ATMOSPHERIC AEROSOLS AND THEIR INFLUENCE ON AIR QUALITY IN URBAN AREAS

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Abstract. The quality and pollution of air and its impact on the environment and particularly on human health, is an issue of significant public and governmental concern. The emission of the main air pollutants (sulfur dioxide, nitrogen oxides) has declined significantly but the trends in concentrations of a particulate matter are less clear and this pollutant still pose a risk to human health. The studies on the quality of air in urban atmosphere related to suspended particles PM10 and PM2.5, and first measurements of their mass concentrations have been initiated in our country in 2002, and are still in progress. The results of preliminary investigations revealed the need for the continuous and long-term systematical sampling, measurements and analysis of interaction of the specific pollutants – PM10 and PM2.5 as well as ozone, heavy metals in the ground level. Survey of some basic knowledge and features of atmospheric particles will be given and the results of air quality assessment in Belgrade will be presented as well.

Key words: Atmospheric particulate matter, urban air quality, PM10, PM2.5, mass concentration.

INTRODUCTION

Atmospheric particles – aerosols – are some of the key components of the atmosphere. They influence the energy balance of the Earth's surface, visibility, climate, human health and environment as a whole. According to World Health Organization (WHO), ozone, particulate matter, heavy metals and some hydrocarbons present the priority pollutants in the troposphere. The results of the long-term studies confirm that the adverse health effects are mainly due to particulate matter, especially small particles - less than 10 microns in diameter, PM10 [1]. According to the 1999/30/EC Directive [2], the countries-members are obligated to reduce the emission of the particles in urban areas by some 50% over the existing levels in order to meet the health-based limit values by 2005 and 2010. Within the European programme for monitoring and evaluation of the long-range transmission of air pollutants (EMEP), measurements of PM10 and heavy metals, as highly toxic species have been introduced.

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Atmospheric aerosols

Atmospheric particles are a complex mixture of organic and inorganic substances, suspended in the atmosphere as both liquids and solids, and they cover a very wide range from a few nm in diameter to 100 or more µm. They vary also in shape, chemical composition, and optical properties. Particle size is one of the key parameters that govern the transport and removal of particles from the air, their deposition within the respiratory system and is associated with the chemical composition and sources. Sizes of some typical atmospheric particles are presented in Table 1.

Table 1. Sizes of some typical atmospheric particles

<table>
<thead>
<tr>
<th>Description</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Very Small</td>
<td>paint pigments, tobacco smoke, dust, sea-salt particles</td>
</tr>
<tr>
<td>0.01 to 5 micrometers (µm)</td>
<td></td>
</tr>
<tr>
<td>Larger</td>
<td>cement dust, wind-blown soil dust, foundry dust, pulverized coal, milled flower</td>
</tr>
<tr>
<td>5 to 100 µm</td>
<td></td>
</tr>
<tr>
<td>Liquid (Mist)</td>
<td>fog, smog, mist, raindrops</td>
</tr>
<tr>
<td>5 to 10,000 µm</td>
<td></td>
</tr>
<tr>
<td>Of Biological Origin</td>
<td>viruses, bacteria, pollen, spores</td>
</tr>
<tr>
<td>0.001 to 0.01 µm</td>
<td></td>
</tr>
<tr>
<td>Of Chemical Formation</td>
<td>atmospheric sulphur dioxide oxidizes producing sulfuric acid; the acid attracts atmospheric water forming small droplets (haze). Metal oxides form when fuels that contain metals are burned.</td>
</tr>
<tr>
<td>0.001 to 100 µm</td>
<td></td>
</tr>
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</table>

Atmospheric particles generally occur in two distinct modes: the fine (<2.5 µm) mode and the coarse (2.5 - 10.0 µm) mode. **Fine particles** have an aerodynamic diameter less than 2.5 µm (PM₂.₅) and differ from coarse particles in origin and chemistry. The fine or accumulation mode is ascribed to growth of particles from the gas phase and subsequent agglomeration. This fraction is composed of varying amounts of sulfate, ammonium and nitrate ions, elemental carbon, organic carbon compounds, water, and small amount of soil dust, and trace species (Pb, Cd, V, Ni, Cu, Zn, Mn, Fe etc). This size fraction is generally man-made. Their lifetime is from days to weeks, travel distance ranges from 100 s to >1000 s km and they are associated with decreased visibility (haze).

**Coarse particles** are mainly formed by mechanical forces such as crushing, grinding, and abrasion of materials of geological origin. Pollen and spores are also included in the coarse particle range. Generally, coarse particles normally consist of aluminosilicate and other oxides of crystal elements, and major sources including fugitive dust from roads, industry, agriculture, construction and demolition, fossil fuel combustion; the lifetime being from minutes to hours, and their travel distance varies from <1 km to 10 km.

Airborne suspended particulate matter can be either **primary** emitted directly into the atmosphere or **secondary** in origin i.e. formed in the atmosphere from gaseous species by either homogeneous or heterogeneous chemical reactions. Due to these different emission sources, particles have different chemical composition and size distributions. In the urban environment, most secondary particulate have a predominantly man-made origin and occur as sulphates and nitrates. Primary particles are emitted either by natural or anthropogenic processes.
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Atmospheric particles are emitted either by natural or man-made (anthropogenic) processes. The main natural sources of airborne particulates are sea spray and soil re-suspension by the wind and atmospheric turbulence, Saharan dust and volcanoes storms. These result in a natural background concentration that varies according to local sources or specific weather conditions. In most European countries, industrialization results in anthropogenic sources predomination, especially in urban areas. The most significant of these are traffic, power plants, combustion sources (industrial and residential), industrial fugitive dust, loading/unloading of bulk goods, mining activities, human-started forest fires and, non-combustion sources such as building construction and quarrying.

The results of a number of studies have shown that emission of natural origin exceeds emission from anthropogenic sources in global scale by factor of 4 to 5 [3]; however according to some estimations [4], emission from anthropogenic sources will, up to 2040, reach the level of the natural emission mainly as a consequence of fossil fuel combustion with high increase rate in China and India.

**Anthropogenic sources**

**Road transport**

Particulate emissions from road transport come up as direct emissions from vehicle exhausts, tire and brake wear and re-suspension of road dust and in urban areas, and it is the major source of particles. The size distribution of these particles is bimodal, with particles of 0.01 to 0.05 µm in the nucleation mode in the case of freshly emitted soot particles and, of some 0.05 to 2.5 µm in the accumulation mode in the case of older coagulated soot particles. Particles emitted from tire-wear are produced by abrasion processes and their sizes are in the range 3 to 30 µm. The chemical composition of these particles may also be very different from those derived from combustion. Particulate matters also enter the atmosphere from dust on the road surface which is entrained by the motion of the vehicle along the road. It may come originally from deposited atmospheric dusts, material carried onto the road by vehicles or erosion, or the wear of the road surface itself.

**Stationary combustion sources**

Stationary combustion sources involve domestic sources, large combustion sources (power stations running with coal, oil and gas) and industrial plants.

**Domestic coal burning** was traditionally a major source of particles during winter months. Nowadays, however, abatement strategies decreased the significance of this source in a quite a number of European cities.

**Industrial emissions** - The contribution of this source to ambient particulate material vary depending on the location of the industry and the abatement technology adopted. Particles emitted from industrial sources have been found to be in the size range 0.5 to some 100 µm, depending on the nature of the source.

**Coal and oil fired power stations** usually have electrostatic filters which remove, in average, 99.5% of particulate emissions. Therefore, only the fine fraction, which can be transported by wind, contributes to an increase in ambient levels of suspended particulate matter in other areas. Power stations proved to be the main stationary source of sulphur dioxide in Europe.

Combustion in coal-fired power stations, domestic coal burning and industrial emissions have increased the presence of heavy metals such as Hg, Mo, Se, As, Cr, Mn, Ti; oil combustion effected the increase of concentrations of Va, Ni, Sn. All these elements are proved to have a great negative effect on health and environment.
Physical characterization of aerosols

Physical characterization of atmospheric particles includes determination of size, size distribution, shape, optical features, elemental, molecular and isotope structure. All these properties profoundly influence the behaviour of atmospheric particles, and their effects on health and environment. The effect of particle size is strongly dominant as it influences the aerodynamics, respirability, lifetime and removal from the atmosphere. The particle shape controls the toxicity and respirability. Special importance in characterization of particles has the size distribution the knowing of which can indicate the possible source.

The atmospheric particles show evidence of the three major modes [5]. The first (nucleation mode) is attributable to the nucleation process and contains a very large number of particles of 10 nm in diameter. The mass in this component is often a small fraction of the total aerosol mass concentration. In the second component, the accumulation mode, particles, roughly in the size range 0.05 to 2 μm diameter are long-lived in the atmosphere since the removal mechanisms are least efficient in this region; they are important tracers for long range transport and efficient light-scatterers, so they are often dominant in optical effects such as visibility. The third peak corresponds to particles with diameters between 10 μm and 100 μm; they are shorter-living, very variable according to local conditions, and likely to travel distances typically of metres to hundreds of kilometers according to size and wind speed. They may contribute substantially to aerosol mass, although the number of such particles is often small.

Chemical characterization of particles

It is well established that chemical contents influence the transport and transformation processes of atmospheric particles; thus chemical characterization of atmospheric particles has an important role in better understanding of their behaviour and influence. The majority of particles of industrial origin contain significant quantities of some potentially dangerous trace elements. As the result of condensation and adsorption processes, the elements as As, Cd, Co, Cr, Mn, Ni, Pb, Se, S, Sb, Tl and Zn can be found on the particle surface. Special attention is paid to the surface chemistry in order to get detailed informations for better understanding of behaviour and influence of some ambient pollutants adsorbed on particulate surfaces.

Instrumental neutron activation analysis (INAA), photon-induced X-ray fluorescence (XRF), particle-induced X-ray emission (PIXE), atomic absorption spectrophotometry (AAS), inductively-coupled plasma with atomic emission spectroscopy (ICP/AES), inductively-coupled plasma with mass spectroscopy (ICP/MS), and scanning electron microscopy with X-ray fluorescence (SEM/XRF) are the sensitive methods that are usually used for analysis of contents of suspended atmospheric particles. They all are aimed to determine trace elements, which is connected with difficulties relating to small concentration measurements, unknown nature of chemical species as well as a fact that due to coagulation, condensation, and adsorption of gases, each single particle presents a complex agglomerate.

Dispersion

Dispersion of the atmospheric particles in the air is affected by meteorological conditions (wind speed, wind direction and atmospheric stability), the emission height (e.g. ground level sources such as road traffic or high level sources such as tall chimneys), local and regional geographical features, the source (e.g. fixed point, such as a chimney, or a diffuse number of sources such as cars and solvents). Meteorological conditions can be described as either stable or unstable, where the stability is determined by wind (which stirs the air) and heating effects
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(which cause convection currents). Atmospheric stability affects pollution released from ground level and elevated sources differently. In unstable conditions, ground level pollution is readily dispersed thereby reducing ground level concentrations. Elevated emissions, however, such as those released from a chimney, are returned more readily to ground level, leading to higher ground level concentrations. Stable conditions mean less atmospheric mixing and therefore higher concentrations around ground level sources, but better dispersal rates, and therefore lower ground level concentrations, for elevated plumes.

Importance of aerosols for human health

A series of epidemiologic studies has clearly shown the causative interconnection between particles and health effects; frequency rates of chronic obstructive respiratory diseases seem to be increasing. The World Health Organization (WHO) as well as different authorities in Europe and the US, recognized the potential risks of atmospheric particulate matter, PM to public health, and atmospheric pollution by particles has become an important policy theme. Many studies have generally accepted that the ability for particles to cause health effects is dependent on their size [6]. In spite of the fact that particles up to 100 µm enter the body through breathing, only very small particles, below 5 µm aerodynamic diameter can reach deep into the lung and these very small particles have the main potential for causing health effects. The current focus of health-related sampling of particulate matter is on particles with aerodynamic diameter less than 10 µm (PM₁₀) but recent research pointed out the great health effect of fine particles PM₂.₅, and even PM₀.₁. The importance of chemical composition of fine particles is also outstanding.

Four main fractions are defined: inhalable fraction (E) defined as the mass fraction of total airborne particles, which is inhaled through the nose and/or mouth and for ambient atmosphere is given by:

\[
E = 0.5 (1 + \exp[-0.06D]) + 10^{-5} U^{2.75} \exp(0.05D)
\]

where D is the aerodynamic diameter of the particle and U is the wind speed (up to 10 m s⁻¹). Thoracic fraction, defined as the mass fraction of inhaled particles penetrating the respiratory system beyond the larynx (median aerodynamic diameter of 10 µm); respirable fraction, defined as the mass fraction of inhaled particles which penetrate to the unciliated airways of the lung with a median aerodynamic diameter of 4 µm, and "high risk" respirable fraction for the sick, and infirm or children with a median aerodynamic diameter of 2.5 µm.

Air Quality standards

The Council of the European Union has adopted Directive 1999/30/EC [1] of 22 April 1999 relating to limit values for sulphur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter PM₁₀ and lead in ambient air. The formal proposal obligated EU countries to closely monitor air quality throughout their territory, to make detailed action plans for the most polluted areas and to provide the public with up-to-date information on all of four pollutants. The proposed limit values were based on previously adopted World Health Organization (WHO) guidelines for SO₂, NO₂ and lead. Commission Decision of 16 January 2003 [7] concerning guidance on a provisional reference method for the sampling and measurement of PM₂.₅ under Directive 1999/30/EC was adopted. It was also proposed that where possible, sampling points for PM₂.₅ shall be co-located with sampling points for PM₁₀. For the first time, air quality limits were predicted to prevent damage to crops and buildings. The limit
values for PM$_{10}$ are 50 $\mu$g m$^{-3}$ (24h mean) not to be exceeded more than 35 times per year, and 40 $\mu$g m$^{-3}$ as an annual mean; these limits have to be achieved by January 1, 2005.

In our country, limit values are still related to total suspended particles and for urban areas daily limit amounts 120 $\mu$g m$^{-3}$ and mean annual value is 70 $\mu$g m$^{-3}$ [8].

AIR QUALITY STUDIES IN THE BELGRADE URBAN AREA

Sampling of suspended particulate matter, PM$_{10}$ and PM$_{2.5}$ started in July 2002 and are still in progress at three sites in the very urban area of Belgrade: roof of the Rectorat Building of the Belgrade University at Student Square (at a height of about 20 m); roof of the greenhouse at about 6 m height in the Botanic Garden, 50 m far from heavy-traffic streets; and on the platform above entrance stairs to the Faculty of Veterinary Medicine at the height of about 4 m from the ground, facing a very busy street about 5 m far in horizontal line and close to the big junction Autokomanda with a highway. This sampling point can be considered as traffic - exposed.

Suspended particles were collected on Pure Teflon filters, Whatman (47 mm diameter, 2 $\mu$m pore size) and Pure Quartz, Whatman, (47 mm diameter) filter papers, using the low volume air sampler Mini-Vol Airmetrics Co., Inc., (5 l min$^{-1}$ flow rate). The duration of each sampling period was 24 hours. The filter samples were sealed in plastic bags and kept in portable refrigerators, in horizontal position during transport back to the laboratory. Particle mass was gravimetrically determined by weighting loaded and unloaded filters (stored in Petri dishes) after 48 hours conditioning in a desiccator, in clean room Class 100 at the temperature T=20°C and constant relative humidity Rh around 50%. A semi-micro balance, Sartorius, type 162, with a minimum resolution of 0.01 mg, was used to weight filters. For a quality assurance procedure, the quality of sample collection was determined by collecting blank samples in the field and by three control filters [9]. During the sampling, conventional meteorological parameters were regularly recorded at the Meteorological Station of the Hydro-Meteorological Institute of Republic of Serbia located inside central urban area.

RESULTS AND DISCUSSION

Daily mass concentrations of 105 PM$_{10}$ and 49 PM$_{2.5}$ samples were determined by gravimetric analysis of filters that were exposed to urban air in Belgrade from June 2003 and June 2003. A seasonal variation was found as higher concentrations both for PM$_{10}$ and PM$_{2.5}$ occurred in autumn-winter period (October, November, December) which could possibly be attributed to the higher traffic density and combustion of fossil fuels for heating during winter, as well as to the prevailed meteorological conditions e.g. inverted layers, low temperature and stagnation of air masses. Higher winter PM$_{10}$ concentrations were also recently presented in some other studies of European cities [10-13]. In general, determined PM mass concentrations have been found to be considerably higher compared to EU standard (40 $\mu$g m$^{-3}$).

The PM mass concentration levels in Belgrade urban air and in some European cities are presented in Table 2. showing that our annual mean PM mass concentrations exceed the values obtained in some other European cities.
Table 2. Annual mean PM mass concentrations (µg m⁻³) in urban air in Belgrade and some European cities

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<tbody>
<tr>
<td><strong>PM₁₀</strong></td>
<td>77</td>
<td>103 (w)</td>
<td>48</td>
<td>38</td>
<td>60</td>
</tr>
<tr>
<td><strong>PM₂.₅</strong></td>
<td>61</td>
<td>68 (s)</td>
<td>34</td>
<td>30</td>
<td>/</td>
</tr>
</tbody>
</table>

The winter episode with simultaneous sampling of PM₁₀ and PM₂.₅ run at the Faculty of Veterinary Medicine, showed that PM₁₀ and PM₂.₅ concentrations data are very well correlated (Pearson's coefficient R=0.99), indicating the same source for fine and coarse particles. The relative contribution of fine, PM₂.₅ to inhalable particles, PM₁₀, was determined for the period with simultaneously measurements of both fractions. On average, the mass percentage of PM₂.₅ was 78% of PM₁₀ i.e. 62% in summer and 85% in winter period. During the episode with intense photochemical processes, in summer, this ratio reached the value of 96% and during the high pollution period with the highest mass concentrations for PM₁₀ and PM₂.₅ particles (November, December), the value was up to 88%. Similar data have been obtained in some other cities as well.

Statistic analysis of daily mass concentration and relevant meteorological parameters such as daily mean values of temperature, relative humidity, precipitation, atmospheric pressure, wind speed and direction, were performed; negative correlation with wind speed was observed giving the prominence to the efficiency of the atmospheric horizontal mixing as a dilution mechanism.

![Fig. 1. Mass concentrations of PM₁₀ and PM₂.₅ with respect to wind directions](image)

Mass concentrations of PM₁₀ and PM₂.₅ with respect to wind directions for whole measuring period are presented in Fig.1. For both seasons, the PM concentrations were higher when prevailing wind directions was south-west. One of the possible explanations might be
that the most polluted location, Faculty of Veterinary Medicine, is opened from S-SW direction where the big crossroad with a highway is. Another reason could be the influence of the great source of air pollution, the complex of coaled fired power plants of Nikola Tesla A and Nikola Tesla B - Obrenovac, 20 km south-west from Belgrade, which is significant source of secondary sulfate aerosols [16]. Air-back trajectories model was applied to determine the main sources of pollution in the Belgrade area and the results confirmed the assumption that the dominant source of particles was local traffic, individual power stations and the complex of coaled fired power plants 20 km far from Belgrade [17]. Physical and chemical characterization of PM particles done with scanning electron microscope [18] have indicated the presence of soot, particles with high content of Si, sulfate, particles enriched with heavy metals and biological particles.

The results presented in this work, are related only to the part of integrated project "Air quality studies in urban areas" which includes also measurements of heavy metals concentration in PM, bulk atmospheric deposition, soil and plant leaves; natural and man made radionuclides (Be-7, Cs-137, Pb-210), and ground level ozone.

CONCLUSION

Air quality investigation in Belgrade urban area has shown, that the annual PM mass concentrations, in comparison to majority of European cities are significantly higher. The main sources of suspended particle are traffic, power stations, local heating and dust re-suspension. Project and investigation are in progress. The obtained results and further investigations will substantially improve our knowledge in estimating parameters that define transport, distribution and interaction of pollutants from the sources of pollution to human population and are aimed for finding effective solutions to improve air quality and for a sustainable development in urban areas. Special attention has to be paid to errors related to possible contamination of samples, data processing, and analysis of results.

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ATMOSFERSKI AEROSOLI I NJIHOV UTICAJ NA KVALITET VAZDUHA U URBANIM SREDINAMA

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U tipičnoj atmosferi koja nas okružuje i stalno se menja, nalazi se suspendovani čestični materijal. Ispitivanja su pokazala, da je pored SO<sub>2</sub> i O<sub>3</sub> visok nivo čestičnog materijala najdominantniji oblik zagađenja, kao i da čestični materijal na dugoročnoj osnovi nanosi štetu više nego i jedan drugi poluant. Procesi industrijalizacije i sve veća naseljenost uticali su na emisiju znatnih količina opasnih i štetnih materija, polutanata; visoke koncentracije kako čestičnog materijala u gradovima tako i gasovitih polutanata su uglavnom posledica emisije iz termoelektrana, velikih i/ili malih industrijskih postrojenja, lokalnih izvora grejanja i dr. Važan izvor emisije polutanata je saobraćaj i to kako putem emisije izduvnih gasova i čestica tako i emisijom koja nastaje kao posledica kočenja i abrazije površinskih slojeva puteva. Polutanti u vazduhu mogu da formiraju smog i kisele kiše, izazovu respiratorne i druge zdravstvene probleme, uništavaju zaštitni ozonski omotač u gornjim slojevima atmosfere i utiču na klimatske promene. Kvalitet vazduha u urbanim sredinama ima veliki značaj, i na regionalnom i lokalnom nivou, i utiče na transport polutanata i procese transformacije. U radu će biti dat pregled opštih pojmovna i karakteristika atmosferskih aerosola kao i neki rezultati njihovog ispitivanja u urbanom delu Beograda sa ciljem određivanja kvaliteta vazduha.