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Seasonal variability and source apportionment of metals in the atmospheric deposition in Belgrade

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ABSTRACT

The primary objective of this study is to assess anthropogenic impacts on the environment by determination of element atmospheric depositions. Bulk depositions were collected monthly, from June 2002 to December 2006, at three urban locations in Belgrade. Concentrations of Al, V, Cr, Mn, Fe, Ni, Cu, Zn, Cd and Pb were analyzed by atomic absorption spectrometry and the current deposition fluxes of atmospheric metals were established. Fourier analysis was applied in order to investigate seasonal variation of the monthly data set. Nickel, V, Fe and Al showed pronounced seasonal dependence, while seasonal variation of the other elements was not evident. The enrichment factors of Pb, Zn, Cd and Cu were obviously above those who could have been caused by natural processes, indicating a mainly anthropogenic origin. Nickel was intermediately enriched suggesting participation of both natural and anthropogenic sources. The multivariate receptor model, Unmix, was used to analyze a 5-yr element atmospheric depositions data set. Three main source profiles (mixed road dust, oil combustion and metal processing) were identified and the overall average percentage source contributions determined.

1. Introduction

Atmospheric deposition is an important source of toxic substances and the major pathway into the surface environment. Toxic substances include trace metals, such as As, Cd, Hg, Ni, Zn, Cu and Pb, which are emitted into the air from both natural and anthropogenic sources. Major anthropogenic sources of trace metals include vehicular emissions (Cr, Mn, Fe, Cu, Zn, Ba, Pb), stationary fossil fuel combustion (V, Cr, Mn, Ni), non-ferrous metal production (Cu, Zn, Cd) and combustion of gasoline (Pb) (Pacyna and Pacyna, 2001; Bilos et al., 2001; Schauer et al., 1996). Trace metals are persistent and widely dispersed in the environment and their interaction with different natural components may result in toxic effects on the biosphere (Nriagy and Pacyna, 1988; Bargagli, 1998).

Among other factors, the magnitude of atmospheric deposition and the ratio of wet to dry deposition are controlled by emission sources, distance to emission sources and the sampling site and meteorological conditions, e.g. prevailing wind directions, type, frequency and amount of precipitation (Tasić et al., 2001; Avila and Rodrigo, 2004; Motelay-Massei et al., 2005). Since either wet or dry modes may contribute equally to or predominate in total deposition, it appears essential to include both wet and dry deposition in estimations of loading from atmospheric deposition. From a biogeochemical perspective, the characterization of bulk deposition (BD) is relevant for identifying the variability and sources of the atmospheric pollutants (Azimi et al., 2005). Trace elements, such as Pb, Cd and Hg, can be transported over long distances by atmospheric flow and be deposited far from emission sources (Nriagy and Pacyna, 1988; Pacyna et al., 1989; Alcamo et al., 1992). Within the framework of the Cooperative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP), the bulk method has been used as a field measuring method for Pb, Cd and Hg in many countries (Denmark, Ireland, Estonia, Finland, Great Britain, Slovakia and Sweden) (EMEP, 2009).

During the past few decades, many studies on bulk (wet and dry) deposition of metals in urban areas have been widely used to estimate the influence of atmospheric inputs of metals on the surface environment (Golomb et al., 1997; Wong et al., 2003; Motelay-Massei et al., 2005; Azimi et al., 2003, 2004, 2005; Rossini et al., 2005; Papaefthymiou and Anousis, 2006; Sharma et al., 2008). Azimi et al. (2005) determined atmospheric fallout fluxes in order to access spatial variability in the Paris area and to estimate their seasonal changes. Heavy metals distribution showed the importance of the urban center as a source of all pollutants, even elements usually considered as crustal (Al and Fe). In the study of Motelay-Massei et al. (2005), concentrations of Cd, Cu, Ni, Pb and Zn were

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determined in bulk atmospheric deposition collected at five stations in the Saine River basin (France). No seasonal trend was found, except in Paris where domestic heating could explain the higher concentrations measured in winter.

Wong et al. (2003) collected samples of atmospheric deposits at urban, suburban and rural locations, including Hong Kong, to examine elemental associations in atmospheric depositions and to elucidate the potential sources of heavy metal contaminants in the region. Rossini et al. (2005) sampled monthly bulk depositions in four sites inside the Lagoon of Venice. Fluxes of metals (Cd, Cu, Ni, Pb, Hg) of anthropogenic origin were 3–4 times higher in the sites nearest to the urban and industrial area compared to the more distant sites. Spatial variations in elemental deposition rates in southern Greece were studied by Papaefthymiou and Anousis (2006) and indicated that the city situated near lignite power plant had significantly higher deposition rates of many elements compared to the typical urban city.

The aim of this paper is to report the results for atmospheric deposition of Al, V, Cr, Mn, Fe, Ni, Cu, Zn, Cd and Pb from June 2002 to December 2006 in the Belgrade urban area. The spatial variation of the air deposition fluxes was analyzed and metal enrichment factors calculated. According to the available sources, for the first time, the possibility of applying Fourier analysis to monthly BD data was included in order to investigate seasonal variation. The study also attempted to examine element associations and to identify and clarify the potential sources of trace metal contamination in the city.

Receptor modeling, using measurements of pollutant concentrations at one or more sample sites, is a reliable way of providing information regarding source regions of pollution. There are only a few reports applying receptor models to analyze BD data (Azimi et al., 2005; Sharma et al., 2008). This article provides the first demonstration of Unmix receptor modeling on bulk deposition data. It was used to analyze a 5-yr elemental data set for the purpose of source apportionment. The analysis generated source profiles and overall percentage source contribution estimates for source categories.

2. Materials and methods

2.1. Sampling

The capital of Serbia, Belgrade (latitude 44°49′14″ N, longitude 20°27′44″ E), has a population of about 2 million inhabitants and is situated at an average height above sea level of 116.75 m on the confluence of the rivers Sava and Danube. The total number of registered vehicles increased between 2002 and 2006 from 394 540 to 470 396. The largest contribution is from passenger cars (83% in 2006), most of them being from 0–10 years old (41%) or 16–25 years old (40%) (MIRS, 2009). The percentage of new cars (0–10 years old) increased from 2002–2006, as well as the production of unleaded gasoline (NIS, 2006). Nevertheless leaded gasoline is still widely used. There are 18 large heating plants, run on natural gas or crude oil and 59 small plants run only on crude oil. Fuel used for domestic heating consists mainly of coal or crude oil.

Bulk depositions were collected using an open polyethylene cylinder (29 cm inner diameter and 40 cm height) fitted on a stand at about 2 m above the ground. Both rainwater and the fallout of particles were collected continuously for one month periods from June 2002 to December 2006 at three sites in the urban part of Belgrade. The first site was located on the roof of the Rectorate building of the Belgrade University (RB), at 20 m above ground level. The second site was in the Botanic Garden (BG), about 50 m far away from heavy-traffic streets. The third site was a platform placed above the steps to the Faculty of Veterinary Medicine (FVM) at a height of about 4 m from the ground, 5 m away from a street edge with heavy traffic and 200 m away from the main state highway (Fig. 1). Before each sampling period the collection bottles were filled with 20 ml of 10% acidified (HNO_3 65% Suprapure, Merck) ultrapure water. Precautions were taken to avoid sample contamination in both the field and laboratory. Details about the studied sites and sampling procedures are given in Tasić et al. (2009).

2.2. Analysis

After collection the samples were sent to the laboratory for pre-treatment and analysis. Pre-treatment included acid digestion, evaporation to dryness, and dissolving the residue in 50 ml 0.1 M HNO_3. The digested solution was passed through a 0.45 μm nitrocellulose filter (Whatman) and analyzed by atomic absorption spectrometry. Laboratory blanks were below the analytical detection limits for all examined metals.

The concentration of elements, Al, V, Cr, Mn, Fe, Ni, Cu, Zn, Cd, and Pb, were determined by flame atomic absorption spectrometry (FAAS) (Perkin Elmer AA 200) and graphite furnace atomic absorption spectrometry (GFAAS) using a transversely-heated graphite atomizer (THGA; Perkin Elmer AA 600) with Zeeman-effect background correction. For calibration, standard solutions containing all

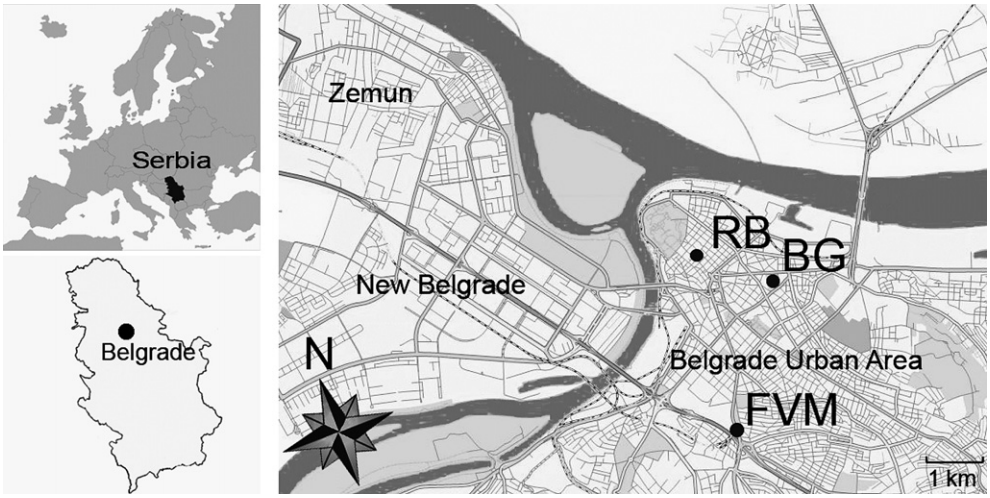

Fig. 1. Location of the three sampling sites in the Belgrade urban area: Rectorate building of the Belgrade University (RB), Botanic Garden (BG) and Faculty of Veterinary Medicine (FVM).