Technical Paper

Physico-Chemical Characterization of PM_{10} and $PM_{2.5}$ in the Belgrade Urban Area

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Abstract

An extensive study on urban aerosols with the aim to determine the sources and provide a physico-chemical description of PM_{10} and $PM_{2.5}$, present in the urban air of Belgrade, was performed. Daily aerosol samples were collected in four seasonal episodes at three representative places in the urban area of Belgrade in the period of 2002-2004. Suspended particles were sampled on pure Teflon filters by using a Mini-Vol air sampler (Airmetrics Co., Inc.; 5 L min^{-1} flow rate) and were analyzed by a JEOL JSM-5300 SEM via an energy dispersive X-ray microanalysis system (EDX). The airborne particulate matter was characterized from a physico-chemical point of view to supply information on the particle composition and the compounds carried on their surfaces. The combined use of microanalysis and statistical methods enabled identification of several groups of particles such as: soot, sulfates, Si-rich, metal-rich and biological particles.

Key words: particulate matter, urban air, characterization, SEM/EDX

Introduction

Suspended atmospheric particulate matter, PM_{10} and $PM_{2.5}$ (aerodynamic diameter less than 10 μm and 2.5 μm, respectively) are today a key issue in contemporary air pollution research. Their effect on public health and their activity in heterogeneous chemistry have been well recognized.[1, 2] Many studies have confirmed the hypothesis that apart the size, also the chemical composition of the particles and their capacity to carry potentially toxic substances (such as organic substances or metallic compounds) adsorbed on their surfaces has a crucial role. Some epidemiological data also seem to indicate possible seasonal effects of the particulate matter on human health. Therefore, the study of the mass concentrations, physico-chemical characteristics, their possible sources, as well as the spatial and temporal variation of atmospheric aerosol particles gained in significance and resulted in an increased interest in the use of analytical techniques capable of measuring the size, morphology, and chemical composition of individual aerosol particles. Such data are essential for the understanding of particle formation, transport, transformation and deposition mechanisms as well as the impact of particles inhaled by a respiratory system. This is especially important for urban aerosols, whose variety of size and composition make complete characterization a difficult task.

Scanning electron microscopy (SEM) coupled with Energy-Dispersive X-ray analysis (EDX) is a powerful tool for the characterization and source apportionment of atmospheric particulate matter and several applications to environmental studies have been reported in the literature.[3-8] Emission X-ray spectra under electron beam excitation allow a qualitative analysis of particles observed on the SEM images, providing an information on the size, size distribution, morphology and chemistry of particles as small as few nanometers. Hence, it might disclose information about possible emission source that cannot be determined through ordinary bulk chemical analysis.

The aim of the present research was to study the composition of PM_{10} and $PM_{2.5}$ and their physico-chemical characteristics in the very urban area of Belgrade. The results of the gravimetric analysis of PM samples (PM_{10} and $PM_{2.5}$) are previously presented [9, 10] and reported that the mass concentrations had high average values in comparison with other European cities. Strong seasonal variation has been indicated as well. The main sources of airborne particulate matter were the traffic emission, road dust re-suspension, and individual heating emissions. After mass concentration measurements, qualitative chemical analysis of daily PM samples was done with scanning electron microscope and energy dispersive spectrometry. Presented results have been involved in the project of an integral

monitoring "Air quality Studies in Urban Areas: Heavy Metals, Radionuclides and Their Interaction in the Atmosphere" which also includes the measurements of heavy metal concentrations in the PM, bulk atmospheric deposition, soil and plant leaves, natural and man-made radionuclides (Be-7, Cs-137, Pb-210), ground level ozone, and SO_2 concentrations.

Experimental

24-h atmospheric aerosol samples have been collected in four seasonal episodes at three representative locations in the very urban area of Belgrade from July 2002 and are still in progress. Sampling sites are located about 5 - 10 m away from heavy traffic streets. Suspended particles, PM_{10} and $PM_{2.5}$, were sampled on Pure Teflon filters, Whatman (47-mm, 2 μm pore size) and on Teflon coated glass filters, Whatman (47-mm) by using a Mini-Vol air sampler (Airmetrics Co., Inc.; 5 L min^{-1} flow rate) positioned at 2 m height. The filter samples were sealed in plastic bags and were kept in portable refrigerators, in the horizontal position during transportation back to the laboratory. All filters have been weighted with a microbalance for determination of the mass concentrations. Quality assurance procedure was provided by simultaneous measurements of three control filters, which were kept together with the samples at the temperature of 20° C and humidity of 50% in a desiccator. One PM sample per episode was analyzed with the SEM/EDX according to the EPA Guidelines.[11] Prior to analyses three small sections of the filters (5 x 5 mm^2) were mounted on the SEM stubs and then coated with 10 nm layer of high purity gold using vacuum evaporator (Balzers/Union FL-9496). Afterwards, the filters were analyzed by a JEOL JSM-5300 SEM via an energy dispersive X-ray microanalysis system (EDX). The SEM observations were carried out at magnifications up to 15,000X; the electron beam energy was 30 keV, and probe current of the order of 100 μA. Both, high and low magnification spectra were examined on secondary electron images. The PM size distribution was determined by counting particles on the SEM images recorded randomly over the filter. Ten photomicrographs were arbitrarily taken under low resolution conditions and about 300 particles per PM sample were assessed for their morphology and about 50 particles for the X-ray spectral analysis (visual selection of particles with various shape and size). The elemental composition of selected particles in the secondary electron images was deduced from an energy dispersive X-ray spectrum (EDS) in the energy range of 0 – 20 keV, collected from the selected particles for a spectrum acquisition time of 100 s. The total X-ray count rate was between 1000 and 2000 counts s^{-1}. The elements observed were: Al, Si, C, S, N, Cl, P, K, Ca, Na, Mg, Cr, Fe, Cu, Zn, Ni, Cd, As, Ti and V, with detection limit of 1 wt %. It is necessary to mention that as the most of the urban particles are of a complex shape, quite different from an ideal flat sample, this may lead to an over- or underestimation of actual element concentration, while it still enables an identification of the most important particle types.

Results and discussion

Atmospheric PM_{10} and $PM_{2.5}$ sampled at three representative sites in the urban area of Belgrade were analyzed with scanning electron microscopy coupled with energy-dispersive X-ray analysis with the aim to identify their origin.

The relative size distribution of particles on $PM_{2.5}$ samples for all sampling sites has shown a huge peak at about 0.1 μm, (anthropogenic sources) with a second broader mode around 1 μm as presented on Figure 1. The similar size distribution was obtained in the case of PM_{10} particles, but with the presence of coarse particles. Classification of the present particles was based on the morphology and chemical composition of particles, typically expressed in terms of EDX peak-to-background values for the elements of interest as well as to the particle classification rules described in US-EPA.[11]

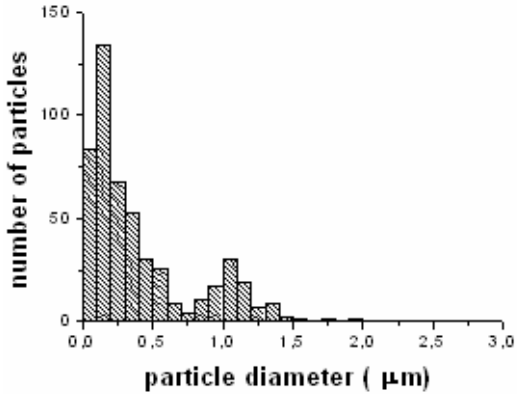

Figure 1. Particle size distribution of $PM_{2.5}$ sample

According to their morphology, two main particle categories were observed: particles of natural sources include materials of organic origin (pollen, bacteria, fungal spores etc.). This category also includes suspended soil dust (mostly minerals) such as the angular-shaped material. Particles from anthropogenic sources, mostly emitted from high temperature combustion processes are characterized by their spherical shapes and smooth surfaces. This type of particles occur as individual particles but also in an aggregate form, as agglomerates of similar-sized particles and individual large particles carrying several smaller attached particles.

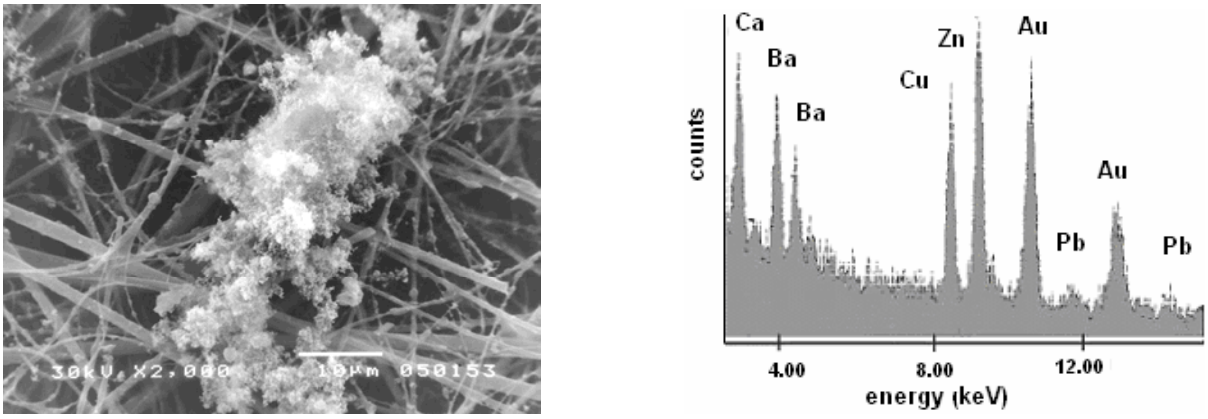

Figure 2. High resolution SEM image and X-ray microanalysis spectra of fly ash particles agglomerate from fossil fuel combustion process

Related to the chemical composition and morphology, the analyzed particles were classified into the most abundant groups such as soot, Si-rich particles, sulfates, metal-rich and biological particles. The SEM photomicrographs of some characteristic particles and their X-ray spectra are presented in Figures 2-5. *Soot* is present as agglomerates of many fine spherical primary particles. This kind of aggregate has an irregular morphology of various shapes. The X-ray microanalysis show traces of S and sometimes of Na and K. The surface of carbonaceous particles acts as a catalyst for SO_2 photochemical oxidation producing ammonium and alkaline metal sulfates. C-rich particles are mainly resulting from the vehicular traffic and, during winter, from the heating systems. This kind of particles usually contains also heavy metals what is presented in Figure 2.

The most of *silica particles* (probably Si oxides) and aluminosilicates (containing Al, Si, K, Fe, and Ca) present in the coarse fractions have irregular forms and come from soil. Spherical aluminosilicates that dominate in the size fraction below 1 μm are anthropogenic fly ash (e.g. coal combustion).[8,12] In Belgrade urban area, this type of particles originates mostly from individual heating emissions and coal-fired power plant (Nikola Tesla A, B, Obrenovac). One of these particles with its X-ray microanalysis spectra is shown in the Figure 3.

Sulfates are characterized by a strong S line in the X-ray spectrum and mostly by the presence of Ca, or Fe, Pb and K. These particles are formed as a result of the reaction in the atmosphere between sulfur compounds and other substances. They predominate in the fine fraction and have round forms. Sulfate clusters, often with sharp edges are mainly composed of Ca sulfates; they arise from the reactions between Ca carbonate materials and sulfurous compounds and have been found in the coarse particle range.

Oxides of Al, Zn, Cu, Ni, Pb, Ti, with spherical morphology, abundant in the sub-micrometer range, are identified as anthropogenic fly ash. Many particles, which could not be classified into one of these groups, found in the coarse particle range, were mixed aggregates, irregularly shaped, consisting of soil and road dust: Si, Al with minor constituents such as C, Fe, Mg, Ca, Ba, Pb, K, S, Zn, Ni, Cu, Ti. Coarse metal-rich particles of irregular form, liberated in industrial processes, were

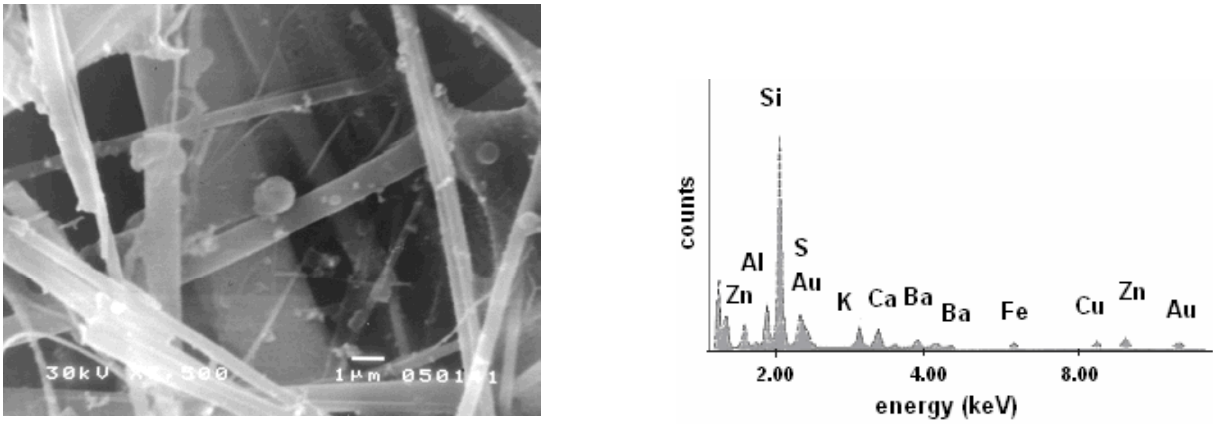

Figure 3. High resolution SEM image and X-ray microanalysis spectra of an aluminosilicate fly ash particle from the $PM_{2.5}$ sample

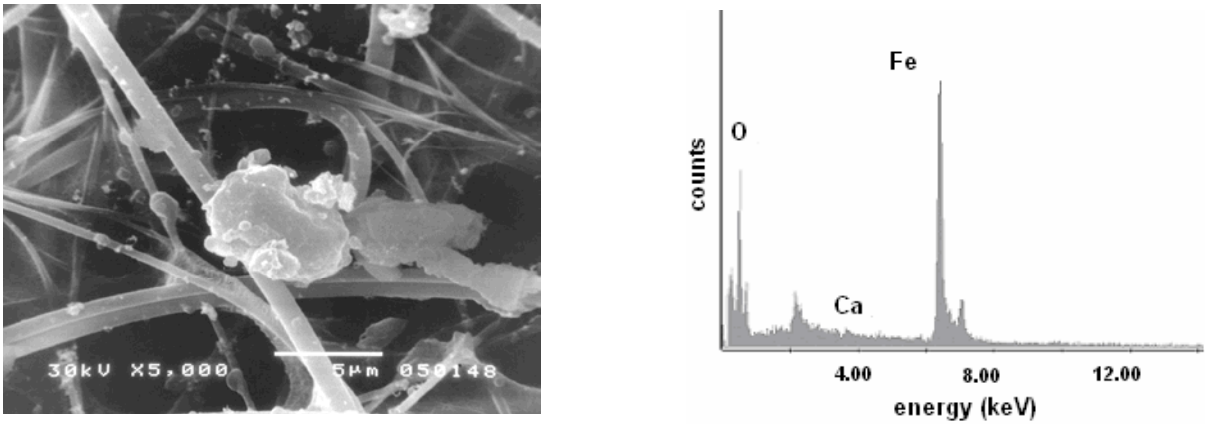

Figure 4. Coarse Fe-rich particle from the $PM_{2.5}$ sample, November 2003 and X-ray microanalysis spectra

also found (Figure 4). Biological particles (pollen, bacteria, fungi, spores etc.) are recognized (by their characteristic morphology[13]) as important constituents of the coarse particle fraction in the PM_{10} samples, especially during summer period and an example of such a particle is presented in Figure 5.

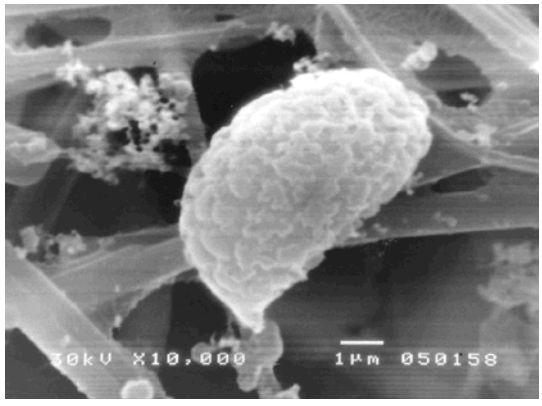

Figure 5. SEM image of a biological particle

Conclusions

24-h atmospheric aerosol samples have been collected at three representative sites in the very urban area of Belgrade from July 2002. All filters have been weighted with a microbalance for the mass concentration determination. After coating with gold under vacuum, particles were analyzed by a scanning electron microscope with energy dispersive X-ray spectroscopy; the size, size distribution, morphology and chemical composition of individual particles were examined.

The relative size distribution of atmospheric particles has shown a huge peak at about 0.1 μm, with a second broader mode around 1 μm for $PM_{2.5}$, as well as the presence of the mode of coarse particles in PM_{10} samples. Several groups of particles such as soot, sulfates, Si-rich particles, metal-rich particles, and biological particles are recognized as the most abundant particles. The SEM/EDX analysis, i.e. morphology and chemical characterization showed that the main sources of the PM particles in Belgrade urban area are: traffic emission, fossil fuel combustion from various processes, and soil and road dust re-suspension.

The results presented in this paper are in correlation with our previously experimental published results,[9] related to gravimetrical determined PM mass concentrations. On the basis of the analysis of the influence of meteorological parameters on PM mass concentrations, seasonal variations and statistical analysis, the main pollution sources were identified. Mean $PM_{2.5}/PM_{10}$ ratio being 0.78 indicated that PM_{10} primarily consisted of fine particles originating from anthropogenic sources.

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Povzetek

V urbanem okolju Beograda je bila opravljena obsežna raziskava aerosolov, da bi določili vire in fizikalno kemijske lastnosti prisotnih PM_{10} in $PM_{2,5}$. V obdobju 2002-2004 smo dnevno zbirali aerosole na treh značilnih lokacijah v Beogradu, v štirih različnih letnih obdobjih. Suspendirane delce smo vzorčili s teflonskimi filtri s pomočjo vzorčevalnika Mini-Vol (Airmetrics Co., Inc., pretok 5 L min^{-1}) in jih analizirali z energijsko disperzijskim rentgenskim sistemom (EDX) za mikroanalizo JEOL JSM-5300 SEM. S fizikalno-kemijsko karakterizacijo zračnih partikulatov smo dobili podatke o njihovi kemijski sestavi in snoveh na njihovi površini. Kombinacija mikroanalize in statističnih metod je omogočila identifikacijo različnih delcev kot so saje, delci z visoko vsebnostjo silicija, kovin ter delci biološkega izvora.