

Evaluation of the levels and sources of trace elements in urban particulate matter

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Abstract An assessment of air quality of Belgrade, Serbia, was performed by determining the trace element content in airborne daily PM_{10} and $PM_{2.5}$ samples collected from a central urban area. The ambient concentrations of Zn were the highest in $PM_{2.5}$ ($1,998.0 \text{ ng m}^{-3}$). Multivariate receptor modelling (principal component analysis and cluster analysis) has been applied to determine the contribution of different sources of specific metallic components in airborne particles. The obtained results showed that vehicle traffic and fossil fuel combustion in stationary objects were the main sources of trace metals in Belgrade urban aerosols.

Keywords Trace elements · PM_{10} · $PM_{2.5}$ · Urban air · Pollution sources · Statistical analysis

Introduction

Trace elements are released into the atmosphere by human activities, such as combustion of fossil fuels and wood, high temperature industrial activities and waste incinerations. Natural emissions are mainly from volcanoes, wind erosion, forest fires and the oceans. The combustion of fossil fuels constitutes the principal anthropogenic source for Be, Co, Hg, Mo, Ni, Sb, Se, Sn, and V. It also contributes to anthropogenic release of As, Cr, Cu, Mn, and

Zn. High percentages of As, Cd, Cu, Ni, and Zn are emitted from industrial metallurgical processes. Exhaust emissions from gasoline may contain variable quantities of Pb, Cu, Zn, Ni, and Cd (Pacyna and Pacyna 2001; Samara et al. 2003). 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 (Dockery and Pope 2006). A better understanding of particle size distribution and chemical composition is essential for assessing the health risks through inhalation (Li et al. 2003).

The objective of this study was to evaluate, for the first time, the trace metal concentrations in PM_{10} and $PM_{2.5}$ in the Belgrade urban atmosphere and to identify the main sources by principal component analysis (PCA), cluster analysis (CA) and analysis of meteorological conditions effects. 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.

Experimental

Particulate matter with aerodynamic diameter $<10 \mu\text{m}$ (PM_{10}) and $<2.5 \mu\text{m}$ ($PM_{2.5}$) was collected at two sites in an urban area, during the period from June 2003 to July 2005. The first sampling point was at an height of about 20 m, on the roof of the Rector's Office building of Belgrade University in Student Square, situated near the small city-park and the square with very high traffic density. As this sampling point is in the prime city centre, and the airflow is not blocked by any direction, it can be considered as representative for urban-background. The second sampling site was at the Faculty of Veterinary Medicine, at an height of

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about 4 m, a few meters away from a heavy traffic street and close to the big junction Autokomanda with the main state highway. The air distance between these two sampling points was about 2.5 km. Meteorological parameters were provided by the Hydro-Meteorological Institute of the Republic of Serbia.

Suspended particles were collected on Pure Teflon filters (Whatman, 47 mm) using two MiniVol air samplers (Airmetrics Co. Inc., 5 l min⁻¹ flow rate) provided with PM₁₀ and PM_{2.5} cut-off inlets. A total of 273 (209 PM₁₀ and 64 PM_{2.5}) valid daily samples were taken during the 2-year period. A detailed description of the sampling sites, sampling methodology, and the climate of Belgrade, was given in our previous work (Rajšić et al. 2004). After completion of gravimetric analysis, PM samples were digested in 0.1 M HNO₃ on an ultrasonic bath (Kyotani and Iwatsuki 2002) and analysed for a set of trace elements by graphite furnace atomic absorption spectrometry (GFAAS) using the transversely-heated graphite atomizer (THGA; Perkin Elmer AA 600) with Zeeman-effect background correction. For quality assurance, NIST standard reference material 2783 was used.

Multivariate analysis

Multivariate analysis, PCA, and CA were used to identify the possible emission sources of trace elements. PCA with varimax normalized rotation was also applied, which can maximize the factor loadings across variables for each factor. Factor loadings >0.71 are typically regarded as

excellent and <0.32 as very poor (Nowak 1998). In this study, all principal factors extracted from the variables with eigenvalues >1.0 were retained, as suggested by the Kaiser (1960). As a complementary analysis to PCA, CA was applied to the concentration data using Ward's method, with Euclidean distances as the criterion for forming clusters of elements and also to determine when two clusters were sufficiently similar to be linked.

Results and discussion

PM₁₀ and PM_{2.5} mass concentrations

Descriptive statistics for daily mass ($\mu\text{g m}^{-3}$) and trace element (ng m^{-3}) concentrations in PM₁₀ (a) and PM_{2.5} (b) sampled in urban Belgrade are presented in Table 1. The first emerging point is the high mean and maximum level of PM₁₀ and PM_{2.5}. The PM₁₀ mean mass concentration during the 2-year period ($68.4 \mu\text{g m}^{-3}$) exceeded the proposed annual limit of $40 \mu\text{g m}^{-3}$ (EU Directive 1999/30/EC). Of more concern was the mean PM_{2.5} concentration of $61.4 \mu\text{g m}^{-3}$, which was three times higher than the EC annual limit of $20 \mu\text{g m}^{-3}$ (EN 14907 2005).

Trace metal concentrations

The results for the total mean concentrations of individual metals indicate iron as the most abundant metallic element

Table 1 Statistical parameters of daily mass ($\mu\text{g m}^{-3}$) and trace elements concentrations (ng m^{-3}) in PM₁₀ (a) and PM_{2.5} (b) in Belgrade urban area from June 2003 to July 2005

(a)	PM ₁₀	Pb	Cu	Zn	Mn	Fe	Cd	Ni	V	Al	Cr
N	209	210	210	210	210	210	210	210	210	210	167
Mean	68.4	46.5	71.3	1,389.2	20.8	1462.9	1.4	17.7	36.6	873.8	10.2
SD	46.4	128.5	118.7	2,313.4	15.9	1,911.9	2.2	17.7	48.8	914.1	11.4
Maximum	333.8	1,525.0	947.5	17,239.6	72.7	20,283.0	17.7	107.7	282.4	6104.2	58.0
Minimum	2.8	0.5	0.2	2.1	0.2	0.5	<d.l.	0.4	0.6	2.1	0.1
Median	57.6	19.1	42.4	400.2	14.6	746.7	0.5	12.0	10.8	598.5	7.5
98th percentile	193.0	322.4	556.6	7,018.3	62.4	5,749.1	7.9	71.6	166.2	4126.9	46.3
(b)	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	1,998.0	15.2	1,081.2	0.9	28.4	59.8	1,180.3	6.2
SD	52.5	27.0	19.2	1,846.4	13.7	1,360.3	1.2	43.1	56.3	1,657.4	3.8
Maximum	286.6	193.9	99.6	6,642.4	50.7	5,996.5	4.8	315.0	248.5	7,875.0	26.0
Minimum	8.8	0.5	0.2	115.2	2.1	49.7	<d.l.	0.4	5.2	159.1	1.6
Median	51.9	13.5	17.4	1,153.3	10.1	488.4	0.4	17.3	50.2	500.7	5.9
98th percentile	237.3	66.8	80.6	6,101.7	47.9	5,380.6	4.1	107.9	208.7	7,307.3	13.2

N number of samples; SD standard arithmetic deviation

(1,462.9 ng m⁻³) in the PM₁₀. Zinc and Al concentrations in this fraction were very high, amounting to 1,389.2 and 873.8 ng m⁻³, respectively. The highest mean concentration in PM_{2.5} was 1,998.0 ng m⁻³ for Zn, followed by Al and Fe. Concerning Cu, a heavy metal characterised by its toxicity, relatively high mean values of 71.3 ng m⁻³ in PM₁₀ and 20.8 ng m⁻³ in PM_{2.5} were obtained. This trace element is associated with industrial activities, but in urban areas, road traffic (diesel engines and wearing of brakes) could be the most important source. Aluminium concentration was higher in PM_{2.5} than in PM₁₀. Although Al and Fe are typically crustal elements, if coupled with other elements, they can indicate the presence of anthropogenic sources, such as the steel production industry. The mean Ni concentration of 28.4 ng m⁻³ in the PM_{2.5} fraction was above the target value of 20 ng m⁻³ for PM₁₀ (Directive 2004/107/EC). Mean concentrations of Pb, Cd, V, and Mn did not exceed the current air quality guideline values (WHO 2002). Comparison with other studies, from different sites in industrial and urban areas, around the world, showed that the level of Zn in Belgrade urban area is higher than the values reported for most urban areas (Bem et al. 2003; Puxbaum et al. 2004). The mean value for V is also very high compared to those for downtown Athens (Manalis et al. 2005) and Zurich (Hueglin et al. 2005). The Pb concentrations obtained here were lower than the several other sites but had the same level as in Athens and Zurich. The seasonal variations of the trace metals in PM₁₀ and PM_{2.5} were also analysed. In winter, when domestic heating becomes a significant source of particles in the area, the amounts of all elements were elevated. The sources for the elements exhibiting winter enrichment are mostly connected with fossil fuel combustion in heating units. The exceptions were Cu, Cr, and Cd, which suggest that some local industrial source of these elements is more influential during the summer. The higher mean concentration of Al during the cold period indicated another anthropogenic source besides the main natural one. Comparison of trace element concentrations in PM from two different sites in the urban area of Belgrade showed, as expected, much higher concentrations for all elements at the Autokomanda (a traffic-exposed site) than at Student Square, except for Cr and Cd.

Correlation coefficients

In order to investigate the extent to which metal concentrations are related to road traffic, the relevant data set for carbon monoxide (CO), nitrogen oxides (NO_x) and sulphur dioxide (SO₂) for the whole PM sampling period were provided by the Institute of Public Health of Belgrade and correlated with PM data. Pearson's correlation coefficients

between meteorological parameters, combustion-related gases, PM mass and trace element concentrations in PM₁₀ and PM_{2.5} are calculated. As products of fossil fuel combustion, CO, NO, NO₂, and SO₂ were the most closely correlated ($r = 0.70$ – 0.95). The highest correlations among the trace elements in PM₁₀ were between V and Ni ($r = 0.69$), Al–Mn ($r = 0.66$), Zn–Mn ($r = 0.56$), Fe–Mn ($r = 0.55$) and Al–Zn ($r = 0.54$). Generally, mass concentrations of PM_{2.5} were positively correlated with the pollution gases, CO ($r = 0.80$), NO ($r = 0.74$), NO₂ ($r = 0.70$), and SO₂ ($r = 0.65$) and V ($r = 0.40$). The correlation of NO₂ with particle mass was more prominent than for SO₂, showing that particles from traffic emissions predominated. Lead was most closely connected to Cr ($r = 0.56$), Zn to Mn ($r = 0.82$), Al to Zn ($r = 0.66$), and Cu to Ni ($r = 0.49$).

Regarding correlations between metal concentrations and wind speed, only Cu and Cd in PM_{2.5} were significantly negative correlated with wind speed ($r = -0.36$, $r = -0.34$), suggesting that Cu and Cd are mostly from local sources. Vanadium and Ni were strong negatively correlated with temperature ($r = -0.56$, $r = -0.29$). This result supports the presumption that those elements originate from combustion of fossil fuels in heating units.

Principal component analysis and cluster analysis

Principal component analysis was applied to assist in the identification of pollutant sources. Factor loadings, with a varimax rotation for PM₁₀ and PM_{2.5} were calculated. Four factors were obtained for PM₁₀ (Table 2a), accounting for 73.5% of the total variance. Factor 1, dominated by Mn, Zn, Fe, Al, and Ni, accounted for 26.1% of the total variance and can be attributed to road dust. Its bulk matrix is soil, while correlation with other metals indicates some other sources, such as tire tread, brake-drum abrasion, yellow paint, etc. This factor is interpreted as representing road dust resuspension, which includes soil dust mixed with traffic related particles. Factor 2 is highly loaded with the fuel oil markers V and Ni and accounted for 17.4%. Factor 3, including Cu, Cd, and Pb, also accounted for 16.8% and may be associated with road traffic emission, as Cu and Cd are associated with diesel engines and wearing of brakes while Pb probably comes from exhaust emission, since road vehicles use leaded gasoline, or diesel fuel. Factor 4 accounted for 13.2%, with Cr and Pb as the main components and is most likely due to traffic exhausts. For PM_{2.5} data (Table 2b), four main groups may be identified, explaining 78% of the total variance. Factor 1 with the components Zn, Al, Mn, and Fe reflects resuspended road dust. Factor 2 has considerable loadings for Cr and Pb, possibly related to emissions from traffic and oil refineries.

Table 2 Principal component analysis after varimax rotation for the trace elements analyzed in PM₁₀ (a) and PM_{2.5} (b)

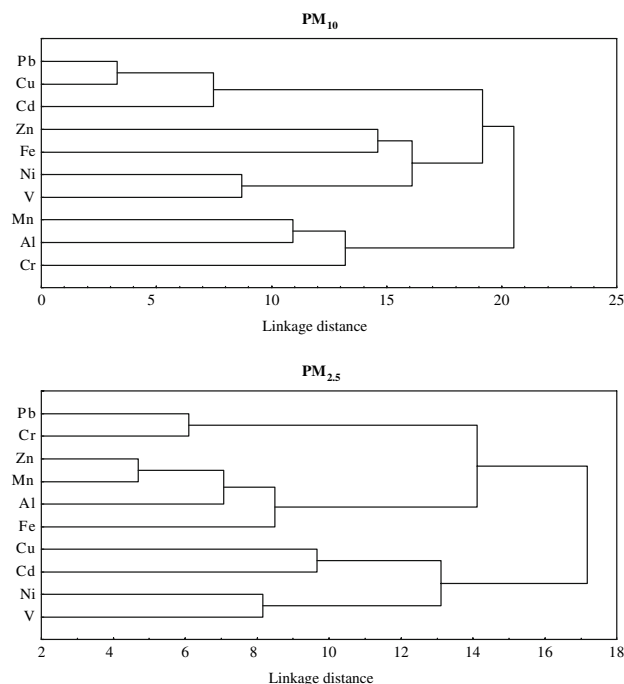
Element	Factor 1	Factor 2	Factor 3	Factor 4
(a)				
Pb	-0.07	0.04	0.41	0.72
Cu	0.01	0.13	0.86	0.02
Zn	0.78	0.09	-0.12	0.01
Mn	0.84	0.16	0.08	0.27
Fe	0.77	-0.03	0.04	-0.13
Cd	-0.08	-0.11	0.79	0.03
Ni	0.32	0.85	0.19	-0.01
V	0.02	0.94	-0.13	-0.05
Al	0.74	0.23	-0.14	0.22
Cr	0.24	-0.11	-0.2	0.81
Variance (%)	26.1	17.4	16.8	13.2
(b)				
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
Variance (%)	29.0	17.8	17.7	13.5

PCA loadings >0.5 are marked in bold

The third component is related to oil combustion as expressed by high factor loadings for Ni and V. The fourth component is probably characteristic of emissions by vehicles using diesel fuel and local industry (high loadings for Cu and Cd). Thus, the results of PC analysis indicate that resuspended road dust and fossil fuel combustion play the most significant roles.

The results of CA for the variables, trace elements in PM, were obtained as dendograms displaying four main clusters. In the dendogram for PM₁₀ (Fig. 1) 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 mainly associated with oil burning and emission from heavy fuel oil, while the fourth group includes Mn, Al, and Cr with a soil origin. All groups are connected at some distance, suggesting that the main sources of metals in PM₁₀ are fossil fuel combustion (traffic or stationary units) and resuspended dust, which is a mixture of soil and road dust.

The dendogram for trace elements in PM_{2.5} (Fig. 1) points to several groups connected to each other at some

**Fig. 1** Dendogram resulting from Ward's method of hierarchical cluster analysis of the trace elements in PM₁₀ and PM_{2.5}

distance. The first group contains only Pb and Cr, probably from leaded gasoline vehicular exhaust and may be also from the oil refinery in Pančevo, 25 km northeast of Belgrade. The second group containing Zn and Mn is closely connected with Al and Fe and, all together, they represent road dust. The third group includes Cu and Cd and is connected with the fourth group (V and Ni) at a higher level suggesting perhaps a common source for these groups. These results imply that the main source of trace elements in urban PM_{2.5} is traffic, with a considerable portion of resuspended road dust, and products of other fossil fuel combustion processes.

Enrichment factor analysis

In order to differentiate between the trace elements originating from human activities and those of natural origin, we calculated the enrichment factor (EF) in particulate matter (PM) for each element, according to the relation:

$$EF_{\text{element}} = \frac{(C_{\text{element}}/C_{\text{Fe}})_{\text{PM}}}{(C_{\text{element}}/C_{\text{Fe}})_{\text{crust}}}$$

using Fe as the referent element and the continental crustal composition given by Mason (1966). C_{element} and C_{Fe} are concentrations of element and Fe in PM and Earth crust. According to the degree of enrichment (Wang 2005; Tomašević et al. 2005), the elements are grouped as

follows: Zn, Cd and Pb, elements with a toxic character, were highly enriched ($EF > 100$) confirming that anthropogenic sources prevail; Cu was intermediately enriched (EF between 10 and 100); EF s for V and Ni were higher than 10 during the heating season. The enrichment factor for Zn was the highest (678 for PM_{10} and 1,320 for $PM_{2.5}$); EF for Cd was 237 for PM_{10} and 196 for $PM_{2.5}$ and for Pb 122 for PM_{10} and 75 for $PM_{2.5}$.

Meteorological parameters influence

The relation of trace element contents in PM with the prevalence of winds from different sectors was studied in an effort to elucidate the transport of metal particles from various zones of the city. The data set for the 2-year period was divided into 16 main wind directions. The most frequent wind directions were south-east (33%) and west (33%). The maximal PM_{10} ($334 \mu\text{g m}^{-3}$) and $PM_{2.5}$ ($287 \mu\text{g m}^{-3}$) mass concentrations and maximum concentrations of V and Ni occurred on 20/21 December 2003 (Autokomanda) with wind blowing from the south sector. Several local heating plants and the thermo-electric plant in Lazarevac (about 40 km distant) are situated in that direction.

For Zn, the most abundant metal in $PM_{2.5}$, maximum concentrations were connected with a wind blowing from the ESE direction, suggesting a possible influence from the steel industry complex in Smederevo, 40 km far from Belgrade.

Concerning the dependence of trace element concentrations on wind speed, 42% of the days had calm conditions, with a daily mean wind velocity under 2 m s^{-1} . The maximum concentration of Cu was also found during the calm days, indicating that local sources predominated. High concentrations of Pb in PM_{10} were observed when the wind was blowing from the WSW sector, indicating a contribution from the complex of coal-fired power plants (Nikola Tesla A, and Nikola Tesla B; Obrenovac, 20 km southwest of Belgrade), but in the fine fraction of suspended particles ($PM_{2.5}$) a high Pb content was connected with the north-easterly direction oil refinery, Pančevo. If we separate the days with calm conditions from the days with stronger winds, the highest Pb concentrations occurred when conditions were calm (wind speed $< 2 \text{ m s}^{-1}$) suggesting that road traffic was the most significant source of Pb in particles in the central area of Belgrade during the sampling period.

To obtain some quantitative measure of how much each direction contributed to metal contents in the Belgrade atmosphere, mean concentrations were multiplied by wind direction frequency. The PM mass concentration rise showed the prevailing transport from western and south-

eastern segments. The same trends were found for each separate metal.

Conclusion

In this work we demonstrated how to define the sources of ambient trace metals in particles using multivariate receptor modelling and meteorological analysis. The meteorological parameters revealed that higher trace element concentrations were associated with calm conditions, suggesting a great influence of local sources. The appearance of stronger W, SE and NE flows was responsible for the particles transported from the thermoelectric plants, refineries, chemical and steel industry. The PCA and CA showed that the main sources of trace metals in PM_{10} and $PM_{2.5}$ are combustion processes, e.g. emissions from mobile and stationary units, with the major contribution from traffic and resuspended road dust.

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References

- Bem H, Gallorini M, Rizzio E, Krzeminska M (2003) Comparative studies on the concentrations of some elements in the urban air particulate matter in Lodz city of Poland and in Milan, Italy. *Environ Int* 29:423–428
- Dockery DW, Pope III CA (2006) Critical review: health effects of fine particulate air pollution: lines that connect. *J Air Waste Manage Assoc* 56:709–742
- Hueglin C, Gehrig R, Baltensperger U, Gysel M, Monn C, Vonmont H (2005) Chemical characterization of $PM_{2.5}$, PM_{10} and coarse particles at urban, near-city and rural sites in Switzerland. *Atmos Environ* 39:637–651
- Kaiser HF (1960) The application of electronic computers to factor analysis. *Educ Psychol Meas* 20:141–151
- Kyotani T, Iwatsuki M (2002) Characterization of soluble and insoluble components in $PM_{2.5}$ and PM_{10} fractions of airborne particulate matter in Kofu city, Japan. *Atmos Environ* 36:639–649
- Li N, Sioutas C, Cho A, Schmitz D, Misra C, Sempf J, Froines JR, Nel A (2003) Ultrafine particulate pollutants induce oxidative stress and mitochondrial damage. *Environ Health Perspect* 111:455–460
- Manalis N, Grivas G, Protonotarios V, Moutsatsou A, Samara C, Chaloulakou A (2005) Toxic metal content of particulate matter (PM_{10}), within the greater area of Athens. *Chemosphere* 60:557–566
- Mason B (1966) Principles of geochemistry. Wiley, New York
- Nowak B (1998) Contents and relationship of elements in human hair for a non-industrialized population in Poland. *Sci Total Environ* 209:59–68
- Pacyna JM, Pacyna EG (2001) An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide. *Environ Rev* 9:269–298

- Puxbaum H, Gomiscek B, Kalina M, Bauer H, Salam A, Stopper S, Preining O, Hauck H (2004) A dual site study of $PM_{2.5}$ and PM_{10} aerosol chemistry in the larger region of Vienna, Austria. *Atmos Environ* 38:3949–3958
- Rajšić FS, Tasić DM, Novaković TV, Tomašević NM (2004) First assessment of the PM_{10} and $PM_{2.5}$ particulate level in the ambient air of Bgrade city. *Environ Sci Pollut Res* 11:158–164
- Samara C, Kouimtzis Th, Tsitouridou R, Kanias G, Simeonov V (2003) Chemical mass balance source apportionment of PM_{10} in an industrialized urban area of northern Greece. *Atmos Environ* 37:41–54
- Tomašević M, Rajšić S, Đorđević D, Tasić M, Krstić J, Novaković V (2005) Heavy metals accumulation in tree leaves from urban areas. *Environ Chem Lett* 61:753–760
- Wang X, Sato S, Xing B, Tamamura S, Tao S (2005) Source identification, size distribution and indicator screening of airborne trace metals in Kanayawa, Japan. *J Aerosol Sci* 36:197–210