

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.

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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

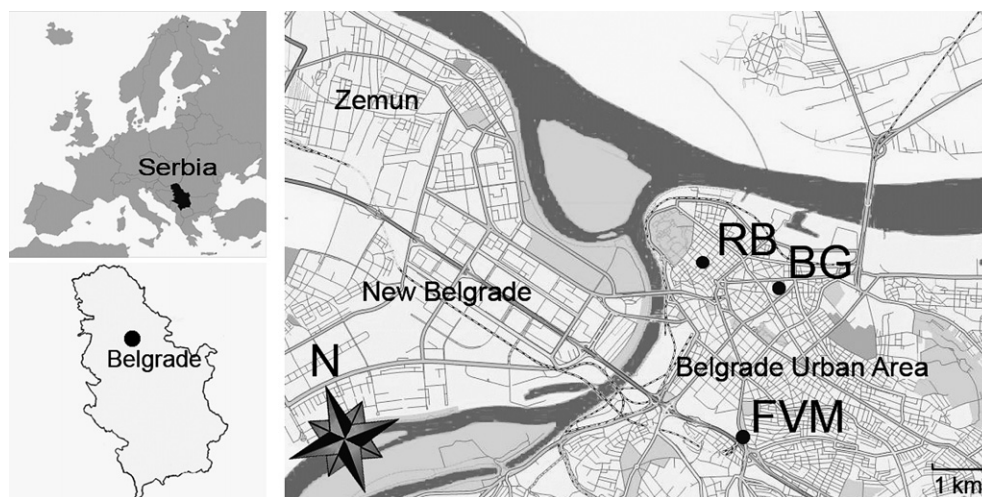


Fig. 1. Location of the three sampling sites in the Belgrade urban area: Rectorate building of the Belgrade University (RB), Botanic Garden (BG) and Faculty of Veterinary Medicine (FVM).

metals of interest were prepared using Merck certified atomic absorption stock standard solutions containing 1000 mg l⁻¹ metal in 0.5 M HNO₃ and Milli-Q quality deionized water, without addition of matrix modifier. Detection limits for the metals found to be: 0.04 ng ml⁻¹ for Cd, 0.1 ng ml⁻¹ for Cr, 0.2 ng ml⁻¹ for Cu, 0.5 ng ml⁻¹ for Pb, 2 ng ml⁻¹ for Zn, 0.4 ng ml⁻¹ for Ni, 0.2 ng ml⁻¹ for Mn, 5 ng ml⁻¹ for V, 0.5 ng ml⁻¹ for Fe and 2 ng ml⁻¹ for Al. Standard practices for the handling of trace metal samples were implemented.

For quality assurance, standard reference material NIST 2783 was used. It contains an urban dust PM_{2.5} aerosol fraction deposit from a mixed industrial urban area, collected on two polycarbonate membrane filters with corresponding blanks. The obtained recoveries in two runs were within ±15% of the certified values for Cd, Cr, Cu, Pb, Zn, Mn, V and Fe concentrations. Lower recoveries were observed for Ni (58%) and Al (74%) probably due to incomplete solution of the deposit. The whole analytical procedure is described in detail by Rajšić et al. (2008).

Data treatment included calculation of the monthly deposition fluxes of Al, V, Cr, Mn, Fe, Ni, Cu, Zn, Cd and Pb. To calculate the daily element atmospheric depositions per unit area (µg m⁻² day⁻¹) in each season, the total mass of metal was divided by the number of sampling days, and the cross sectional sampling area of the container. In order to estimate annual atmospheric inputs, the daily deposition fluxes were multiplied by the number of days in a year.

2.3. Enrichment factors

Enrichment factor (EF) analysis was used to investigate the relative contribution of anthropogenic sources with respect to those of natural origin. Calculation of element enrichment factors in our samples was based on standardization of the measured element against a reference element. Reference elements are often characterized by low occurrence variability and the most commonly used are Al, Ti and Fe.

The EF was calculated as follows: $EF = (Xi/Al)_{\text{sample}} / (Xi/Al)_{\text{crust}}$, where Xi is a given element concentration and aluminum (Al) is assumed to be predominantly from the Earth's crust. The average amounts of the elements in the crust are found in Mason (1966). According to the degree of enrichment the elements can be considered as highly enriched (EF > 100), intermediately enriched (10 < EF < 100) and less enriched (EF < 10) (Berg et al., 1994; Wang et al., 2005).

2.4. Source apportionment and seasonal variation

Receptor models are mathematical procedures for identifying and quantifying the sources of ambient air pollutants and their effects at a site (receptor) primarily on the basis of concentration measurements at the receptor, and generally without need of emissions inventories and meteorological data. Multivariate receptor models (Principal Component Analysis, Positive Matrix Factorization) have been already used for source apportionment of heavy metal atmospheric deposition studies (Wong et al., 2003; Sharma et al., 2008; Tasić et al., 2008, 2009). In this study the multivariate receptor model, Unmix, was used (EPA Unmix Version 6.0; U.S. Environmental Protection Agency, 2007). The concepts underlying Unmix have been described in a geometrical and intuitive manner (Henry, 1997) and the mathematical details are presented elsewhere (Henry, 2003).

The spectral analysis was used to reveal monthly variations of the elemental bulk deposition. We calculated the discrete Fourier transform, X, of the time series by using the fast Fourier transform (FFT) algorithm. The periodogram for a finite time series was then calculated as the squared magnitude of X

$$\Phi(\nu_k) = |X(k)|^2 = \left| \frac{1}{\sqrt{N}} \sum_{t=0}^{N-1} x_t e^{-2\pi i \nu_k t} \right|^2$$

where $k = 0, 1, \dots, (N-1)$, N is the number of observations; x_t is the segment time series; and $\nu = k/N$ (Choi et al., 2008). The periodogram indicates the strength of the signal as a function of frequency, while its spectrum over the frequency range corresponds to the variance of the time series data (Marr and Harley, 2002). The spectrum $\Phi(\nu_k)$ contains a background value $\Phi_0(\nu_k)$ determined by a “red noise” fit to the spectrum (Gilman et al., 1963). We used the power spectrum with a red noise background in our analysis because most climatic and other geophysical time series tend to have larger power at lower frequencies (Ghil et al., 2002). The significance of the spectral peaks in a periodogram is usually assessed by comparing $\Phi(\nu_k)$ to $\Phi_0(\nu_k)$.

The spectra of the power density (periodogram) were calculated separately for time series data for each sampling site. The final periodogram of atmospheric bulk deposition fluxes for each element was obtained by averaging the corresponding periodograms over the three sampling sites.

3. Results and discussion

3.1. Elemental atmospheric bulk deposition fluxes

A total of 140 atmospheric deposit samples were collected monthly from June 2002 to December 2006 at three sites in Belgrade, RB, BG and FVM, and metal (Al, V, Cr, Mn, Fe, Ni, Cu, Zn, Cd, and Pb) monthly fluxes were calculated. For ease of comparison, seasonal and annual atmospheric metal deposition fluxes were obtained from these data.

The average daily element bulk depositions (µg m⁻² day⁻¹) for all sampling sites showed that the most abundant metal was Fe (1627), followed in order by Al (901), Zn (113.5), Cu (94.5), Mn (71.8), Pb 59.4, V (54.1), Ni (31.0), Cr (4.5) and Cd (0.6). This order of element abundance is similar to those already obtained for bulk deposition in other urban studies (Sandroni and Migon, 2002; Azimi et al., 2004; Motelay-Massei et al., 2005).

Wide variation in the monthly deposition rates of all elements was observed, which explains the high standard deviations for the average deposition fluxes. This may be attributed mainly to weather conditions (temperature inversion layers, low temperature and stagnation of air masses) that strongly affected the dispersion and deposition of air pollution, as well as to variation of pollutants emission. Additional, the obtained seasonal pattern could be possibly attributed to the higher traffic density and combustion of fossil fuels for heating during winter.

The annual bulk deposition fluxes of the analyzed metals averaged for all sampling sites in this study were compared with data from different areas (urban, suburban and rural) (Table 1).

The annual bulk deposition fluxes of Cu, Ni, V, Mn and Pb exceeded the corresponding data from these studies. The largest contributors to the high loading for these elements were road traffic, heavy oil combustion and industrial activities. The most probable sources of Cu were vehicle related particles, such as brake abrasion, corrosion of metallic parts of cars, together with industrial and incinerator emissions (Pacyna and Pacyna, 2001; Rajšić et al., 2008). Confirmation of the presence of elevated concentrations of Ni in many soil samples from certain locations in Belgrade (Ecological Bulletin, 2008), points to a geological origin, followed by emission from fossil fuel combustion processes (Ni and V). Elevated Ni contents at all sites and high Cu contents at the RB site were obtained previously after evaluation of the levels and sources of trace elements in urban particulate matter (Rajšić et al., 2008) and a moss survey (Aničić et al., 2009). Besides dominant natural

Table 1
Annual bulk deposition fluxes ($\text{mg m}^{-2} \text{yr}^{-1}$) in different regions.

Location	Period	Fe	Al	Zn	Cu	Mn	Pb	V	Ni	Cr	Cd	References
Belgrade	2002–2006	594	329	41.4	34.5	26.2	21.7	19.70	11.3	1.64	0.22	This study
Paris	2001–2002			30	6.0		4.2		0.62		0.24	Motelay-Massei et al. (2005)
Pearl River Delta, China	2001–2002	555		104	18.6	8.98	12.7	2.09	8.35	6.43	0.07	Wong et al. (2003)
Massachusetts Bay	1992–1993	140	17.0	7.80	2.50	3.40	1.80		1.50	2.70	0.27	Golomb et al. (1997)
Lake Michigan	1993–1994			6.00	1.87	2.81	1.59	0.14	0.61	0.20	0.45	Sweet et al. (1998)
North Sea	1993–1994			6.50	1.24		3.52					Injuk et al. (1998)
Mediterranean Coast	1988–1993		144		2.60	5.72	3.77		0.57		0.31	Guieu et al. (1997)
Northern France	2001–2002			15.6	3.90		2.20		1.50		0.05	Azimi et al. (2004)
Southern Scandinavia	2002–2005			6.9	1.0		1.0	0.5	0.3		0.05	Hovmand et al. (2008)
North-East Spain	1995–1996			21.5	0.50	3.20	0.63	0.47			0.54	Avila and Rodrigo (2004)
Varanasi, India	2003–2004			52.5	6.68		0.98				1.38	Sharma et al. (2008)
French Riviera	1997–1998		141	41.2	1.28		1.20		1.10	0.62	0.06	Sandroni and Migon (2002)

sources, Mn can be emitted from motor vehicles and the steel industry (Furusjo et al., 2007). High Pb values are the consequence of the still widely used leaded gasoline (NIS, 2006).

The mutual relationship of metals was assessed by estimating Pearson's correlation coefficients between concentrations during the whole sampling period (total number of samples $N = 140$). The most significant correlations ($p < 0.05$) were found between Al – Fe ($r = 0.78$), V – Ni ($r = 0.68$), Al – Ni ($r = 0.65$), Al – Mn ($r = 0.65$), Fe – V ($r = 0.63$), Al – V ($r = 0.61$), Fe – Mn ($r = 0.61$), Ni – Cd ($r = 0.58$), Cr – Mn ($r = 0.58$) and Zn – Fe ($r = 0.57$). Predominantly of crustal origin, Al, Fe and Mn, were also correlated with many elements of anthropogenic origin from traffic and the steel industry (Herngren et al., 2006; Hien et al., 2001; Furusjo et al., 2007; Rajšić et al., 2008).

3.2. Enrichment factors (EFs)

Enrichment values for the elements in the bulk deposition samples are shown in Fig. 2. Averages for all the years and for all sampling sites were calculated with Al as the reference, since it was the element with the lowest anthropogenic influence among the analyzed elements. The high EF values for Pb, Cd, Cu, and Zn (> 100) pointed to significant anthropogenic sources, mainly originating from traffic and industrial activities (Pacyna, 1984; Sharma et al., 2008; Hou et al., 2005). Vanadium and Ni were moderately enriched with EF between 10 and 100. These elements have mainly anthropogenic origin but also some contribution from soil dust. Iron, Mn and Cr, with EFs below 10 were mainly of crustal origin, but slightly enriched, as crustal weathering remained an important source of these elements.

3.3. Spatial and seasonal variation

In general, element bulk deposition fluxes, BD ($\mu\text{g m}^{-2} \text{day}^{-1}$), showed large variations between different sampling locations due

to differences in traffic density, microclimatic conditions and the presence of unidentified local sources (Rajšić et al., 2008; Tasić et al., 2008). As expected, the BD values were highest at the FVM site, being 2753, 1331, 155.5, 111.2, 105.3, 90.1, 65.8, 7.5 and $0.8 \mu\text{g m}^{-2} \text{day}^{-1}$ for Fe, Al, Zn, Mn, V, Pb, Ni, Cr and Cd, respectively. High bulk deposition values of Fe, Zn, V, Pb, Ni and Cd in samples at FVM were expected, as this sampling site suffered from a heavy traffic load at the highway intersection with frequent congestion. The most significant correlations between elements ($p < 0.05$) were Al – Ni ($r = 0.75$) and Ni – Zn ($r = 0.68$). At this site, high correlation coefficients were also found between Cd and Ni ($r = 0.68$), Cd – V ($r = 0.64$), Cd – Al ($r = 0.61$) and Cd – Pb ($r = 0.58$), probably as a result of heavy vehicles traffic and road dust just resuspension (Sternbeck et al., 2002; Thorpe and Harrison, 2008).

The higher mean deposition value for Cu ($166.5 \mu\text{g m}^{-2} \text{day}^{-1}$) in samples at RB, compared to the other locations (BG – $43.2 \mu\text{g m}^{-2} \text{day}^{-1}$; FVM – $75.3 \mu\text{g m}^{-2} \text{day}^{-1}$) could indicate the presence of site specific sources. This is in accordance with the results of Pearson's correlation analysis. The most significant correlation coefficients ($p < 0.05$) were found between V – Ni ($r = 0.78$) and V – Fe ($r = 0.71$) as a result of the great influence of fossil fuel combustion (Manoli et al., 2002). No significant correlation coefficient was found between Cu and other metals, confirming the consumption of some specific Cu source. As the sampler was positioned at the height of 20 m above ground, the airflow was not blocked in any direction.

At the BG site, the bulk collector was mounted in the middle of the garden, protected from the direct influence of traffic. Element bulk deposition fluxes had lower values when compared to the FVM and RB sites, except for Al as a tracer of soil origin. The most significant correlation coefficient ($p < 0.05$) was between V – Ni ($r = 0.88$) but high values were also found between the crustal elements: Al – Fe ($r = 0.75$), Al – Mn ($r = 0.71$), Fe – Cr ($r = 0.69$) and Al – Cr ($r = 0.64$). Although, all three sampling sites were

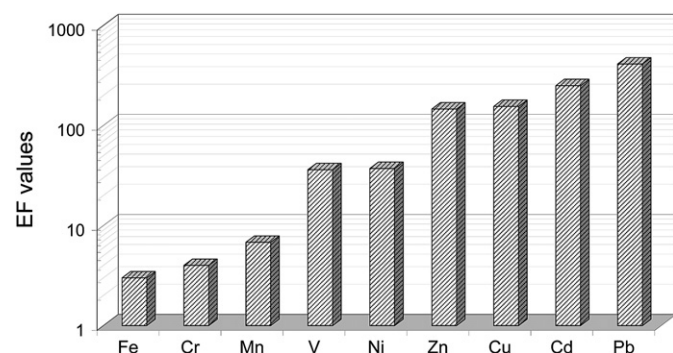


Fig. 2. Enrichment factors of elements in bulk deposition samples.

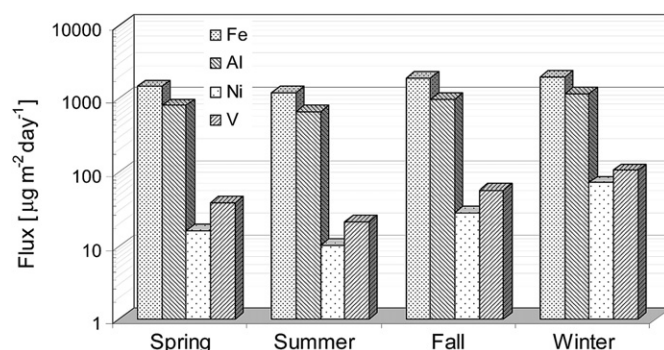


Fig. 3. Seasonal average values of bulk depositions for Ni, V, Fe and Al.

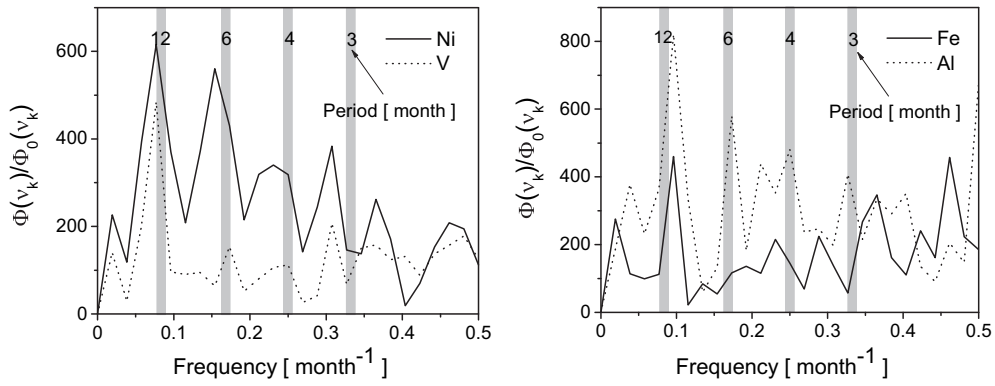


Fig. 4. Average of the power spectra of the monthly bulk depositions of Ni, V, Fe and Al divided by the background value for the three sites.

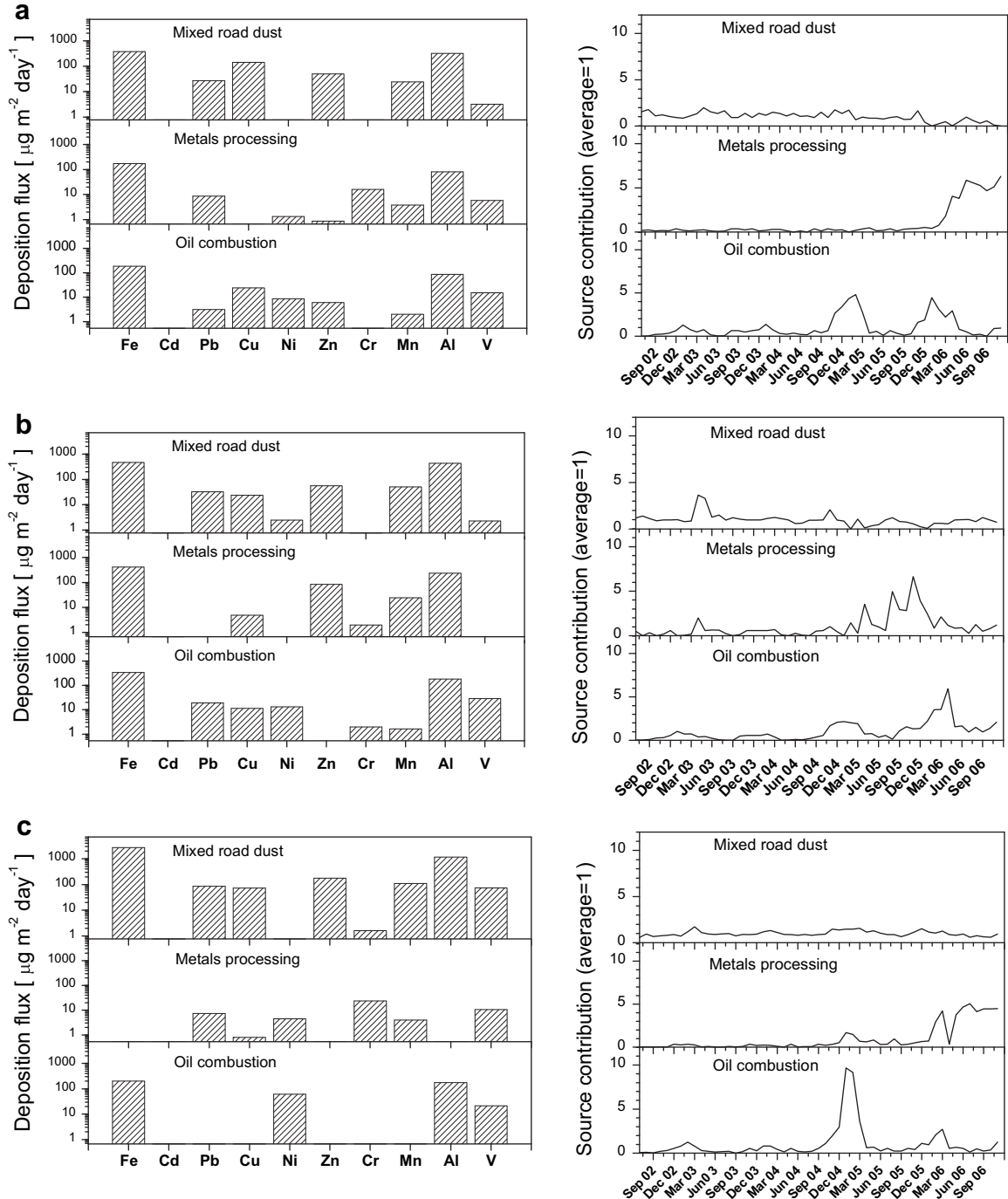


Fig. 5. Source profiles and the time series plot of source contributions resolved from the RB (a), BG (b) and FVM (c).

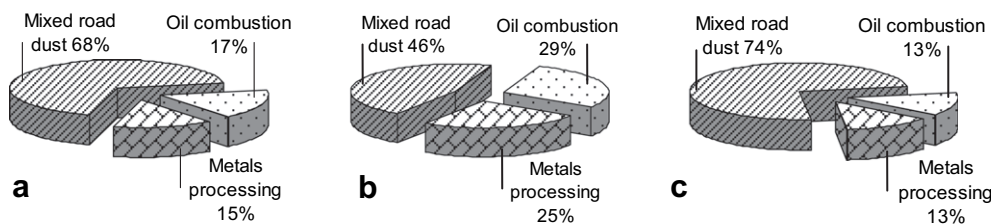


Fig. 6. Average source contributions at: a) RB, b) BG, c) FVM.

situated in the central urban area, element BD fluxes significantly depended on the bulk collector position.

In general, seasonal variation of metal concentrations in BD is associated with the nature of the sites, so seasonal trends were difficult to recognize because of the number of variables: intensity of rainfall, wind direction and mixing depths. The analysis of seasonal differences of elemental BD in the Belgrade atmosphere showed pronounced seasonal dependence for V and Ni, as well as a less pronounced but significant trend for Fe and Al (Fig. 3). The deposition fluxes of V and Ni were 5 and 7 times higher, respectively, during winter than in summer due to the combustion of fossil fuels (fuel oil, coal) in power plants, heating plants and individual heating facilities. The increase of Fe and Al atmospheric loads was mostly connected with fossil fuel combustion in heating units as another anthropogenic source besides the main natural one (Herngren et al., 2006; Hien et al., 2001; Furusjo et al., 2007). Seasonal variations of the other elements (Zn, Mn, Pb, Cr, Cu and Cd) were not evident.

Since seasonal differences of bulk depositions for some elements were confirmed, we applied spectral analysis to investigate the periodicities. The persistence of spectral peaks with 3, 6 and 12 month periods was investigated, as they can be considered to be markers of seasonal cycles.

In Fig. 4 the averages of three periodograms, for each sampling site and each frequency were calculated for Ni, V, Fe and Al and are indicated by solid (dashed) lines. On average, 13-month and 3.4-month spectral peaks exist for both Ni and V. Other strong spectral

peaks occurred at frequencies of 0.15 months⁻¹ (6.5 month), 0.23 month⁻¹ (4.3 month) and 0.36 month⁻¹ (2.8 month) for Ni, and 0.17 month⁻¹ (5.9 month) for V. The periodogram for Al indicated significant spectral peaks at frequencies 0.095 month⁻¹ (10.5 month), 0.17 month⁻¹ (5.9 month), 0.25 month⁻¹ (4 month) and 0.32 month⁻¹ (3.1 month), while the periodogram for Fe showed strong peaks at 0.095 month⁻¹ (10.5 month), 0.23 month⁻¹ (4.3 month), 0.28 month⁻¹ (3.5 month) and 0.36 month⁻¹ (2.8 month). These results confirm the existence of significant spectral peaks for some elements within a reasonable range period, indicating pronounced seasonal cycles of approximately 3, 6 and 12 months. Spectral analysis was shown to be a useful tool for investigating seasonal cycles of atmospheric depositions.

3.4. Source apportionment

The Unmix receptor model was applied to the data set for bulk deposits and three sources were identified for all sampling sites. Source profiles and the time series plots of source contributions resolved from the RB, BG and FVM are presented in Fig. 5(a–c) respectively.

The factor giving high loadings for Pb, Cd, Mn, Fe, Zn, Al and Cu, can be identified as mixed road dust. Previous studies have indicated that road traffic can contribute metals through different pathways, e. g. combustion products from fuel, wear products from tires, brake linings and road construction materials, crustal particles and resuspended road dust (Sternbeck et al., 2002; Vallius et al., 2003;

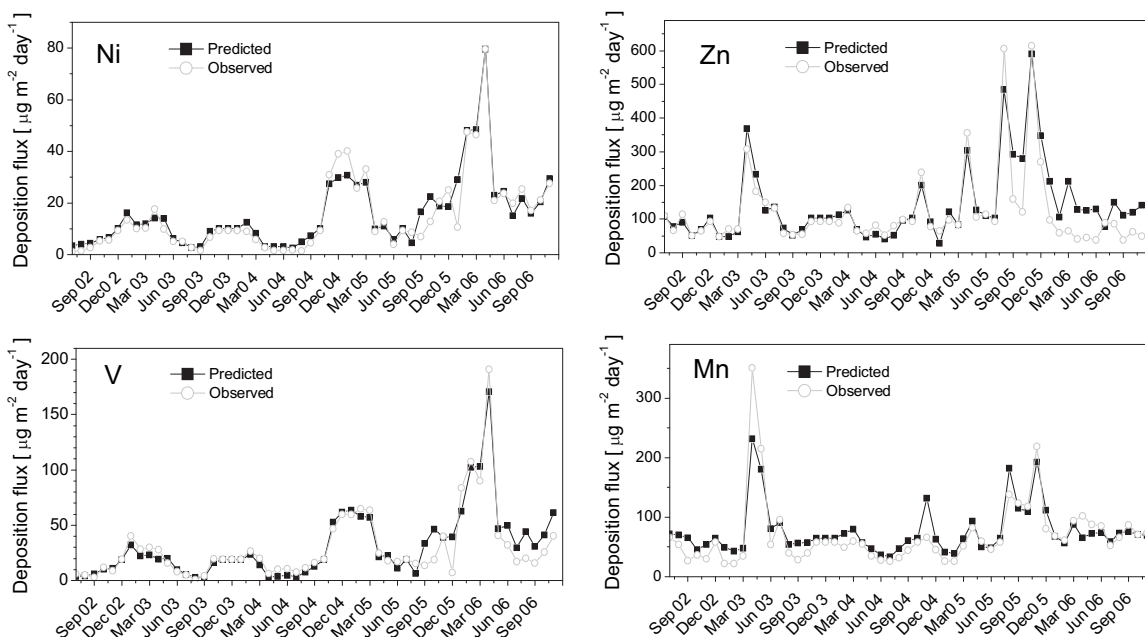


Fig. 7. The time series of observed and Unmix predicted bulk deposition fluxes of Ni, V, Zn and Mn at BG.

Pakkanen et al., 2003; Amato et al., 2009). The chemical profile of this factor represents products from wear of brake pads (Cu, Fe, Zn), tires (Zn), other metallic parts of cars and motor exhaust (Ni, Zn, Pb, V and Cd). The high Mn concentrations, especially at FVM may point to a diesel source, as Mn is a fuel additive normally used by diesel truck operators to prevent engine fouling. Iron and Mn are crustal elements, which may have been present in dust resuspended by traffic; Fe is also related to heavy-duty diesel emissions (Ramadan et al., 2000). The time series plot of the contribution shows a slight decrease without marked seasonal variation. This factor was most dominant at all sites, with the greatest contribution at FVM as the most traffic oriented location.

Oil combustion is a major source of V and Ni according to Pacyna and Pacyna (2001) and Manoli et al. (2002). The Unmix model resolved the source with high loadings of Ni and V for all sampling sites with similar seasonal variation including a strong winter maximum. It appeared to be a very significant atmospheric pollution source in Belgrade and probably reflects an urban region where residual oils are common fuels for utility and industrial sources. The time series plot of its contribution showed an increase in 2004 and 2006 for the RB, BG and FVM sites.

The factor characterized with a high loading of Cr and weaker loadings for Zn, Fe, Cu, Cd, Ni, Pb and V was resolved as specific metal processing (Querol et al., 2007; Pacyna and Pacyna, 2001). The largest total amounts of Cr released into the atmosphere by human activity are from metallurgical industries in the form of particles. The next most important source of atmospheric Cr is coal combustion. While Zn, Fe, and Mn are elements characteristic of steel production, Cu and Zn may be attributed to non ferrous metallurgy. The time series plot of their contribution showed a significant increase in 2006 for both the RB and FVM sites at the same time. One of the reasons was remarked enhance in traffic intensity, especially transportation of merchandise which showed increase from 2002–2006 for 50% (SEPA, 2007). Also, possible explanation could be the increasing production in US Steel Serbia, Smederevo (about 50 km SE from Belgrade).

Average source contributions at the sites discussed are presented in Fig. 6.

The time series plot of observed and Unmix predicted atmospheric fluxes at BG for Ni, V, Zn and Mn are given in Fig. 7. Correlation coefficients were 0.96, 0.94, 0.90 and 0.92 respectively at $p < 0.05$. Regression analyses between the observed and predicted elemental atmospheric fluxes for each sampling site indicate that the resolved factors effectively reproduced elemental BD values (correlation coefficients for all other metals ranged from 0.70 to 0.91). The coincidence of predicted and observed fluxes is reasonably well due to the very long period of measurement which generally improve the Unmix modeling results.

4. Conclusion

The present study aimed to characterize both quantitatively and qualitatively the atmospheric fluxes of Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn over the Belgrade urban area for a 5-year period (2002–2006). Annual bulk deposition fluxes of Cu, Ni, Mn, V, Al, Pb and Zn exceeded corresponding data from other sites, reflecting strong anthropogenic inputs through urban and industrial activities.

Element enrichment factors indicated that Fe, Cr and Mn are mostly of crustal origin, while, Zn, Cu, Cd and Pb are strongly of anthropogenic origin with EF values from 146 to 413.

The Fourier transformation was used to reveal monthly variations of the element bulk deposition fluxes. Spectral peaks with significant periods of about 3, 6 and 12 months confirmed the persistence of seasonal cycles. Significant seasonal variation of some elements (Ni, V, Al, Fe) indicated the impact of fossil fuel

combustion in power plants and small heating units. In addition, Unmix multivariate model identified three sources: mixed road dust, oil combustion and metal processing.

The results confirmed that spectral analysis and the Unmix method can be successfully applied for analysis, not only of daily pollutant concentrations as already used in many studies, but also of monthly deposition samples.

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