix is carbonaceous with relatively high percentage of sulphur), the electron beam was positioned on the particle's center and an EDX spectrum was acquired for 20 s. X-ray microanalysis data set (151 particles for the sample A and 201 for the sample B) are used to classify particles into groups with chemically similar composition and to determine the presence of heavy metals, employing the software package STATISTICA.

3. Results

Observations with SEM show well–known morphology of fly-ash particles – cenospheres: they appear hollow, thin-walled and extremely fragile, irregularly rounded to spherical, porous with a skeletal structure and numerous holes irregularly distributed on their surface (Figure 1). Cenospheres in both samples have approximately the same morphology and similar chemical composition; the noticeable difference is in their size: in fly ash A their size vary from 80μm to 200μm and in fly ash B from 50μm to 100μm; also in fly ash B some cenospheres are partly constituted of metallic compositions, that is not case for the fly ash A in which just μm-sized heavy metal particles are present inside the cenospheres. For both samples we confirmed the presence of heavy metals: Fe, V, Ni, Ti, Cr, Zn. Metallic particles can be assigned to one of the following categories: a) alumino-silicates, b) oxides of Fe, c) oxides of V, and d) mixed oxides of Fe, V, Ni and other metals. Their relative proportions vary considerably between samples: Fe and V are constantly present in both samples, with different percentage ranges from 1% to 60%. Ti and Cr are present in traces in sample A, but significantly higher in sample B: Ti (1% - 2%) and Cr (1% - 5%). Ni is significantly lower (0.5%-8%) in sample A than in sample B (3% - 51%). For both samples Zn is present in traces.

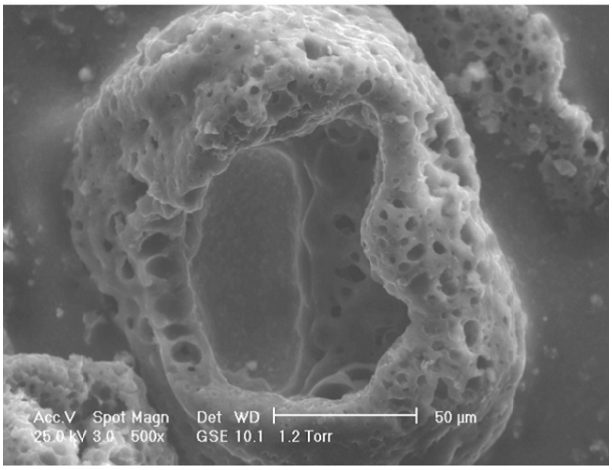

Figure 2 Typical SEM image of one particle emitted by heavy oil burning power plant.

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EU FRAMEWORK AND DAUGHTER DIRECTIVES AND CURRENT SERBIAN LEGISATION ON AIR POLLUTION MONITORING AND MANAGEMENT

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1. Introduction

Although integral Law on Environmental Protection (1) came in force few years ago, the legal basis for the establishing contemporary air pollution monitoring system in the Republic of Serbia (RS) has been based on old Law on Environmental Protection (2). It is expected that air quality monitoring and management in RS will be more harmonized with EU after the Law of Air Protection which is in procedure to be adopted.

Current regulations on the air quality control consist of Regulation on Imission Limit Values, Imission Measurement Methods, Criteria for Setting up Measurement Points and Data Recording (3, 4) and the Program of Air Quality Control, that has been updated every two years (5). The first document established limit values, threshold alert and episodic pollution criteria for notified substances. Limit values are different for urban areas, rural areas and recreation areas. Substances are grouped as inorganic and organic substances, heavy metals (HM) in suspended particulate matter (SPM) and carcinogenic substances. Permanent air pollution measurements in the monitoring network in urban areas are performed during one-year period. Indicative measurements should last six months or less in of vicinity point sources of pollution and at dense traffic roads. The minimal capturing period is 1 hour for gases and 24 hours for total suspended particulate matter (TSP). For the measurement methods, notified in the annex of the regulation there are described procedures for sampling, analysis and levels of accuracy. The height of the sampling sites was between 1.5 and 10 meters above the ground level. The results of measurements were reviewed monthly and annually as average concentrations, characteristic percentiles (C_{50}, C_{95} and C_{98},) and number of days that are exceeding limit values.

The monitoring of the immision given in the Program of Air Quality Control was performed by two monitoring systems: (a) the basic network of hydrometheorogical stations and (b) the local urban monitoring network. The National Hydrometeorological Institute performs programs of air monitoring at their stations as part of the network of 27 meteorological stations and urban meteorological stations where they measure air pollutants (SO_2, NO_2, O_3, soot and green house gases) and precipitation (cations, anions and heavy metals). The measurements performed at the local urban monitoring network are performed by the Municipal Health Institutions or Centers. According to current Program (5) there are 82 measuring stations, sampling sites, in the local urban network of monitoring stations in 43 cities, for monitoring the major air pollutants (soot, SO_2, NO_X, TSP, O_3, CO, deposited

matter). SO_2 and soot have been captured at almost all and NO_2 at most sites. There are also mandatory measurements, of specific pollutants for the purpose of control of air pollutants from industrial sources, at 45 measuring stations in 23 cities. The Program includes control of next specific pollutants, between 2 and 14 specific pollutants are collecting per site: PAH, acrolein, NH_3, HCl, H2S, phenol, benzene, toluene, xylene, Pb, Cr, Ni, Cd, As, formaldehyde, CS_2, Hg, total HC, mercaptane, atrazine, HF, ethyl acetate, Mg, CO_2, Zn, Al, methanol.

2. Comparison of some components of air quality managemement in EU and RS

The adoption of the Framework and Daughter Directives on ambient air quality assessment and management (6, 7, 8, 9, 10) in the EU, introduced a number of useful changes that improved quality assurance and control (QA/QC) of ambient air monitoring. QA/QC of ambient air quality monitoring is a set of measures that enable accurate, precise, credible and time consistent measurements; representative data of ambient air pollution; results that are comparable; high data sampling, evenly distributed; optimal use of resources; etc (11). It also encompases other components, QA/QC covers network design, sampling site selection, method of sampling and analysis selection, equipment selection. The criteria of air quality control were set; giving limit values and concentrations for an averaging period that represents acceptable level of pollutants in ambient air.

Framework and Daughter Directives introduce concept of zones, with agglomeration that are special zone types with more than 250000 inhabitants. Zones are basic territorial units where compliance of limit values should be checked as well as a regime for monitoring. To demonstrate compliance with limit values, monitoring should be performed by measurement or modeling. The most stringent regime is where maximum concentrations are above 70% of limit values and the least stringent regime is in a zone where maximum concentration are below 50% of limit value (12). Depending on the established regime in the zone, high quality measurement, modeling technique, objective estimation or indicative measurement is performed.

In RS territories local urban monitoring network coincide with municipalities but different monitoring regimes are not strictly recognized. In RS legislation there are proposed mandatory measurement and also measurements for duration of six months or less to obtain data in busy traffic streets and areas where there are several air pollutant sources located. The last measurement has some elements of preliminary and supplements measurements in Member States, but they are not defined and performed in an equivalent manner.

Network design

The EC Daughter Directives give proposals for a number of fixed sampling points of pollutant measurements for diffusive sources depending on the population of the agglomeration or zone and the concentration of pollutant. The number of sampling points in the vicinity of point sources should be calculated taking in account emission densities and potential exposure of population. In RS the number of sampling points is established according to the annual program (5). It establishes a number of sites for major and specific air pollutants. Bearing in mind that SO_2 is captured at all almost sites it seems there are enough fix sites for measuring such air pollutant taking into account criteria for determining the minimum number for fix measurements according to the EC Daughter Directive. Soot is also captured at all 60 sites in RS. According to Program (5) NO_2 is

captured at 64 sampling points, SPM and HM including Pb are monitored at 69 sites, O_3 at 11 and CO at 8. In current regulation in RS benzene is only monitored in 12 towns, but in the Program it is not clear if it is obligation to be captured at all sampling sites in that town.. Diffusive point monitoring has not yet been established. The distribution and number of sampling points for the measurements pollutants from points sources needs to be remodeled in RS legislative, taking in account wide range of air pollutants.

The Daughter Directives described the framework for macroscale and microscale location of sampling points. There are same specific rules about macroscale and microscale location of capturing particular air pollutants, which include selecting representative locations that would give characteristic of air pollution in urban, kerbside, industrial, residential and rural areas. In current RS Regulation (3) the distribution of sampling points would depend on the area where air pollution would be controlled, distribution and type of sources, density of population, orography and meteorological conditions. There are other requirements that specify site selection, although limit values are specified for urban, uninhabited and recreation areas.

The main part of air pollution monitoring system in Member States (MS) as well as other development countries are network of automatic monitoring station. In RS automatic monitoring stations have been established only in Belgrade (3 sites), Pancevo (2 sites), Bor (2 sites), Smederevo (2 sites) and Zrenjanin (1 site). Such sites are established through different programs and there are part of local municipal or industrial monitoring systems and they don't belong to monitoring system of RS It may be underlined that automatic monitoring of PM10 is performed only at: two sites in Belgrade Metropolitan, two sites at Pancevo and one site in Zrenjanin. In upcoming period there will be established 25 automatic monitoring sites that will be installed all over the RS at location of basic network of meteorological stations. Equipment will be procured in the framework of ongoing CARDS program.

Monitoring methods

In developing countries the basic rule for choosing monitoring methods for air pollution control is the availability of equipment and the limited level of financial assistance. Monitoring methods that may be recognized in RS regulation are only active sampling methods (2), while passive samplers, continual monitoring methods (automatic analysers and remote sensors), modeling and objective estimation do not exist in the regulations. It is well known that the simplest methods that meet monitoring objectives should always be selected. There are numerous situations where it would be possible to use diffusive (passive) sampling or only modeling tools. Automatic, continual monitoring may also be necessary under defined requirements. The diffusive sampling method has been adopted in MS and many other counties all over the world, but in RS it has been contained either in regulation or in the practice of air pollution quality control. Only in one case where diffusive sampling method was applied is in Pancevo. That project have been performed by Institute for Air Pollution from Rome, Italy and funded under Italian Ministry of Environmental Protection.

Table 1. presents sampling media and methods of air pollutants analysis that were used in RS in comparison with reference methods adopted in EC Daughter Directives.

Compilation of air pollution results

Air pollution control data are analyzed monthly and annually and presented as statistical parameters and chart diagrams. According to regulation it is necessary to have not

less than 75% of all data capture for the reporting period in comparison of 90% in EC Daughter Directives. Values of uncertainty and minimum time coverage are not defined in RS regulation.

3. Comparison of criteria of air quality control in EU and RS

The criteria for assessment of air quality in urban areas in EU are limit values used for protection of human health (hourly, daily, yearly) and threshold values (alert and information). In the Framework Directive (6) there are an established lists of atmospheric pollutants that are to be taken in consideration. In Daughter Directives (7,8,9,10) there are critera for assessment of air quality for several pollutants: SO_2, NO_2, PM_{10}, Pb, CO , C_6H_6 , O_3, As,Hg, Cd, Ni and PAH. In Table 2. and 3.there are notified limit and threshold values for the averaging period of air pollutants in the EC Directives and compared with relevant values in RS regulatory (3,4).

The RS critera for assessment air quality in urban areas are partly harmonized with the EU, but only hourly limit value for the protection of human health for SO_2 are the same. But in the EU the number of exceedances of the SO_2 hourly limit value per calendar year is 24 times. The critera that has the same limit value but a different averaging period is the hourly limit value for the protection human health for CO. Averaging period in EU is 8h, and 1h in RS regulations. There are some critera where the averaging period is the same, but the limit values are different. Limit and target values as well as refernce period for HM and Benz(a)pyrene are same. The questions is could the results be compared: in RS sampling is performed in TSP and EU in PM10

Table 1. Methods of sampling and analyzing air pollutants due to RS and EU regulation

Republic of Serbia				EU	
Air pollutant	Sampling media	Analysis	Relevant Standard	Analysis	Standard
SO_2	Acidimetric, Tetrachloromercurate and thorin method	Spectro-photometer	ISO 4220 ISO 6767 ISO 4221	Fluorescence	EN14212
NO_2	Wet method with solution of trietanolamin	Modified Griess-Saltz-man method	ISO 6768	Chemi-luminescence	EN14211
CO	Sampling bag or continual capturing	IR spectrometry		Non-dispersive IR spectrometry	EN14666
C_6H_6	Sampling bag	GC	VDI 2453 Provisional ISO 8	GC	EN14662 parts 1-3
SPM	Fibreglass membrane filter	Derenda Gravimetric		-	
PM_{10}	ß absorption FH 621-R Horiba 2002 EPA &TÜV/UBA			PM10 reference sampler (EN12341)	EN12341

Pb, As, Cd, Ni	Fiberglass membrane filter	AAS		PM10 reference sampler + analysis by AAS or ICP-MS	EN14902
O_3	Automatic monitor	UV photometry		UV photometry	EN14665
Benz(a) -pyrene	GF/A Whatman & PUF	GC MSD		PM10 reference sampler + analysis by LC-fluorescence or GC-mass spectrometry	
Soot	Filter paper	Reflectometer		-	

Table 2. Limit values in EU and RS regulations for protection of human health

Compound	EU			RS	
	Limit value	Reference period	Number of exceedance of per year	Limit value	Reference period
SO_2	350 μg/m^3	1h	24	350 μg/m^3	1h
	125 μg/m^3	24h		125 μg/m^3	24 h
	20 μg/m^3	1y		50 μg/m^3	1 y
NO_2	200 μg/m^3	1h	18	150 μg/m^3	1h
	40 μg/m^3	1y		85 μg /m3	24 h
	30 μg/m^3	1y		60 μg /m3	1 y
CO	10 mg/m^3	8h		5 mg/m^3	24 h
C_6H_6	5 μg/m^3	1y		5 μg/m^3	1 y
TSP	-			120 μg /m^3	24 h
PM_{10}	50 μg/m^3	24 h		-	
	40 μg/m^3	1y	35		
Pb	0.5 μg/m^3	1y		1 μg/m^3	24 h
soot	-			50 μg/m^3	24 h

Table 3. Target values in EU and releveant values in RS regulations for protection of human health

Compound	EU			RS	
	Threshold value		Reference period	Threshold value	Reference period
NO_2		400 μg/m^3	3 h	300 μg/m^3	1h
		40 μg/m^3	1 y	85 μg /m3	24 h
		30 μg/m^3	1 y	60 μg /m3	1 y
CO		10 mg/m^3	8 h	10 mg/m^3	1 h
O_3	Long term objectives	120 μg/m^3	8 h		
	Alert treshold	240 μg/m^3	1 h	200 μg/m^3	1 h
	Information alert	180 μg/m^3	1 h		
Benz(a) pyrene		1 ng/ m^3	1 y	1 ng/ m^3	1 y
As Cd Ni		6 ng/m^3 5 ng/m^3 20 ng/m^3	1 y	6 ng/m^3 5 ng/m^3 20 ng/m^3	1y

4. Conclusion

Between 1996 and 2004 EU has adopted Framework and four Daughter Directives of air quality control that replaced the old generation of directives from eighties, where there were involved new elements in QA/QC. Basic concept of the new approach consists of the Framework Directive for air pollutants and Daughter Directives for particular groups of pollutants. The legislation of air quality control in Republic of Serbia is going to be replaced with new laws and regulations which will be harmonized with the current EU QA/QC structure and practice. We need to harmonize alter limit and threshold values where they are higher than in the EU. More extensive assessment requirements would be involved. Methods of measurements, sampling and analyzing pollutants need to take into account procedures proposed in relevant EN standards (Table 1.). Air quality monitoring, direct measurement of air quality is important part of urban air quality assessment program and sill not exit in RS regulation and practice. For the improvement in air quality monitoring it is necessary to established complete emission inventory as well as to use more air pollution modeling techniques. It is also necessary to include indicative methods of measuring like diffusive sampling methods for indicative and supplementary measurements. One of the priorities should be to captured respirable aerosols, aerosols less than 10μm. Limit and target values for HM are same in EU and RS, but they are not comparable as in SPM is sampling in RS and control of PM10 is still not involved. One of the main differences that RS air quality monitoring have to harmonized with EU is sampling and control of PM10 and analyzing quantity of HM and Benz(a) pyrene in appropriate manner from PM10.

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QUALITY ASSURRANCE AND THE USE OF A REFERENCE LABORATORY

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1. QA/QC

Air quality monitoring must satisfy certain minimum quality requirements and standards. Measurements, regardless of where and by whom they are carried out, must be comparable to those conducted elsewhere. This is secured through a comprehensive Quality Assurance and Quality Control programme (QA/QC). QA/QC may be regarded as a chain of activities designed to deliver credible and accurate data. NILU delivers written procedures and routines for the quality control of the operation and maintenance of instruments and programmes.

NILU also provides training of key personnel in operation, calibration and maintenance as well as undertake audits of the systems when required. The procedures developed to handle ambient air quality measurements contain several levels of controls. In field operations will be established:

- Station Manuals including Standard Operational Procedures (SOP) for instrument installations, maintenance, controls etc.,
- Zero span checks and calibration routines

2. Purpose of the QA programme

The primary purpose of the Quality Assurance (QA) Programme is to provide an overview of the project, describe the need for the measurements, and define QA/QC activities to be applied to the project, all within a single document. The QA programme should be detailed enough to provide a clear description of every aspect of the project and include information for every member of the project staff, including samplers, lab staff, and data reviewers. The QA programme facilitates communication among clients, data users, project staff, management, and external reviewers. Effective implementation of the QA programme assists project managers in keeping projects on schedule and within the resource budget.

3. QC Activities

Quality Control (QC) is the overall system of technical activities that measures the attributes and performance of a process, item, or service against defined standards to verify that they meet the stated requirements established by the customer; that are used to fulfil requirements for quality.

In the case of the Ambient Air Quality Monitoring Network, QC activities are used to ensure that measurement uncertainty is maintained within established acceptance criteria for the attainment of the Data Quality Objectives (DQO).

4. Data Quality Objectives (DQOs)

DQOs are qualitative and quantitative statements derived from the outputs of the DQO Process that:

1) Clarify the study objective;

2) Define the most appropriate type of data to collect;
3) Determine the most appropriate conditions from which to collect the data; and
4) Specify tolerable limits on decision errors which will be used as the basis for establishing the quantity and quality of data needed to support the decision.

5. The Reference Laboratory

Operation of an air quality monitoring network based on automatic monitors will normally require the establishment of a National Reference Laboratory (NRL), which can take care of:

- Auditing,
- Measurement standard methods,
- Reference standards (gases and traceable standards) and
- International comparison studies.

The objectives of the Reference Laboratory are to contribute to the assurance of quality of the specified analyses, tests and measurements, by assisting the monitoring institutions in matters concerning quality assurance and quality of measurements, including the provision of external quality control services. The Reference Laboratory shall advise the Authorities by assuring the quality of measurements provided by the monitoring institutions and conducting audits of the activities of the monitoring institutions.

The Reference Laboratory should be established in an early phase of the development of air quality monitoring systems. The Reference Laboratory will have to be equipped with a complete set of monitors. The first monitors should actually be installed and trained at the selected Reference Laboratory, prior to installing monitors in field. Expert personnel have to be trained to operate the monitors for calibration reasons. Personnel have to be prepared and trained to carry out systematic audits of the monitoring programmes.

Certified reference material has to be made available and all procedures have to be traceable. Primary and secondary standards as well as all reference gases have to be supplied to the different monitoring systems in the system. The Reference Laboratory will have to participate in international proficiency tests, calibrate the reference standards at internationally recognised laboratories as well as conduct national proficiency tests.

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AIR POLLUTION MONITORING NETWORK IN BELGRADE- EVALUATION OF AIR POLLUTION MEASUREMENT SITES

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1. Programme of Air Quality Control

For the purpose of this paper the results of local urban air quality monitoring network were used with special attention on long - lasting investigations of behavior of air pollutants, such as NO_2, SO_2, O_3, black smoke and PAHs in urban air of Belgrade. The aim of this paper was to perform classification of measuring spots, based on detailed analysis of air pollutant concentration analysis and to identify optimal and most representative sampling (analysis) spots in order to perform air quality analysis in greater Belgrade. Concentrations of air pollutants were analyzed in the samples of air taken from measuring spots within a local urban network in Belgrade, for perod 2001 and 2004.

There are 17 semiautomatic, 3 stationary and 2 mobile automatic stations within local urban network. Sampling is done 24 h every day in the year by semiautomatic devices. Determination of NO_2, SO_2, and black smoke is done in laboratory by clasical physical and chemical methods and that is 24h, daily values. Sampling by automatic devices is continual like three and thirty minutes mean values. Mean concentrations of air polutants is colected by central serever several time during the day. All procedure is automatic and measurements were done using HORIBA ambient NOx and O_3 monitors (APNA-360 and APOA-360). The devices give great stability and extremely high sensitivity (F.S. 0.1 ppm). Polutants on Belgrade territory is defined by »Official Gazzete of Republic of Serbia«, No 54/92. Pollutants in ambient air is examined according to informations about main pollutant sources and importance of pollutants for population exposure.

1. Criteria for selection of monitored air pollutants

The main pollutants in ambient air of interest in urban setting in current air quality monitoring network of Belgrade are presented in Table 1.

The legal basis for the adoption of the Programme of Air Quality Control in the Territory of Belgrade, Serbia is contained in the Law on Environmental Protection [2], so authorities of Belgrade, within their competence, are obliged by law to provide continuous control and survey of environment.

2. Evaluation of air pollution measurement sites in wider urban area

Analysis of the results from two measuring spots within the local urban network (2001 - 2004) has shown considerable differences in pollutant concentrations in air in wider urban area. The example of these differences are measuring spot in central urban area in Belgrade in Bulevar despota Stefana 54/a street and measuring spot near the Metal Castings Plant in Omladinskih brigada street, on the left riverbank Sava, New Belgrade. Measuring spot in Bulevar despota Stefana 54/a street is located in front of Institute of Public Health of Belgrade. It is canyon street with heavy traffic.

Table 1: The main pollutants in ambient air of interest for Belgrade

Ambient air	Gas components	SO_2, NO_X, NO_2 – 24-hourly averages
		O3 – 24-hour, 4 and 8 hourly averages
		CO – 30 minute, 1 hour ,BTEX 1 hour and 24 hourly averages
	Solid phases in the air	PAH – 3,4 benzo-a-pyrene (BaP) – monthly averages
		Soot, total deposited matter – 24-horuly averages
		SPM (mass conc.) mass concentration, 24-hourly averages 7 day sampling interval
		Pb, Cd, Zn, Mn, Ni, Hg, Cr – monthly averages

We analised air samples in August 2004 (NO_2, SO_2, and O_3 at measurement places in Omladinskih brigade street and NO_2, SO_2, and PM_{10} in air samples in Bulevar Despota Stefana 54a at IPHB). On the basis of those data we can notice differences betwen measurement places IPHB and MCP:

in airpollutants concentrations,

in dynamics, i.e. in appearance of daily maximum and their excat time,

in every diagram we can notice weekend effect, in fact we notice lower concentrations of airpollutants at weekend days when traffic isn`t heavy and emission pollutants in atmosphere is low,

airpollutants concentrations at both measurement places depends on meteorology parameters, in period 26.08.-31.08.06. we can notice low concentration of all aeropollutants due to meteorological conditions.

3. Influence of meteorologic parameters on airpllutant concentrations.

In last week in August in period 26-29.08.04. we can also see decrease concentrations of all aeropollutants. This is result of meteorolgical parameters: air pressure was low, wind speed high and wind direction was south-east.

4. Depending of daily maximum airpollutant concentrations.

We also strengthened relations between maximum and daily (average) concentration of NO_2, SO_2 and O3, and calculated correlation coefficients for all pollutant. Correlation coefficient *r* was the biggest for SO_2 on MCP measurement place. Generaly, correlation coefficients were biger for SO_2 for the both measurement places because SO_2 concentration were less and differences between daily and maximum concentration were less, too.

Value for correlation coefficients are very important for semiautomatic station because we can calculated daily maximum when we have only average value[2].

This difference has caused the need for a detailed analysis. Although we have examined a great number of parametres and samples, the research only gives a framework and directions for future research. Regard to the aim of research we used statistical method

MANOVA 5,6,7,8.

Chart 1: Results of tests of homogenity variance on locations in period 2001-2004

Pollutant	Test				Signification level
	Hartley	Cochran	Bartlett	Levene	
Soot	77.806	0.098	244.915	3.899	0.000
SO_2	-	0.240	690.611	9.026	0.000
NO_2	232,520	0.140	137.696	3.628	0.000

Hypothesis about normal data distribution of samples and it's homogenity is not approved, because variation coefficients weren't under 30% in all cases[7,8].

In spite of these results and regard to the aim of examination, we used method MANOVA.

Chart 2: Results of method MANOVA

Variability source	POLLUTANT					
	SOOT		SO_2		NO_2	
	F-quotient	p-level	*F- quotient*	p-level	F- quotient	p-level
Years	4.073	0.007	*2.548*	0.055	6.826	0.000
Loocations	20.729	0.000	*14.573*	0.000	82.281	0.000
Interaction	3.051	0.000	*1.508*	0.031	5.826	0.000

Results of method MANOVA show that average concentrations of soot and NO_2 in examination period are statistical very different. Also, average concentrations of all pollutants between locations show statistical very significant statistical difference. Differences between average soot values and NO_2 concentrations are statistical very significant in spite of SO_2 average concentrations for the same period. Interaction of factors years and locations caused significant statistical difference in average SO_2 concentration.

All measurement places within local urban network (according received results) classify in four different groups:

the first group – *street regime 1* contains measurement places Gradski zavod, Miloša Pocerca, Ohridska i Dr Subotića,

the second group (*steet regime 2*) Trg JNA, FOM, Ustanička, Svetog Save, Požeška, Obilićev venac, Ljutice Bogdana i Mate Vidakovića,

the third group (*urban regime*): Goce Delčeva, Kraljice Jelene, Olge Jovanović, Biološki institut i Obrenovac,

the fourth group (*suburban regime*): Blok Grge Andrijanovića i Grabovac.

5. Conclusion.

Our research was related to long - lasting investigations of behavior of air pollutants, such as NO_2, SO_2, O_3 and black smoke in urban air of Belgrade. The aim of this paper was to perform classification of measurement sites, based on detailed analysis of air pollutant concentration .

Analysis of the results from two measuring spots within the local urban network (2001 - 2004) has shown considerable differences in pollutant concentrations in air in wider urban area. These were:

in the level of concentrations of pollutants on daily, monthly and annual levels;

in daily dynanamic of occurrence of maximum values of air pollutants;

in concentrations of ozone and nitrogen- dioxide (caused by different pollution sources);

on the observed measuring spots, for all polutants (except ozone) we have established a "week- end" effect;

there is a positive correlation between maximum and average daily concentrations what enables calculation of a daily maximum from the average daily concentration;

Pollutant concentrations in atmosphere also depend on meteorologic parameters. They have been decreased in days with elevated wind speed and decreased atmospheric pressure

average monthly medians for soot concentrations on all locations showed decrease trend in period 2001-2004

average monthly medians for SO_2 and NO_2 concentrations on all locations showed increase trend in period 2001-2003 and in 2004 decrease trend

there are statistic significant differences between all examination years for average soot and NO_2 concentrations

also, average concentration of all examination parameters were significant difference between all locations

interaction of factors years and locations caused statistical signification difference in average SO_2 concentration

interaction of factors years and locations caused statistical signification difference in average SO_2 concentration

average SO_2 and NO_2 concentrations were minimum in 2001 and maximum in 2003

average soot concentration was maximum in 2001 and minimum in 2004

we have performed cluster analysis based on daily 24h medians of air pollutants (black smoke, NO_2, SO_2) concentration in period 2001-2004 (statistical method MANOVA). Euclidean distance and Ward's cluster method were applied and four different regimes were identify by means of hierarchical clustering. These were: the first group – *street regime 1*, the second group – *steet regime 2*, the third group – *urban regime* and the fourth group – *suburban regime*.

Grouping of measurement sites has shown that they are representative for urban environments: street regime (kanyon-like type) that are strongly influenced by traffic. Although we have examined a great number of parametres and samples, the research only

gives a framework and directions for future research. In order to reduce concentrations of air pollutants, it is necessary to perform additional measurements of nitrogen dioxide and ozone concentrations and suspended particles PM_{10} and $PM_{2,5}$ in the zones with street regimes 1.

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AIR QUALITY MANAGEMENT AND ABATEMENT STRATEGY PLANNING

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1. The abatement strategy system

Optimal abatement strategies were developed by the World Bank for four large urban areas in Asia as early as in 1996-97. Air quality measurements combined with models, dose response functions and effect/cost estimates produced a list of the most cost effective actions that could be implemented in Kathmandu, Mumbai, Jakarta and Manila.

The Urban Air Quality Management Strategy (URBAIR) project was undertaken to assist in the design and implementation of policies, monitoring, and management to restore air quality in Asian metropolitan areas. Its goal was to identify the components of a general action plan to manage and control air pollution. Abatement measures in the plan were categorized according to cost-effectiveness, as well as the time required implementing them and when they would become effective.

The air quality management strategy planning tool (AQMS) contains the following main components:

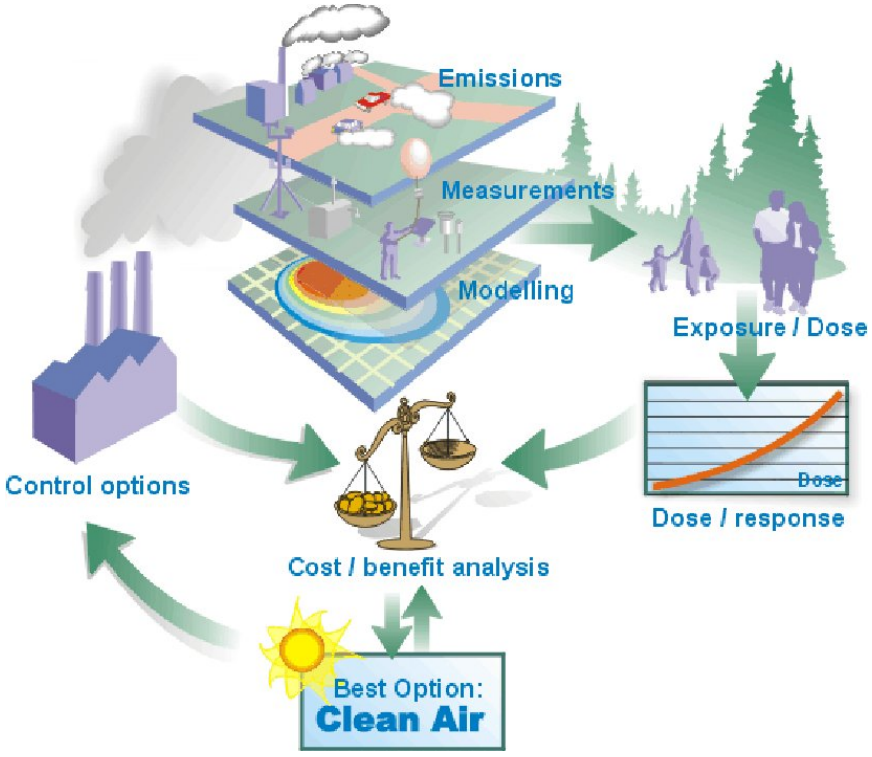
- Air quality assessment
- Environmental damage assessment
- Abatement options assessment
- Cost-benefit or cost-effectiveness analyses
- Abatement measures
- Optimum control strategy

Assessment: Air quality assessment, environmental damage assessment and abatement options assessment provide input to the cost analysis, which is also based on established air quality objectives (e.g. air quality standards) and economic objectives (e.g. reduction of damage costs). The analysis leads to an Action Plan containing abatement and control measures for implementation in the short, medium, and long term. The goal of this analysis is an optimum control strategy.

The AQMS depends on the following set of technical and analytical tasks, which can be undertaken by the relevant air quality authorities:

- Creating an inventory of polluting activities and emissions;
- Monitoring air pollution and dispersion parameters;
- Calculating air pollution concentrations with dispersion models;
- Assessing exposure and damage;
- Estimating the effect of abatement and control measures;
- Establishing and improving air pollution regulations and policy measures.

These activities, and the institutions necessary to carry them out, constitute the prerequisites for establishing the AQMS as illustrated in the Figure below.



The elements of an optimal abatement strategy planning system.

Action plans and implementation*:* Categories of "actions" include the following:

- Technical abatement measures;
- Improvements of the factual database (e.g. emission inventory, monitoring, etc.);
- Institutional strengthening;
- Implementing an investment plan;
- Awareness raising and environmental education.

Monitoring: A third essential component of AQMS is continued monitoring, or surveillance. Monitoring is essential to assessing the effectiveness of air pollution control actions. The goal of an Air Quality Information System (AQIS) is, through thorough monitoring, to keep authorities, major polluters and the public informed on the short- and long-term changes in air quality, thereby helping to raise awareness; and to assess the results of abatement measures, thereby providing feedback to the abatement strategy. This

part of the AQMS will also include institutional building and training in order to assure sustainability in the system established in the area or region in question.

A system for air quality management requires activities in the following fields:

- Inventorying of air pollution activities and emissions
- Monitoring of air pollution, meteorology and dispersion
- Calculation of air pollution concentrations, by dispersion models
- Inventorying of population, materials and urban development
- Calculation of the effect of abatement/control measures
- Establishing/improving air pollution regulations

The implementation of plans and strategies for air quality improvements, in Asian cities as elsewhere, is done through the use of policy instruments by ministries, regulatory agencies, law enforcers and other institutions. Indeed, some of these institutions may well be the same institutions as those, which must be in place to carry out the AQMS analysis described above, which ideally is the basis for the plans and strategies. Thus, the existence of relevant institutions, and an organisational institution structure, is part of the basis for AQMS work.

Different levels of government - national, regional and local - have different roles and responsibilities in the environmental sphere. Air quality standards or guidelines are usually set at the national level, although local government may have the legal right to impose stricter regulations. National governments usually assume the responsibility for scientific research and environmental education, while local governments develop and enforce regulations and policy measures to control local pollution levels.

Institutional arrangements, laws and regulations are important parts of an AQMS. Some roadblocks to successful air quality management in Asia are weak institutions that lack technical skills and political authority; enforcement agencies that often lack both the necessary information and the means to implement policy, and unclear legal and administrative procedures. Countries have their own political and administrative hierarchies and technical expertise that affect institutions, laws and regulations related to air pollution control. AQMS procedures similar to the URBAIR project have been undertaken in other urban areas and regions in China, such as Guangzhou, Yantay and the Shanxi province. One of the experiences from these studies is pointing at the importance of clarity in the organisational structures and the division and description of responsibilities and “lines-of-command”.

2. Applications

The integrated air quality management tool, AirQUIS has been needed in order to select the right decisions for protection of human health as well as materials and the ecosystem from an increasing impact of pollution. Heavily populated and industrialised areas experience a change in impact that is difficult to handle. Not only is the amount of pollution increasing in many areas, but also the composition and complexity is becoming more difficult to monitor, understand and solve.

The AQM system has been applied in several urban areas around the world.

NILU is presently working in

- China (3 cities in Shanxi province, Guangzhou, Yantai ++)
- Vietnam (HCMC and Hanoi)

- United Arab Emirates (Abu Dhabi)
- South Africa (Durban ++)
- Senegal (Dakar)

When abatement options and scenarios are defined, cost-benefit analyses have been used to evaluate the best options to reduce the air pollution load seen from an economic point of view. The results of such analyses can lead to the development of action plans. The AirQUIS exposure estimates can be combined with dose-response relationships in an impact and damage assessment for health, materials and vegetation.

The main goal and objectives for the project in China has been to:

- Develop and establish an environmental management and planning system; based on the AirQUIS technology
- Evaluate, update and improve the air quality monitoring system by additional measurements (parameters and measurement points),
- Transfer tools and knowledge to the extent necessary to enable local institutions and experts to continue the Air Quality Management Strategy work in a qualified fashion.

The existing surveillance system has been improved and upgraded in co-operation with the Chinese partners in order to develop a modern environmental surveillance and information system as well as a planning tool for improved air quality.

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MONITORING AIR QUALITY, OBJECTIVES AND DESIGN

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1. Air Quality monitoring network design

The design of the air quality monitoring network basically involves determining the number of stations and their location, and monitoring methods, with a view to the objectives, costs and available resources.

The typical approach to network design, appropriate over city-wide or national scale, involves placing monitoring stations or sampling points at carefully selected representative locations, chosen on the basis of required data and known emission/dispersion patterns of the pollutants under study. This scientific approach will produce a cost effective air quality monitoring programme. Sites must be carefully selected if measured data are to be useful. Moreover, modelling and other objective assessment techniques may need to be utilized to ''fill in the gaps'' in any such monitoring strategy.

Another consideration in the basic approach to network design is the scale of the air pollution problem:

- The air pollution is of predominantly local origin. The network is then concentrated to within the urban area. (e.g NO_2, SO_2, PM_{10}, CO, benzene)
- There is a significant regional contribution to the problem and more emphasis will be on the regional part. (e.g. Ozone, PM).
- *Large-scale phenomena, such as winter or summer smog episodes in Europe or the Asian dust cloud (local impacts should be avoided).*

Most of the discussions in this presentation will be related to urban air pollution problems. The number of sites will depend upon the size and topography of the urban area, the complexity of the source mix and again upon the monitoring objectives. In Europe the EU Directives specify a minimum number of stations to be established dependent upon the population, and it also indicates what types of areas should be monitored. Some of this background will be referred in the following chapters.

2. Monitoring Objectives

The air quality monitoring programme design will be dependent upon the monitoring specific objectives specified for the air quality management in the selected area of interest. What are the expected outputs of the monitoring activity? Which problems do we need to address?

Defining the output will influence the design of the network and optimise resources used for monitoring. It will also ensure that the network is specially designed to optimise information on the problems at hand.

There might be different objectives for the development of the environmental monitoring and surveillance system. Normally the system will have to provide on-line data and information transfer with direct /automatically/ online quality control of the collected data. Several monitors, sensors and data collection systems may be applied to make on-line data transfer and control possible.

The main objectives stated for the development of an air quality measurement and surveillance programme might be to:

- Facilitate background concentrations measurements,
- Monitor current levels as a baseline for assessment,
- Check the air quality relative to standards or limit values,
- Detect the importance of individual sources,
- Enable comparison of air quality data from different areas and countries,
- To collect data for air quality management, traffic and land-use planning purposes,
- Observe trends (related to emissions),
- Develop abatement strategies,
- Determine exposure and assess effects of air pollution on health, vegetation or building materials,
- Informing the public about air quality and raising awareness,
- Develop warning systems for prevention of undesired air pollution episodes,
- Facilitate source apportionment and identification;
- Supply data for research investigations,
- Develop/validate management tools (such as models),
- Develop and test analytical instruments.
- Support legislation in relation to air quality limit values and guidelines

The relationships between the data collected and the information to be derived from them must be taken into account when a monitoring programme is planned, executed and reported. This emphasizes the need for users and potential users of the data to be involved in planning surveys, not only to ensure that the surveys are appropriate to their needs but also to justify committing the resources.

3. Screening studies and operational sequence

Before a final programme design is presented it is also important to undertake a preliminary field investigation, often referred to as a screening study. This may consist of some simple inexpensive measurements (e.g. using passive samplers) and simple dispersion models. The data will give some information on the expected air pollution levels, high impacted areas and the general background air pollution in the area.

The number of monitoring stations and the indicators to be measured at each station in the final permanent network may then be decided upon based on the results of the screening study as well as on knowledge of sources and prevailing winds.

Once the objective of air sampling is well-defined and some preliminary results of the screening study is available, a certain operational sequence has to be followed. A best possible definition of the air pollution problem together with an analysis of available personnel, budget and equipment represent the basis for decision on the following questions:

1. What spatial density of sampling stations is required?
2. How many sampling stations are needed?
3. Where should the stations be located?
4. What kind of equipment should be used?
5. How many samples are needed, during what period?

6. What should be the sampling (averaging) time and frequency?
7. What additional background information is needed:
   - Meteorology,
   - Topography,
   - Population density,
   - Emission sources and emission rates,
   - Effects and impacts.
8. What is the best way to obtain the data (configuration of sensors and stations)?
9. How shall the data be accessible, communicated, processed and used?

The answers to these questions will vary according to the particular need in each case. Most of the questions will have to be addressed in the site studies and in the selection of sites as addressed below.

4. Site selection

The urban air quality monitoring programme shall normally provide information to support and to facilitate the assessments of air quality in a selected area and to meet the objectives as stated by the users. Some of the objectives have been presented above.

This normally means that for designing a monitoring programme in an urban area several monitoring stations are needed for characterising the air quality in the total region. The areas are generally divided into urban, suburban and rural areas. Measurements should be undertaken in different microenvironments within these areas, where people are living, staying and moving. In a typical urban air pollution measurement programme the microenvironments selected are often classified as:

- Urban traffic,
- Urban commercial,
- Urban background,
- Suburban (traffic and industrial)
- Rural sites (background areas).

When considering the location of individual samplers, it is essential that the data collected are representative for the location and type of area without undue influence from the immediate surroundings. It is important to bear in mind, when measuring air quality or analysing results from measurements that the data you are looking at is a sum of impacts or contributions originating from different sources on different scales.

In any measurement point in the urban area the total ambient concentration is a sum of:

- A natural background concentration,
- A regional background,
- A city average background concentration (kilometre scale impact),
- Local impact from traffic along streets and roads,
- Local impacts from small area sources like open air burning (waste and cooking),
- Impact from large point sources such as industrial emissions and power plants.

To obtain information about the importance of these different contributions it is therefore necessary to locate monitoring stations so that they are representative for the different impacts. We will, in addition to air pollution data, often need meteorological data

to identify and quantify the sources contributing to the measurements. It also will require that more than one monitoring site is needed for characterising the air quality in the urban area, as indicated in Ch4.2.4.2. It is also important to carefully characterise the representativeness of the monitoring sites, and to specify what kind of stations we are reporting data from.

The classification of measurement stations is divided into 3 types of areas; urban, suburban and rural. In each of the areas there may be 3 types of stations; traffic, industrial and background. The background stations are divided into; near-city background, regional and remote background stations.

Descriptions of the areas are given in the Table below:

Table 4.2.1: Typical area classification of micro-environments for air quality monitoring programmes.

Type of area	Description	Type of station
Urban	Continuously built-up area	Traffic
Suburban	Largely built-up area: continuous settlement of detached buildings mixed with non-urbanized areas	Industrial
Rural	Areas that not fulfil the criteria for urban/suburban areas	Background : - Near city - Regional - Remote

When considering the location of individual samplers, it is essential that the data collected are representative for the location and type of area without undue influence from the immediate surroundings.

5. Air Quality Indicators

Air quality indicators have been selected for different environmental issues and challenges. Not all indicators are specific enough to address only one issue. The nature of air pollution involve that some indicators address several issues. Some of the issues that have to be addressed are

- Climate change,
- Ozone layer depletion,
- Acidification,

- Toxic contamination,
- Urban air quality,
- Traffic air pollution.

As can be seen from the list the indicators have to cover all scales of the air pollution problems (in space and time) to address different type of impacts and effects.

The most commonly selected air quality indicators for urban and industrial air pollution are:

- Nitrogen dioxide (NO_2),
- Sulphur dioxide (SO_2),
- Carbon monoxide (CO),
- Particles with aerodynamic diameter less than 10 μm (or 2,5 μm), PM_{10} ($PM_{2,5}$),
- Ozone (O_3).

The US EPA refers to the compounds listed above as the priority pollutants (US EPA, 1990). They are also given in the Air Quality Daughter Directives of the European Union with specific limit values for the protection of health and the environment (EU, 2005). The first three are also given in the World Bank limit values for ambient air pollution. The World Health Organisation guideline values also include the above indicators (WHO, 2005).

6. Other elements in the design

In the design of the air quality monitoring programme we will also have to include measurements of meteorology. Weather stations should be located in order to assess the general wind flow over the study area.

Weather stations do not need to be placed at all air quality sites, but some co-locations will decrease the total cost of these measurements.

Before air quality data can be used to assess the situation in the area it is important assure that the data collected are real concentration values, which may be compared to similar information from other areas and countries. For each pollutant, which is measured as input to the air quality assessment and evaluation, the following main questions may be asked:

- Have suitable quality assurance procedures been set up for all stages and activities?
- Is technical advice available?
- Is monitoring being carried out at suitable locations?
- Have suitable arrangements for data handling and storage been made and implemented?

The documentation to support the credibility of data collection and initial data quality assurance are the responsibility of the data provider. This includes the process of data collection, application of calibration factors, initial Quality Assurance procedures (QA/QC), data analysis, data “flagging”, rollups (averaging) and reporting. A combination of data record notes, data quality flags and process documentation are all part of this first phase of processing. During the data collection phase, one role of the data provider is to assist in

maintaining process credibility and validity of the data.

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MEASUREMENT OF BAP IN TSP AND BLACK SMOKE (SOOT) IN BELGRADE

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are formed during incomplete combustion or pyrolysis of organic material and in connection with the worldwide use of oil, gas, coal and wood in energy production. Additional contributions to ambient air levels arise from tobcco smoking, while use of unvented heating sources can increase PAH concentrations in indoor air. Because of such widespread sources, PAHs are present almost everywhere. The biological properties of the majority of these compaunds are as yet unknown. Benzo[a] pyrene (BaP) is the PAH most widely studied, and abundance of information on toxicity and occurrence of PAHs is related to this compaund. Current annual mean concentrations of BaP ina major European urban areas are in the range 1-10ng/m^3. In rural areas, the concentrations are <1ng/m^3.(1)

Epidemiological studies provide sufficient evidence of the role of inhaled PAU (3,4 benzo(a)pyrene) in the induction of lung cancer (WHO). The risk assessment would imply that about 9 per 100.000 exposed people may die from cancer of the respiratory tract as a result of spending a lifetime in ambient air containing an average level of 1 ng BaP per m^3 mixed with all the other PAH and related substances in coke-oven emissions. No specific guideline value can be recommened for PAHs as such in air. These compaunds are typically constituents of complex mixtures. Some PAHs are also potent carcinogenes, which may ineract with number of other compaunds. In addition, PAHs in air are attached to particles, which may also play a role in their carcinogenicity

2. Method and material

Air samples for analysis of BaP in TSP are collected at six monitoring sites within air quality monitoring network which consists of 16 monitoring sites. Measurement location are selected in accordance with Regulation on Imission Limit Values, Imission Measurements Methods, Criteria for Setting up Measurement Points and Record of Data, Official Journal of Republic of Serbia, 1992/54.

Air samples for analysis of BaP in TSP are collected at height of 1,5-2m for period of 24 hours by high volume sampling equipment, approximately of volume 300 m^3 of air. Air is passing through GF/A glass fibre filter Whatman.

Air samples for analysis of BaP in Black Smoke (soot) are collected at 15-een monitoring sites, at height of 1,5-2m for period of 24hours by British standard semiautomatic equipment. Volume of air is approximately 1,5-2m^3 and sampling media is WHATMAN 1 filter paper. Collected samples are prepared in Laboratory following laboratory SOP and quantitavely analysed by gas chromatography GC-MSD.

Period which was taken in consideration for evaluation is from 2004-2006.year.

3. Results and disscusion

For the purpose of this presentation we have taken in consideration and evaluation results from 2004-2006. Obtained results are processed as annual average, minimum value, maximum value, number of measurements exceeding Limit value and percentage of it. Number of measurement for TSP was from N= 27 in 2004. to N= 69 in 2006. Number of measurement for BS was from N=197 in 2004. to N=192 in2006.

Annual average values were over LV of 1. 0ng/m^3 in botth (TSP and BS) except in TSP in 2004. when annual average was 0.28ng/m^3. Maximum values of BaP in TSP during 2005. (16,34ng/m^3) and 2006. (24,27ng/m^3) were registered at the same measurement site in the wider area of the center of Belgrade in the residental zone located at the left bank of river Danube. The reason for such high concentrations is probably great number of individual heatings using solid fossil fuel. Maximum values of BaP in BS during 2004. (7.94ng/m^3), 2005. (11.38ng/m^3) and 2006. (12.78ng/m^3) were registered in the central parts of Belgrade in the streets which are loaded with very frequent and dense traffic. The evidence that traffic is one of the dominant sousrces of BaP in urban environment can be found in literature (1,2). When speaking about Belgrade, there we have several reasons for which beside individual heatings, traffic is considered to be also the source of BaP and they are: very old individual carpark (average is about 14 to 18 years), buses in public transport use diesel, and quality of fuel is very low or of unknown origin. During winter season i.e. heating season monthly concentrations of BaP in black smoke are siginificantly higer, and all maximum values were registerd in december, winter season. Having this in mind it is clear that BS as the fraction of TSP during winter comes from heating sources. Maximum values of BaP in TSP were registered during october and november, which still is not high heating season.

Measurement of BaP in TSP and Black smoke in Belgrade 2004-2006

Statistical tools	2004		2005		2006	
	TSP**	BS#	TSP	BS	TSP	BS
Number of measurement	27	197	41	164	69	192
Annual average	0,28	1,45	3,62	1,54	2,23	1,55
Minimum value	<0,02	<0,02	0,20	<0,02	<0,02	<0,02
Maximum value	0,56	7,94	16,34	11,38	24,27	12,78
Number of measurement >ILV*	∅	137	17	112	27	59
% of measurement >ILV	∅	69,54	41,46	68,29	39,13	30,72

* ILV (immission limit value) for BaP = 1 ng/m^3
** Total suspended matter
\# Black smoke (soot)

4. Conclusion

The significance of BaP in ambient air from the aspect of health importance, and current results, point out the need for further surviellance of BaP in the air on the territory of Belgrade as well as some more activites in identification of emission sources. It would be very useful to investigate the concentrations of BaP in smaller solid fractions in air pollution preferebly in $PM_{2.5}$ which are also very important as respirable particles. Current air pollution in urban environment specially in aglomerations may be considered as "urban aerosol" which has evidence based adverse health effects to human health. Measurement of BaP in solid fractions (TSP, BS, PM_{10} and $PM_{2.5}$) of air pollution should be continued in order to follow the trends and to undertake measures for reducing identified emmissions and sources.

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AIR QUALITY MONITORING AND ABATEMENT STRATEGY PLANNING IN BELGRADE

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In order to take action to improve Belgrade citizens' health, key stakeholders and local policy makers (Secretariat for Environmental Protection, Secretariat for Health, Secretariat for Transport, City Assembly of Belgrade and other relevant actors) are aware of the environmental risks especially children and adolescents face in the environments in which they live.

Air-quality monitoring programs are formed by a group of experts, guided by national legislation, as well as by the above said intention to focus on the issues of health and environment, by making local monitoring program a practical tool for environmental local policy development and target setting, pollution abatements strategies and measures, and for measuring progress in achieving policy targets and effectiveness of abatement measures.

So, based on this premises, City Assembly of Belgrade is adopting Program of Air Quality Control every two years. In the current program, for the years 2006/2007, three main objectives are set:

- Systematic air quality monitoring
- Targeted or on demand measurements
- Following up health effects of air pollution in the population

Focusing on air pollution health effects, especially at children as the most susceptible part of the population referring to environmental health effects, major attention is paid to particulate matter (PM10 and especially PM2.5) and ground-level ozone. Air pollution by fine particles represents the highest risk to the public health in the UNECE region. The health risk due to air pollution by fine particles is higher than of the other pollutants. The loss of lives due to current levels of air pollution by fine particles is assessed as comparable to the loss of lives due to car accidents. Concerning health impacts, currently in the EU there is a loss in statistical life expectancy of over 8 months due to PM in air, equivalent to 3.6 million life years lost annually.

However, existing data indicate high hazardous environmental exposures and health effects in children, indicating that environmental health risks to children and adolescents are still present. They include the following:

- Air pollution caused by SO_2, CO, NOx, soot, dispersed particles, organic compounds, ozone, PM 10
- Summer and winter smog in urban and industrial areas is not rare;
- Almost all children (97.4%) from 13 to 15 years of age are exposed to second hand tobacco smoke in their homes;
- Lead exposure originated from the leaded gasoline, still in use in Serbia;
- Exposure to heavy metals in some industrially polluted areas (Pb, Hg, Cd, As etc.)

In the EU, air pollution is considered one of the main environmental issues (6th action program *"Environment 2010: Our future, our choice"* and subsequent CAFÉ – Clean Air for Europe - program). Recently, The EU Thematic Strategy on air pollution was launched. This strategy focuses on the reduction of exposure by ozone and particulate matter with

special attention paid to PM2.5.

Unfortunately, our legislation on national level is not demanding monitoring of PM 10 or PM2.5. **Being aware of the above said facts, Belgrade monitoring program made a step forward, and now, at 6 measuring points, automatic stations are installed which monitor the concentrations of the most important pollutants, including PM10 and ground-level ozone.**

The basic rule for air-quality assessment and management policy is: **"What is regulated, must be monitored – what is monitored, can only be regulated effectively".**

Limited resources at the national level are the main obstacle to start up and develop strategic activities in abatement strategy, but, on local Belgrade level our abatement measures consist of several main points:

- Operation of air-quality information system (emission inventories and projections, air quality monitoring, reporting)
- Campaigns on raising public awareness
- Permitting (including environmental impact assessment (EIA) and strategic environmental assessment (SEA)
- Issuing state of the environment reports (monthly and yearly)
- Optimization of standards for health reporting, accounting for environmental and combined health impacts (based on WHO criteria), with introducing set of environmental health and air quality indicators
- Introduction of standards for products that directly affect the environment in the course of their use (road vehicles in public transport, fuels, etc.),
- Implementation of Best Available Techniques and best practices
- Organizational measure in public and road traffic

Our aim is that our Air quality monitoring system should become integrated part of national and international air quality assessment and management systems, completed with the currently missing parts as integration poor air quality monitoring data with emissions inventories and modeling. The whole system should fit DPSIR (driving force, pressure, state, impact, response) framework. When our national standards achieve harmonization with international standards and guidelines, introducing the above said measures and setting local policies will be much easier.

AIR QUALITY MANAGEMENT IN SERBIA : CURRENT STATUS AND PROSPECTIVES

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The atmosphere is usually contaminated by various gas, liquid or solid pollutants. Human exposure to air pollutants may cause a variety of health effects, depending on the type of pollutant, the magnitude, duration and frequency of exposure and toxicity of any specific pollutant. Excessive exposure to air pollutants may cause a wide range of disorders in children and adults, leading to their disability and a significant reduction in life expectancy (WHO, 2005). Besides human population, polluted air may also have adverse effect on all other organisms sharing the ecosystems (EEA, 2003). The most prominent air pollutants include: sulfur dioxide, nitrogen oxides, tropospheric ozone, suspended particles, persistent organic pollutants and allergenic pollen.

Natural sources of air pollution include gaseous emissions from trees, animals and lightning, and gaseous and particulate emissions from volcanic eruptions, soil erosion, wind-blown dust and forest fires. *Anthropogenic* sources of air pollution involve combustion of fossil fuels (thermo power plants, motor vehicles, communal and household heating installations), mining operations (sources of fugitive dust emissions), manufacturing processes (metallurgical plants, chemical plants, oil refineries), agricultural activities (crop spraying, crop-residue burning), etc.

The main sources of air pollution in Serbia include the energy sector (thermo power plants), district heating plants, oil refineries, chemical industry, fossil fuel combustion in households, industry, individual heating boiler plants, traffic, construction industry, waste dumpsites etc. (Government of the republic of Serbia, 2007, SEPA, 2007).

The lignite used as a fuel for thermo power plants in Obrenovac, Lazarevac and Kostolac has low calorific value, high moisture content and its combustion produces high quantities of fly ash, sulfur dioxide and nitrogen oxides. These thermo-power plants are equipped with electrostatic precipitators, but desulfurisation and denoxification facilities are not installed. Important sources of air pollution are oil refineries in Pančevo and Novi Sad, the cement factories in Popovac, Kosjerić and Beočin, as well as chemical plants and metallurgical complexes in Pančevo, Kruševac, Šabac, Smederevo and Bor.

Air pollution attributable to traffic is increasing, especially in major towns, because the old vehicle fleet still uses leaded and low-quality fuels.

During the 90's, a general crisis in economy and public sector affected air quality. Outdated technology and lack of pollution abatement installations and low energy efficiency of industrial facilities are main causes of air pollution in Serbia. Moreover, industrial complexes in Pančevo, Novi Sad, Bor, Niš, Belgrade were heavily bombarded during the 1999 NATO air attacks on Serbia.

In order to improve environmental condition in Serbia, the Serbian Government

proposed and Parliament adopted the new legal framework for environmental protection in 2004. The new laws (the Law on Environmental Protection, the Law on Strategic Environmental Assessment, the Law on Environmental Impact Assessment, and the Law on Integrated Prevention and Pollution Control) are harmonised with the EU Directives on Environmental Impact Assessment (85/337/EEC), Strategic Impact Assessment (2001/43/EC), IPPC (96/61/EC) and Public Participation (2003/35/EC). The Ministry of Science and Environmental Protection Directorate for Environmental Protection (DEP) has the key responsibility in environmental protection.

Reliable information on impacts of the socio-economic growth on environment, ecosystems and, consequently, on public health is essential for framing and implementing sound and effective environmental policy measures and legislation. Therefore, the Serbian Government established in 2004 the Environmental Protection Agency, within the Ministry of Science and Environmental Protection. Cooperating with relevant Serbian authorities, Universities and Scientific Institutions, Serbian Environmental Protection Agency (SEPA) permanently upgrades the national data bank with information on all environmental components (including air quality) in Serbia. The Agency uses the central data bank to publish periodic reports on the environment in Serbia. Reports are directed to decision makers (Republic Government and Republic Parliament), to international institutions, first of all to the European Environment Agency (EEA) and to the widest spectrum of public clients. Reports that are directed to Republic Government represent a valuable tool for developing, adopting, implementing and evaluating environmental policy. Since 2004, SEPA started to cooperate with EIONET (European Information and Observation NETwork), a partnership network of the EEA in order to fulfill reporting obligations that countries have towards international organisations. Contribution of Serbia in development of pan-European environmental data bank was symbolic in 2004. However, in 2006 Serbia achieved significant progress in cooperation with EIONET and EEA.

Law on Environmental Protection predicted several types of economic instruments within financing and fulfillment of the environmental protection objectives: charges for utilization of natural resources, charges for environmental pollution, budget resources and international financial aid, fund for environmental protection and economic incentives. Fund for Environmental Protection was registered in 2005. The Fund's financial means are mainly based on the budget earmarked funds, income from the charges for utilization of wild flora and fauna, charges for motor vehicles, charges for the import of the materials which deplete ozone layer, charges for gases emission and for produced and disposed waste.

Continuous measuring of different parameters enables monitoring of actual air quality in real time. An initial network of automatic monitoring stations in Serbia covers Belgrade, Pančevo, Smederevo, Bor and Zrenjanin. This network will be upgraded by 24 additional urban, suburban and rural monitoring stations.

In this article we reviewed current state and trends of air quality variability in Serbia, and described legal and economic instruments that enable improvement of air quality.

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THE URBAN AIR QUALITY FORECAST SYSTEM FOR NORWAY

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1. Introduction

For the past 6 years the Norwegian Institute for Air Research, the Norwegian Meteorological Institute and the Norwegian Public Road Administration have been producing air quality forecasts for a number of Norwegian cities. An operational Urban Air Quality Information and Forecasting System (UAQIFS) has been developed, the system is shown in Figure 1. Today this UAQIFS is applied in six Norwegian cities including Oslo, Bergen, Trondheim Drammen, Stavanger, and Grenland during the winter season (The "Better City Air" project).

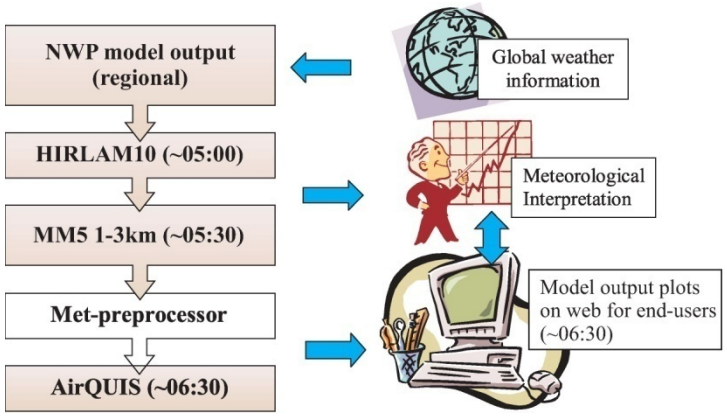

Figure 1. The operational Urban Air Quality Information and Forecasting System (UAQIFS).

2. Background

High levels of PM10, PM2.5, and NO2 occur every winter in Norwegian cities during temperature inversions and weak winds. High levels of PM10 also occur during dry weather conditions, in particular during spring conditions when particulate matter accumulated along the roads due to traffic and usage of studded tires is released. These pollutants may cause health effects to people, especially to asthmatics, allergy sufferers and those who live close to hotspots. Local authorities require a forecast system to help deal with these public health issues.

3. Results

In Figure 2 the forecast for PM10 daily average is shown for a dry January day in the city of Oslo. A comparison between the forecast and measured values of particulates at a measurement station Løren in Oslo for a period during the winter of 2005 is shown in Figure 3.

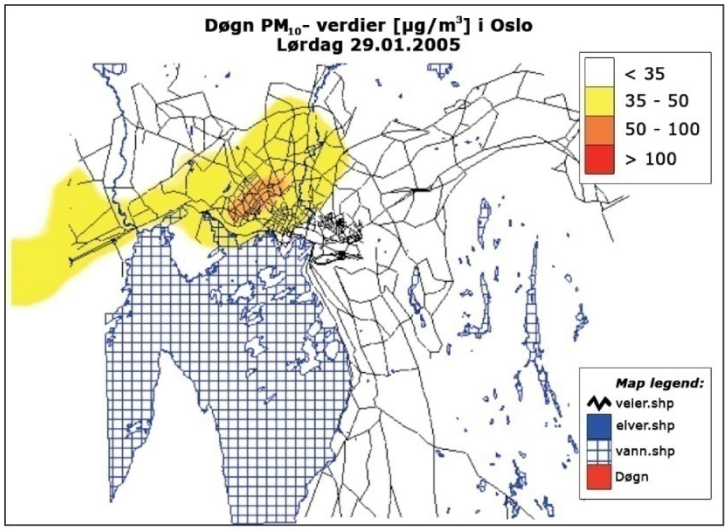

Figure 2. PM_{10} daily averages in Oslo January 29 2005.

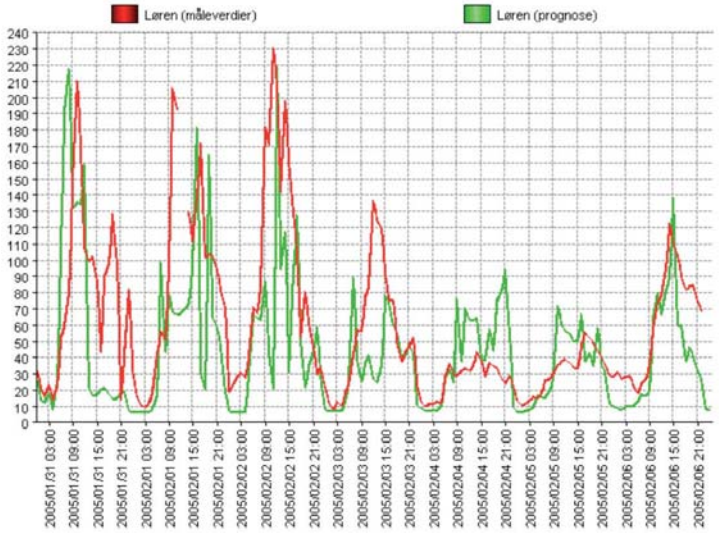

Figure 3. PM_{10} 31 January – 6 February 2005.

4. Forecast index for the public

Each day the results from UAQIFS are published on password protected web pages. The results of the forecasts are split into 4 different classes described as 'little', 'some', 'high' and 'very high' pollution. Each city forecast is based on concentration levels and how many people who are exposed to this concentration. The local authorities use this information to give their recommendations to the public. This index is made publicly available through www.luftkvalitet.info is displayed for the coming day for every 4 hours, Figure 4. The recommendations for the population are also published in local newspapers. A service has also been developed for the distribution of the forecast via SMS. In addition to the forecast information, monitoring data from all stations for up to 30 days can be accessed and viewed. The forecasts are used for health warnings and may be used to plan immediate measures, such as reduction of speed limits, when episodes are predicted.

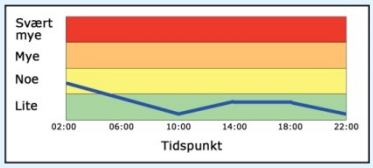

Figure 4. Example of the 24 hour forecast displayed on the public web page for Oslo from 5 February 2005. Forecasts are only available in Norwegian.

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AMBIENT PM10 AND PM2.5 MEASUREMENTS IN DAKAR, SENEGAL

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1. Introduction

The Norwegian Institute for Air Research (NILU) is assisting the Senegalese authorities in establishing an Air Quality Management Centre. As part of the present project, a comprehensive measurement campaign of air pollution were conducted between October 2005 and January 2006 in order to collect background information for designing a permanent air quality monitoring programme.

2. Methodology

As a part of the screening study, PM_{10} and $PM_{2,5}$ were monitored in one heavily trafficated street. The instrument used for daily monitoring PM_{10} and $PM_{2.5}$ was a sequential gravimetric sampler, of type SEQ47/50. The filters are weighed before and after exposure and the concentrations of PM_{10} and $PM_{2.5}$ were determined by NILU. Some samples of PM_{10} and $PM_{2.5}$ were analysed for trace elements, EC/OC and water-soluble components to provide knowledge on the chemical composition of the particulate matter.

3. Results and Discussion

The daily concentrations of PM_{10} exceed the daily EU limit value [1] every day of the sampling period. The PM_{10} values range from 52 to 338 $\mu g/m^{3,}$ with an average value of 133 $\mu g/m^3$. The $PM_{2.5}$ levels in Dakar were also high compared to concentration levels observed in other urban areas in the world [2]. The average $PM_{2.5}$ concentration in the 4 weeks sampling period was 38 $\mu g/m^3$.

The analysis of trace elements identified no exceedances of EU limit and target values [1;3] and WHO guideline values. The elemental carbon/total carbon (EC/TC) ratios indicate that the fine particles in Dakar originate mainly from combustion sources. The average percentage of water-soluble components was 18% for PM_{10} and 15% for $PM_{2.5}$.

4. Conclusions

The measured daily averages of PM_{10} concentration were 2 to 7 times higher than the EU limit values and the daily averages of $PM_{2,5}$ were also high. A large fraction of the $PM_{2.5}$ originates from combustion sources, while a large part of the PM_{10} coarse fraction is soil dust and sea salts. This screening study shows that the major air pollution source in Dakar is traffic, although industry is also an important source in some areas.

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BONDARY LAYER AEROSOL SIZE DISTRIBUTION DATA FROM BIRKENES, NORWAY

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1. Introduction

The Birkenes location (58º 23'N, 8º 15'E) has been part of NILU's nation-wide samplingnet since 1973 and is situated in an area with limited industrial activity and low population density, separated from densely populated and industrialized areas of Europe by the North Sea and Skagerak. Airborne concentrations reaching Birkenes are largely due to long-range transport of air masses from areas 500 – 1000 km away. Thus, as demonstrated by Amundsen et al. (1992), Birkenes is well suited to monitor longrange atmospheric pollution from continental Europe. Van Dingenen et al. (2004) categorized Birkenes as a natural background station in their network of 31 European sites. The station is operated mainly for the Norwegian Pollution Control Authority (SFT), but it also serves as part of the Norwegian contribution to the EMEP network. The size distribution of aerosols is an important parameter that impacts the transport and deposition properties of particles in the atmosphere, their optical properties, and their ability to act as cloud condensation nuclei. Detailed information on particle size distribution can provide valuable information for the validation of air pollution models (EMEP (2003)), for source attribution, and for understanding the formation, transport and deposition of particles in the atmosphere (Tunved et al (2003)).

2. Methods

Particle size distributions (20-630 nm) are measured using a Differential Mobility Particle Sizer (DMPS). The differential mobility analyzer (DMA) is of the Hauke-type with an inner electrode length of 22 cm. A condensation particle counter model TSI3010 is used to count particles downstream the DMA, respectively. Raw mobility distributions were recorded in stepping mode, leading to a time resolution of the measurement of 2 min. Sheath air is provided using a membrane pump in a closed loop set up, where the flow is controlled using a critical orifice. Ambient aerosol was sampled at a flow rate of ca 1 l min-1 through a ca 3 m stainless steel tubing with a ¼ inch outer diameter and rain cover on the top. The inlet height is ca. 2 m above the ground. No dryer was used.

3. Results

The integrated total number concentrations were at the maximum in the late spring and summer and at a minimum in the winter months and the variations are higher in the winter months than in the summer months. In figure 1 the median (small square boxes) are at a higher value than the mean value, due to high peak number concentrations all through the three years of data.

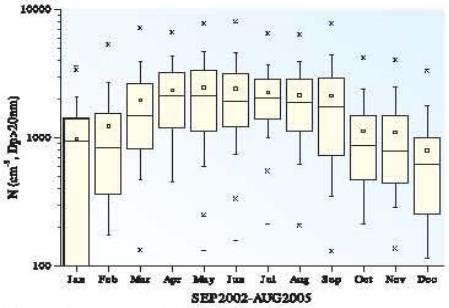

Figure 1: Integrated total number concentrations on monthly basis at Birkenes in the period between September 2002 and August 2005.

The individual size distributions observed at Birkenes were clustered according to shape and number concentrations using kmeans function provided in Matlab. 8 clusters where chosen to capture the different stages of the aerosol lifecycle. 8 clusters proved sufficient to capture aerosol properties likely connectable to typical processes affecting the atmospheric aerosol. The clusters are displayed as cluster 1 – 8 in figure 2. The fraction number of size distributions contribution to each cluster is given at the right of each frame. The clustering resulted in average size distribution properties indicating recent particle formation (i.e. homogenous nucleation (1, 7, 8)) intermediate aged properties (i.e. growing aitken mode, 2 & 3) and two different types of aged aerosols; either aging under influence of clouds and precipitation and aging under the influence of condensation and coagulation only (4 & 6 and 5, respectively).

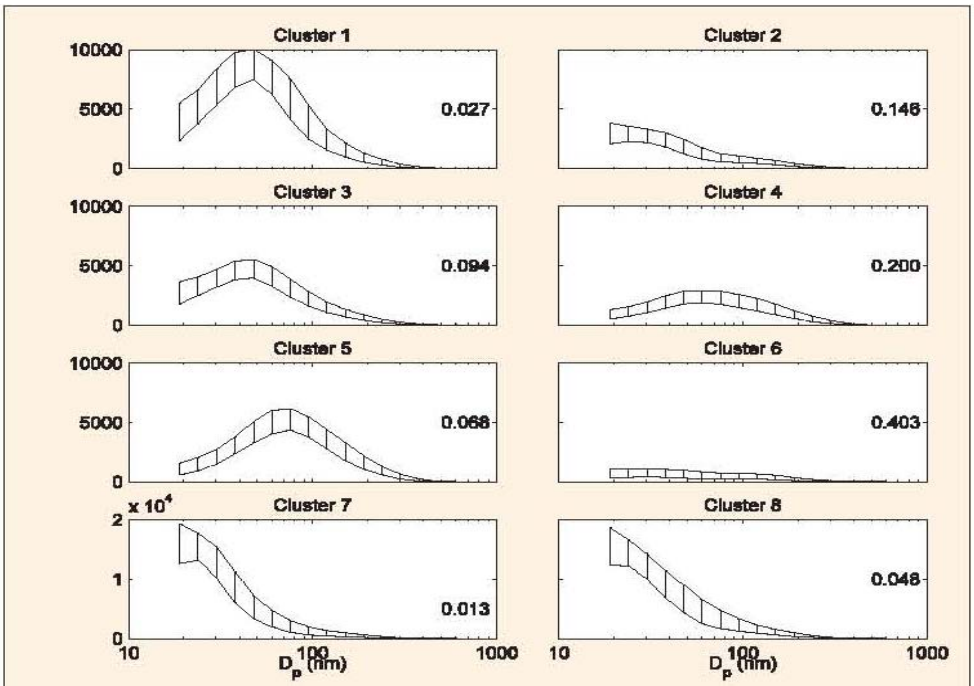

Figure 2: Number size distribution clusters. Fraction number of size distribution contributing to each cluster is given in the figure.

Table 1: Type of particle formation and frequency of occurrence associated with each cluster.

Particle properties	Clusters	Frequency of occurrence (%)
Recent formation (i.e. homogenous nucleation)	Cluster 1 Cluster 7 Cluster 8	2,7 1,3 4,8
Intermediate aged (i.e. growing Aitken mode)	Cluster 2 Cluster 3	14,6 9,4
Aged (i.e. accumulation mode)	Cluster 4 Cluster 6 Cluster 5	20 40,3 6,8

Table 1 shows that almost 70% of the size distributions properties belong to clusters indicating aged or aging aerosols, 25% to clusters indicating intermediate aged aerosols and around 9% that indicating recent particle formation.

The seasonal contribution to each cluster was investigated. Increased global radiation during the summer months increases the photochemical reactions. During fall and winter

the wet deposition rate increases due to more frequent precipitations.

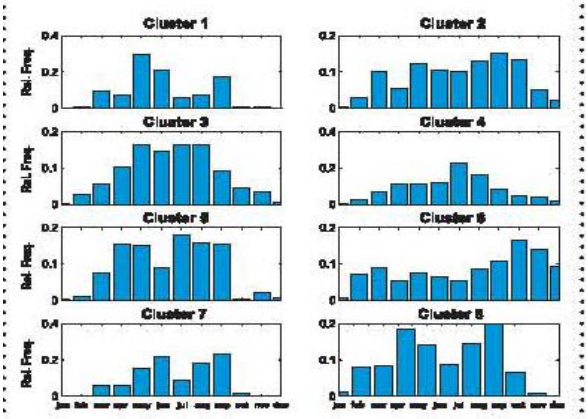

Figure 3: The relative frequency of observations per month for each of of the initial clusters

Cluster 1 and 7 lacks size distributions in the DJF (Dec, Jan, Feb) period, due to lesser nucleation during this period. Cluster 4 and 6 has their contributions spread over the whole year. Cluster 6 (the clearly bimodal distribution) is more well represented during DJF and SON. This is probable due to more frequent precipitation combined with lesser particle formation.

Figure 4 represent the frequency of in cloud events along transport. This is defined as occasions with RH>94%. It is thus clear that bimodal size distribution in cluster 6 is more frequently processed by clouds compared to other cases.

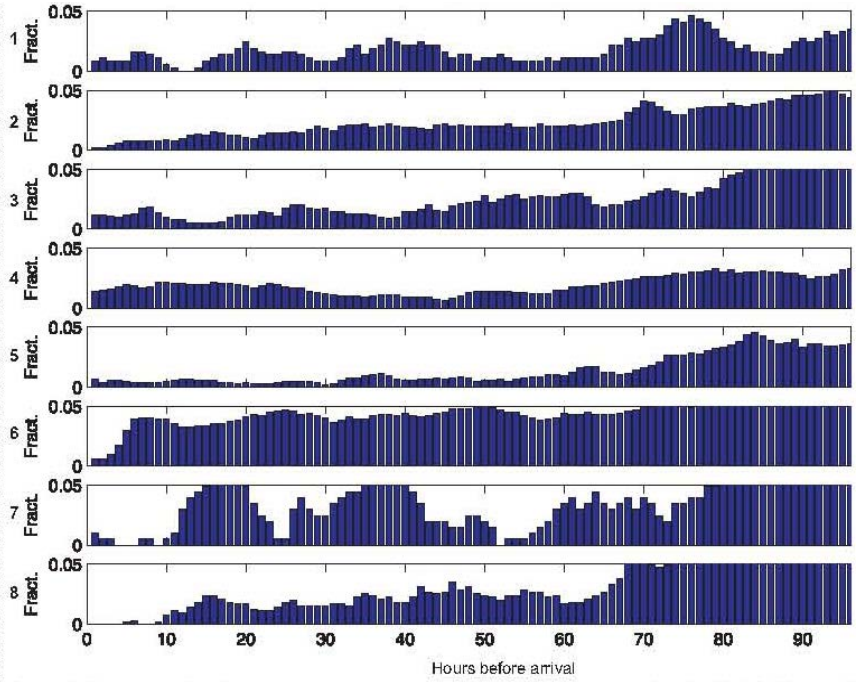

Figure 4: Frequency of in-clouds occasions as derived from the RH>94% profiles from the HYSPLIT4 model, hours before arrival. Corresponding from cluster 1 to 8, from above.

4. Conclusions

Particle size distribution measurements performed at Birkenes, Norway has been investigated during a three-year period between September 2002 and August 2005. The basic behavior of the aerosol number size distribution in terms of seasonal and diurnal variations are similar to what is reported from other Nordic background stations (Aspvreten, Hyytiälä, Värriö, Pallas and Vavihill). The integrated total number concentrations were at the maximum in the late spring and summer and at a minimum in the winter months. Almost 70 % of the size distributions properties belong to clusters indicating aged or aging aerosols, 25% to clusters indicating intermediate aged aerosols and around 9 % that indicating recent particle formation. Recent particle formations (i.e. homogenous nucleation) are almost not observed from December to February, due to lesser nucleation during this period. While aged aerosols are more well represented during September to February.

5. Acknowledgements

The Research Council of Norway provided funding for this work.

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COMPARATIVE STUDY OF VALUES OF TSP AND SOOT SAMPLED SIMULTANEOUSLY IN TOWN OF KOSJERIC

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1. Introduction

Kosjeric is town in western Serbia. There is cement factory „Titan“ in vicinity of the town. Public health institute Uzice is performing air pollution monitoring of several common air polutants- soot and total suspended particles among those since october 2006.

Aim of this study is comparation between values of soot and TSP sampled at same site and same time.

2. Experiment

Sampling of soot was performing by low volume air sampler with Whatman 1 filter paper. Sampling of TSP was performing by high volume air sampler Tecora Eco Puf with Whatman GF/A glass fiber filter.

Both pollutant sampled at the same site and 24 hours period simoultaneosly each days of this study, according Regulation : Pravilnik o GVI.. SlGl RS 54/92.

There is two sampling sites: VODOVOD (village) 600 m distant from point source cement factory „Titan“ and OPSTINA (center of town)2000m distant from same point source.

At site VODOVOD 14 samples taked, both soot and TSP samples.

Sampling period:october 10.2006. till march 22.2007.

At site OPSTINA 24 pair of samples of soot and TSP taked.

Sampling period:october 12.2006. till march 26.2007.

3. Results and Discussion

Site VODOVOD

Air level of soot: I_{soot} having values ranging from 2 to 13 μg/m^3.

I_{TSP} values ranging from 2 to 118 μg/m^3 .

Air quality index for soot AQI_{soot} is good (0-50) all of those days.

AQI_{TSP} :moderate(51-100) 6 days, good (0-50) 8 days

Between I_{soot} and I_{TSP} Correlation Coeff= -0.020577 .Statistic indicates that the model I_{soot} =f(I_{TSP}) explains 0.042% of the variability in I_{TSP}. P-value=0.9443. Since the P-value is greater or equal to 0.10, there is not a statistically significant relationship between I_{TSP} and I_{soot} at the 90% or higher confidence level.

At site OPSTINA

Air level of soot: I_{soot} having values ranging from 3 to 71 μg/m^3 and TSP (I_{TSP})values ranging from 10 to 232 μg/m^3

Air quality index for soot AQI_{soot} is „good“ (0-50)-9days; „moderate“ (51-100) 11 days; „unhealthy for sensitive groups“(101-150) 4 days.

AQI_{TSP} is „good“ (0-50)-4days; „moderate“ (51-100) 10 days; „unhealthy for sensitive groups“(101-150) 8 days and „unhealthy“(151-200) 2 days.

Table1. Table captions should be placed above the table

Site Vodovod					Site Opstina				
date	**I_{soot} [µg/m^3]**	**I_{TSP} [µg/m^3]**	**AQI_{soot}**	**AQI_{TSP}**	**date**	**I_{soot} [µg/m^3]**	**I_{TSP} [µg/m^3]**	**AQI_{soot}**	**AQI_{TSP}**
10-Oct-06	2	58	4	48	12-Oct-06	23	57	46	47
11-Oct-06	3	53	6	44	13.Oct≡16.Oct	29	64	58	54
25-Oct-06	4	67	8	56	17-Oct-06	19	10	38	8
26-Oct-06	9	56	18	47	18-Oct-06	33	80	66	67
17-Nov≡20Nov	10	79	20	66	22-Oct-06	41	74	82	62
20-Nov-06	3	87	6	72	23-Oct-06	18	79	36	66
21-Nov-06	13	94	26	78	24-Oct-06	17	99	34	82
26-Dec-06	4	118	8	99	23-Nov-06	32	101	64	84
15-Jan-07	8	83	16	69	24-Nov-06	53	155	**106**	**129**
18-Jan-07	2	36	4	30	28-Nov-06	48	162	96	**135**
8-Feb-07	6	22	12	18	29-Nov-06	37	143	74	**119**
20-Feb-07	12	2	24	1	1-Dec-06	52	123	**104**	**103**
19-Mar-07	4	56	8	47	4-Dec-06	48	218	96	**182**
22-Mar-07	5	15	10	12	5-Dec-06	39	129	78	**107**
					6-Dec-06	21	232	42	**193**
					7-Dec-06	71	197	**142**	**164**
					9-Jan-07	57	166	**114**	**138**
					21-Jan-07	32	112	64	94
					24-Jan-07	3	49	6	41
					5-Feb-07	38	96	76	80
					28-Feb-07	34	111	68	93
					1-Mar-07	19	73	38	61
					13-Mar-07	23	85	46	71
					26-Mar-07	5	56	10	46

Between I_{soot} and I_{TSP} Correlation Coeff= 0.639893. The R-Squared statistic indicates that the model as fitted I_{soot} =f(I_{TSP}) explains 40.95% of the variability in I_{TSP}. P-value=0.0008nce the P-value in the ANOVA table is less than 0.01, there is a statistically significant relationship between I_{TSP} and I_{soot} at the99% confidence level.

4. Conclusion

At site Vodovod AQI_{soot} vs AQI_{TSP}: 6 days AQI values was qualitatively diferent. Every time AQI_{TSP} showed worse air quality.

At Opstina site 12 days had qualitatively the same AQI for soot and TSP. In other 12 times AQI_{TSP} showed worse air quality.

This means that TSP parameter is more sesitivity then soot parameter for AQI purpose.

The fact that there is not correlation between values of TSP and soot at VODOVOD site means that those two polutants came from different source. TSP probably from cement factory, and soot from houses chimney nearby. Significant correlation between TSP and soot at OPSTINA means that both parameters came from same sources mostly: public heating plant,houses chimney and traffic.

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SEASONAL DISTRIBUTIONS AND FREQUENCY OF PM_{10} EXCEEDING

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1. Introduction

Particulate matter (PM) is an air pollutant and it is considered as a part of total air pollution.

Special attention is dedicated to this pollutant. EU directive for fraction of particulate matter, PM_{10}, is Directive 1999/30/EC. According to this Directive daily limit value is 50 $\mu g/m^3$, and annual acceptable number of daily exceedances is 35. Annual limit value is 40 $\mu g/m^3$. After 2020., according to Directive, annual limit value will be 20 $\mu g/m^3$, daily limit will not change but annual acceptable number of daily exceedances will reduce from 35 on 7 cases durig year. In EEA Core Set of Indicators (CSI 004 - Exceedance of air quality limit values in urban areas) daily limit PM_{10} concentration is also 50 $\mu g/m^3$, [1].

Continuous measurement of PM_{10} exist in Serbia. It started in Belgrade, and then established in several industrial centers. Expansion of automatic PM_{10} monitoring on whole Serbia is expecting when National automatic air quality system will establish.

The aim of this work is consideration of seasonal distribution of concentrations and exceedins of PM_{10}. Started hypothesis for their existence are, besides characteristics of particulate sources (primary and secundary), significant effect of meteorological conditions on PM_{10} concentrations in urban areas.

2. Data and Technique

Continuous PM_{10} data for location Boulevard D. Stefan in Belgrade were analized. (former 29th November street), [2]. Method of instrument's monitor is Beta radiometer with flux of 1 m^3/h.

Data from the period 2004-2006 were processing. Daily mean PM_{10} concentrations are from [3]. Seasonal periods are defined like in climatological practise, for example winter – December, January and February.

3. Results

Results are presented in Table 1. and graphic in Figure 1. Results show significant seasonal variation of PM_{10} concentration. High concentrations of PM_{10} the most frequently occur during winter and autumn. Winter concentrations are in 48% cases higher of EU limit, 50 $\mu g\ m^{-3}$, and during autumn in 44% cases. Exceeded concentrations of EU limit are lower in summer and sprig, in 21 % and 23 % cases. Average concentrations in summer and sprig are comparable but coefficient of daily variations has minimum in summer.

Table 1. Seasonal and annual statistics with probability of daily PM_{10} concentrations exceeding 50 µg/m^3 , Belgrade 2004 – 2006.

parametar	SPRING	SUMMER	AUTUMN	WINTER	Y E A R
Mean, µg/m^3	39.2	39.8	55.1	65.0	50.0
Variation coef., %	22.0	35.6	63.5	83.5	74.4
Min, µg/m^3	56.1	13.4	8.9	8.4	8.4
Max, µg/m^3	138.8	82.7	267.0	420.9	420.9
Probability of exceedance 50 µg/m^3, %	22.9	21.2	44.2	48.4	34.3

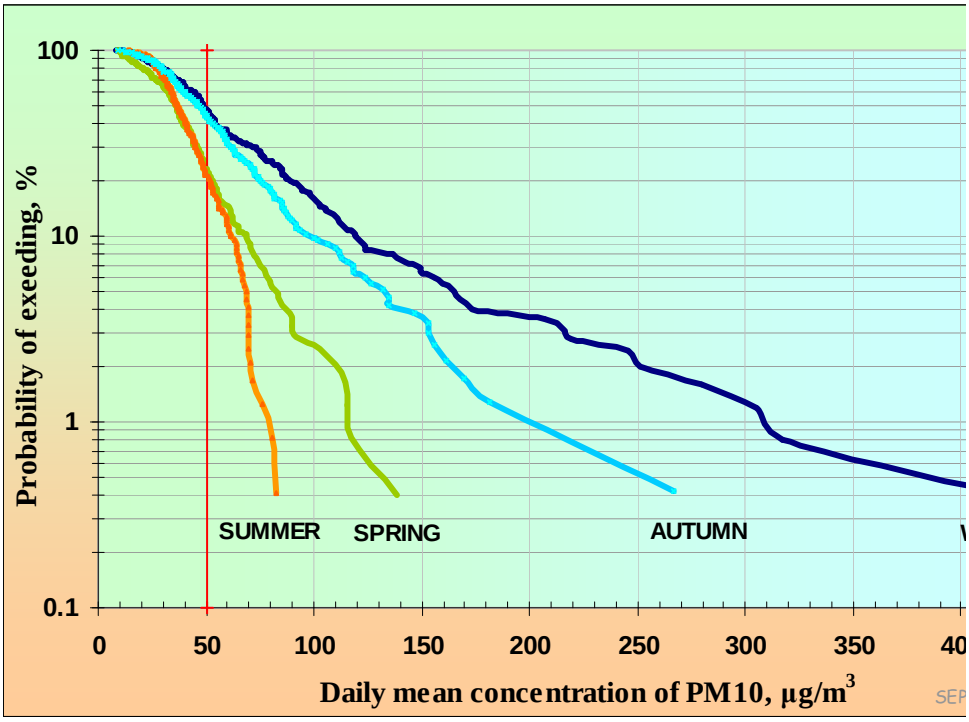

Figure 1. Seasonal distributions of daily PM_{10} concentration, Belgrade 2004-2006.

4. Conclusion

Analysis of daily mean PM_{10} concentration on location Boulevard D. Stefan in Belgrade in the period 2004-2006, indicate on significant seasonal distributions. Frequaency of EU exceedances of daily limit value has maximum in winter and minimum in summer.

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BELGRADE PARTICULATE MATTER DISTRIBUTION FROM BLACK SMOKE DATA

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Many cities have a problem with particulate matter pollution. Very often it is of anthropogenic origin, but a sizable proportion of it may be natural. Belgrade has only one regular PM10 monitoring point, so it is impossible to make any estimates on the distribution of particulate matter across the city based on just this point. However, black smoke (BS) data are known to be related to PM10 concentrations [1, 2], and they are in much better supply across this area.

We have investigated available BS data from all 20 monitoring stations that make up two monitoring networks in Belgrade, and concluded that 17 of them produce reliable results. The results of BS concentrations for years 2003-2006 are summarized in Figs. 1a and 1b. Both the winter and the summer plots of BS (Fig. 1a and 1b, respectively) show a clear "island" of "clean" air around the monitoring station KS, which is expected, as it is an elevated urban background point with lots of green areas. Generally speaking, high BS concentrations seem to be confined to lower parts of the city, where particulate matter naturally accumulates. That indicates natural and traffic as the main sources of this pollution. High summer BS concentrations to the north from the main city area also indicate a strong natural source of this parameter - natural dust, which is quite present in the north, towards the Pannonian Plain. In winter, there is an "island" of high BS pollution around the city centre, where most of the individual and poorly filtered heating sources are situated (Fig. 5a). In that period, district heating plants in the western parts of the area apparently add the seasonal contribution as well [3].

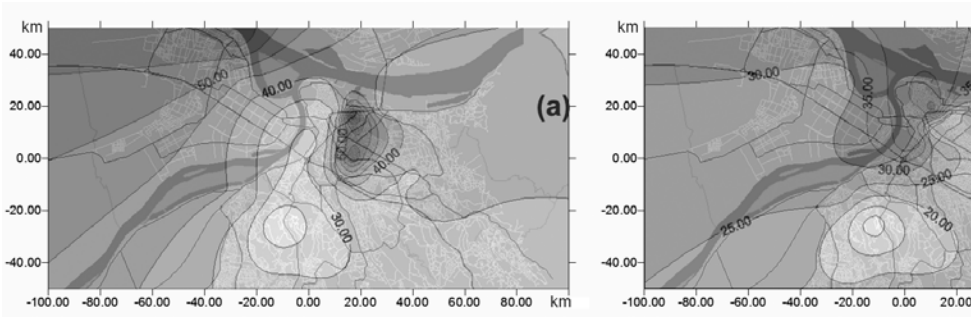

Figure 1. Spatial distribution of BS in (a) winter and (b) summer. Based on the measurements of 17 stations, the iso-concentration lines are indicated in μg/m^3.

The situation is somewhat unusual at the only station in the city centre that presently monitors PM10 (but also BS, simultaneously). At this point e.g. the BS exceedence percentage is not significantly different in the two seasons, and even higher during the non-heating season. This is an indication that at this particular spot the dominant source of BS is traffic. Unlike BS, PM10 values show a great difference between the seasons, such that heating adds a significant contribution to the overall concentration of PM10 particles. Some studies have shown that mineral based particles (diameter around 50 μm) originate either from the combustion processes (e.g. lead compounds from gasoline engines) or from brake and clutch lining wear [4]. These larger particles than 10 μm can appear in the material measured as BS, but not in the filtered PM10 material. PM10 particles mostly originate from various stationary combustion processes, transport, wind erosion, and resuspended road dust [5]. The results in Fig. 2 show that at this location the dominant source of PM10 in winter is stationary combustion (heating). This means that PM10 is here a better indicator of combustion processes than BS itself, which actually better reflects traffic activity.

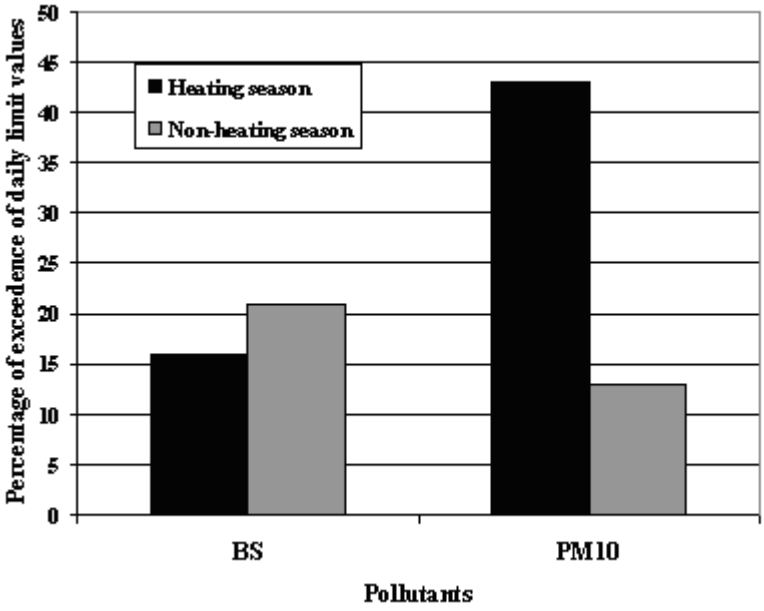

Figure 2. Exceedence of daily limit values for BS and PM10 in 2005 during heating and non-heating season at the BDS station (central).

At the moment, there is only one PM10 monitoring point, in the centre of the city. More such points are planned in the near future, and should help elucidate the sources of

Belgrade particulate matter.

Acknowledgements. This work was supported by the Ministry of Science and Environment, Republic of Serbia, project no 142065.

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INFLUENCE OF LEAD IN SUSPENDED PARTICLES ON BLOOD LEAD LEVELS OF CHILDREN LIVING IN THE VICINITY OF A SECONDARY LEAD SMELTER

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1. Introduction

Lead is an environmental contaminant that is ubuquitously found and as such is of worldwide public health concern (1,2). The adverse chronic health effects of low doses of lead include disruptions of haematological and both peripheral and central neurological functions. For several reasons, children represent the population at highest risk. Results of surveys on biological monitoring of blood lead concentrations in children in various countries have been published. Additionally, relevant investigations in children living close to a point-source have been carried out(3,4). Little is known about lead exposure and its associated health risks in Serbia, which is of particular concern in areas adjacent to known point sources of lead emissions. Therefore, a study was conducted of both lead air pollution and blood lead concentrations in children living around a battery reclamation plant.

2. Experiment

The village of Zajaca is situated in western Serbia, with a population of barely 2000 inhabitants, some 140 kilometers from the capital of Serbia, Belgrade, and comprises solely of a metallurgy industrial complex, surrounded with residential homes of the employees and their families. Village is located in a narrow valley, along the banks of the river Jadar.

The survey was conducted from June 1998 to March 1999. A total of 146 children aged 1 to 13 years were examined, and divided in 3 groups according to the level of environmental exposure by living in Zajaca, or the control site Lipnicki Sor, some 20 km away. The other criterion was paternal occupational exposure. Of the total 146, there were 72 exposed children (living in Zajaca), 37 partly exposed (not living in Zajaca, with paternal occupational exposure), and 37 non-exposed (control, living in Lipnicki Sor). Air samples were taken on previously determined sites, according to the distance of the homes and only school from the point source of lead emission (4 in Zajaca, and 1 in Lipnicki Sor). Samples were collected and sent to the Ecotoxicologycal laboratory of the Institute of Public Health of Serbia «Dr Milan Jovanovic Batut» to be analyzed on lead content with atomic absorption spectrometry (AAS) method. Blood samples were collected by the finger prick, and samples treated at -20°C, and lead measurements carried out with AAS method within one week.

3. Results

Figure 1 shows maximum monthly values of Pb in suspended particles, both in Zajaca and Lipnicki Sor ($\mu g/m^3$). As calculated, values of lead were significantly higher in samples taken in Zajaca, close to the smelter than in Lipnicki Sor. Table 1 shows blood lead

concentrations in the subgroups investigated. They were significantly higher (F=51,936, df =2, p<0,001) in children residing close to the battery reclamation plant (<1 km) than in those living on the further location of Lipnicki Sor. Blood lead concentration (µg/dl) of exposed children were related with the values of Pb in suspended particles (µg/m^3), and presented as correlation for both summer and winter periods. Analyzing the correlation between above mentioned values, log.trendline shows that any rise of Pb in suspended particles(µg/m^3) in Zajaca is followed with an increase of blood lead concentrations in exposed children, in both seasons, with the correlation quotient $R^2 = 0.4502$ in summer, and $R^2 = 0.5466$ in winter measurements.

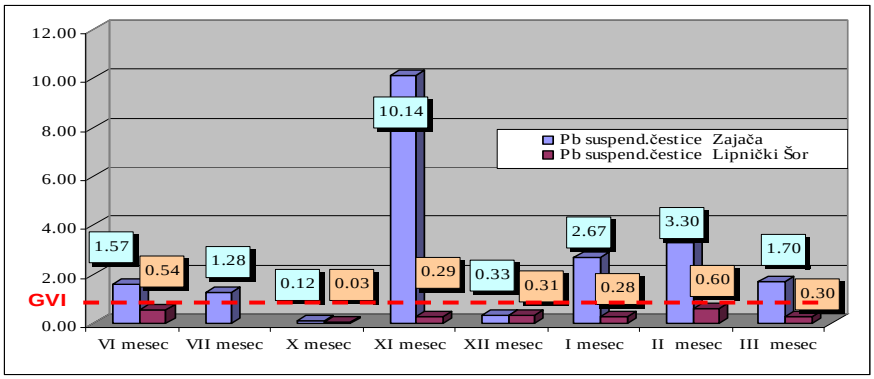

Figure 1: Maximum monthly values of Pb in suspended particles (µg/m^3)

Table 1: Blood lead in the subgroups of investigated children (µg/dl)

Pb µg/dl	N	Mean Values	SD	95% Confidence Interval		Min.	Max.
				lowest	highest		
Exposed	72	15.806	5.602	14.489	17.122	3.581	27.552
Partly Exposed	35	9.532	2.928	8.526	10.538	4.244	17.678
Non-exposed	39	7.364	3.089	6.363	8.366	2.174	13.434
Total	146	12.047	5.858	11.089	13.005	2.174	27.552

4. Discussion

The baseline value of blood lead concentration has been reported as being 4 and 6 µg/dl (2), and WHO recommended that 98% of a population should have values below 20 µg/dl and 50% below 10 µg/dl. In this study 84.7% of exposed children had its values above 50%. In a similar study in Mexico this percentage is even higher (92.8%) (4). According to Yankel et al. it is suggested that average monthly values of Pb in suspended particles above 2.0 µg/m^3 contribute significantly to the rise of blood lead levels in children (5).

5. Conclusion

1. Environmental presence of lead is proven in air samples (suspended particles, $\mu g/m^3$), taken in the vicinity of the active smelter (500m), being of higher statistical significance than values from the control site (Lipnicki Sor), some 20 kilometers away from the facility.
2. Value of lead in suspended particles ($\mu g/m^3$) sampled in Zajaca are correlated with blood lead concentrations (μg/dl) in exposed children living in the factory's neighbourhood, with high statistical significance.

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EXAMINATION OF AIR QUALITY AT MEASUREMENT SITE NEAR ELEMENTARY SCHOOL „ JEFIMIJA“ (RAJKOVAC, OBRENOVAC)

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Air is a complex physical and chemical system, with many processes due to the presence of pollutants[1,2,3]. The pollution of urban air is familiar to any city dweller. It can often be seen and smelled. These processes have a huge influence on the pollutants and health. That is why it is very important to spot these processes and pollutants in air, which very often change their primary form and participate in different chemical reactions[2,3,4].

The biggest source of air pollution in Obrenovac community is electric thermopower plant TENT “Nikola Tesla”. That was the reason for Ecological fund of Obrenovac to ask IPH, Belgrade to perform measuring of air pollution (specifically PM_{10}) in the vicinity of elementary school “Jefimija” Rajkovac, in period from 27.12.2005 to 25.01.2006.

All measurements were done using HORIBA ambient monitors: for NOx APNA-360; for SO2 APSA-360; for CO APMA-360; for hydrocarbon APHA-360. The devices give great stability and extremely high sensitivity O3 (F.S. 0.1 ppm). At the same time, meteorological parameters were registered by automatic meteo station, like temperature, pressure, wind speed, wind direction and relative humidity. Measurements of PM_{10} were done using ambient monitor FH62 I-R.

Imission limit values of air pollutants in ambient air in Republic of Serbia are defined by »Official Gazzete of Republic of Serbia«, No 54/92[5,6,7]. Pollutants in ambient air are monitored or measured according to informations about main emission sources, expecting level of concentartion and importance of pollutants for population exposure.

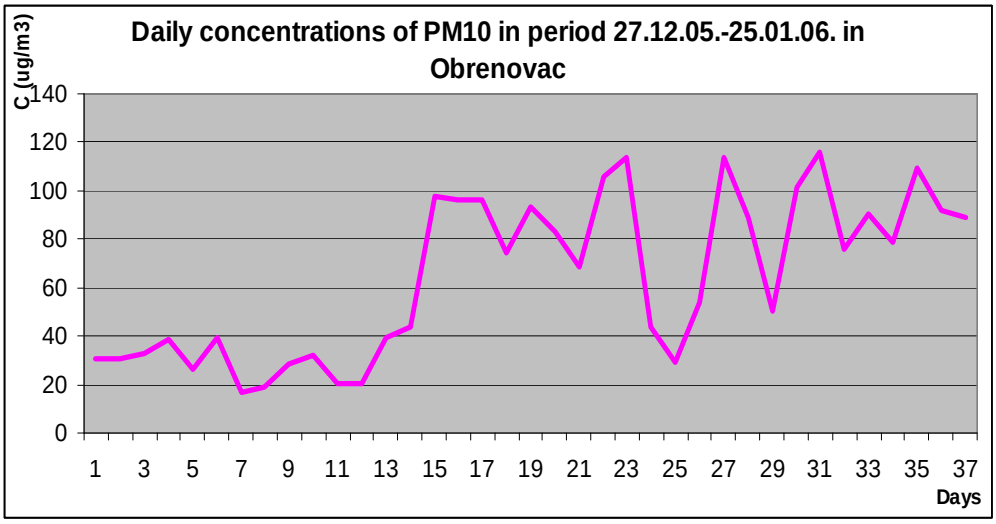
The results obtained for PM_{10} (suspended particulate <10microns) were compared with ILV (imission limit value) according to the National regulation. Daily concentrations of PM_{10} were also compared with appropriate limit value in EU regulations taking in considerstion their significance for human health and whats more, the future harmonization of National regulation in this field with EU Directives[8,9,10].

On the basis of registered results we noticed following:

- Average daily values of CO concentrations were in range 0,32-3,77 mg/m^3 and they were not above 5 mg/m^3. Minimum one hour value was 0,22 mg/m^3 and maximum 5,8 mg/m^3 on 27. 12.2005. in 9:30h;
- Average daily values of NO_2 concentrations were in range 2,3-61,1 µg/m^3 and they were not above ILV (85 µg/m^3). Minimum one hour value was 0,6 µg/m^3 and maximum 137,7 µg/m^3 on 11.01.2006. in 12:30h;
- All values of total hydrocarbon concentrations were very low;
- Average daily values of SO_2 concentrations were in range 1,1-53,7 µg/m^3 and they were not above maximum allowed concentration (150 µg/m^3). Minimum one hour value was 0,7 µg/m^3 and maximum 121,7 µg/m^3 on 27.12.2005. in 8:30h;
- Average daily values of PM_{10} concentrations were in range 16,8-113,9 µg/m^3 (chart 1) and they were not above imission limit value according to Serbia regulation (120 µg/m^3). Maximum value was 293,0 µg/m^3 on 25.01.2006. at

midnight. According to EU regulation LV of PM_{10} for 24h is 50 µg/m^3 what put 51,61% of measurements obove i.e. exceeding the limit value.

Chart 1: Daily concentratios of PM_{10} in µg/m^3



According to the registered results, we can conclude that:

- Daily average 24h concentrations of CO, NO_2 and SO_2 were not above ILV in indicated period;
- Maximum of CO, NO_2 and SO_2 concentration were registered in period of the day when the frequency and density of traffic were increased;
- PM_{10} concentration were not above maximum allowed concentration according to Serbia regulations;
- We concluded that increased one hour concentrations of PM_{10} were classified in time of silent-period with low wind speed;
- 51,6% measurements of PM_{10} were above LV according to EU regulation;
- There are increased concentration of suspended particulate in air and in order to reduce concentrations of this air pollutant, it is necessary to examine their chemical sructure and presence of toxic matter in it.

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MODELILNG ASHES DISTRIBUTION THROUGH ATMOSPHERE AT SHORT DISTANCES IN THE VICINITY OF THERMAL POWER PLANTS IN OBRENOVAC

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1. Abstract.

Coal thermal power plants Nikola Tesla "A" and "B" (TENTA and TENTB in the next text) located in Obrenovac near Belgrade, in routine operation emit to the environment great quantities of flying ashes from three chimneys 150m, 220m and 280m tall. During strong winds thermal power coal depots and ashes/slag depots could be significant air pollution sources of fine dust aerosols. Size of coal depots surface is 13.2ha and 8.4ha for TENTA and TENTB respectively, and 400ha and 200ha for ashes/slag depots.

Establishing of a fully automated environmental monitoring system is in progress for both thermal power plants. Main parts of the system are:

Automated measuring devices for ash emission rates placed in all three chimneys

A module for mathematical modeling ash and coal particles lifting from coal and ash/slag depots

An automated meteorological station

Automated measuring devices for particulate meters concentration in the air placed on three locations at the territory of Obrenovac

An appropriate air dispersion mathematical model

There are two processes we have to model, dust lifting and its transport downstream from the sources (chimneys and ash/slag/coal depots).

2. Model for ashes lifting

If surfaces of ashes/slag depots are not protected with water mirror, i.e. if surfaces of ashes and coal depots are sufficiently dry 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.

Several authors have pointed out saltating (sandblasting) as the most important mechanism for lifting dust aerosols to the atmosphere. It can be presented as:

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

where:

q -instantaneous horizontal (saltation) mass flux (g cm^{-1})

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})

u_{*tv} -threshold shear velocity (cm s^{-1})

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

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:

$U(z)$ -wind speed at height z

k -von Karmann's constant (0.4)

z_0 -roughness height (cm)

D -displacement height (cm)

In order to calculate lifting of dust from ash and coal depots, surfaces of depots are divided into numerous numbers of smaller cells characterized by its coordinates and surface characteristics.

3. Mathematical model for air pollution distribution assessment

Presented module of dust lifting is a part of a more complex air pollution distribution algorithm for air pollution distribution assessment in the vicinity of thermal power plants TENT A and TENT B, near Belgrade. Algorithm is based on Gaussian straight line air pollution distribution model for routine releases, presented by equation:

$$C(x,y,z)=\frac{Q}{2\pi\sigma_y\sigma_z u}\exp\left(-\frac{1}{2}\frac{y^2}{\sigma_y^2}\right)$$
$$\left\{\exp\left[-\frac{1}{2}\frac{(z-H)^2}{\sigma_z^2}\right]+\exp\left[-\frac{1}{2}\frac{(z+H)^2}{\sigma_z^2}\right]\right\} \quad (3)$$

Where:

$C(x,y,z)$	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
u	average wind speed

To account for gravitational settling of heavy aerosols emitted from chimneys we modified heights of emission H with the term:

$$\left(H-\frac{v_s x}{u}\right) \quad (4)$$

Where

v_s	terminal velocity
x	downwind distance

4. Comments and conclusions

Numerical modelling of dust lifting from ashes/slag/coal depots of thermal power plants TENT A and TENT B in Obrenovac appears to be useful tool in assessing dust emission, especially in the situation when we have not appropriate measuring devices for such aim. Intention of this paper is to present a simple method for determining dust lifting using mathematical modelling, meteorological data and data attributed to surface characteristics of ashes and coal depots. Dust lifting is input parameter for an air pollution dispersion model, which is constitutive part of a fully automated air quality monitoring system which

establishing in Obrenovac is in progress. Three control air quality monitoring points located in the vicinity of dust sources will bi used for controlling both, results of dust lifting modelling and results of dust dispersion modelling.

5. References:

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