An assessment of air quality in Belgrade urban area: PM\textsubscript{10}, PM\textsubscript{2.5} and trace metals

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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, present in the urban air of Belgrade, was performed. Air aerosol samples for PM\textsubscript{10} and PM\textsubscript{2.5} and trace metals were collected during June 2002 to July 2005 at representative locations in urban Belgrade area. Mass concentrations of PM\textsubscript{10} and PM\textsubscript{2.5} were determined gravimetrically, concentrations of 10 elements (Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn) were determined with graphite furnace atomic absorption spectrometry and source identification was carried out by Principal Factor Analysis. The mean PM\textsubscript{10} mass concentration of 68.4 \(\mu\text{g m}^{-3}\) exceeded the EC annual limit value of 40 \(\mu\text{g m}^{-3}\); 68 \% exceedance of the proposed PM\textsubscript{10} daily limit value (50 \(\mu\text{g m}^{-3}\)) was obtained and the mean PM\textsubscript{2.5} mass concentration of 61.4 \(\mu\text{g m}^{-3}\) was more than 3 times the EC annual mean value of 20 \(\mu\text{g m}^{-3}\). The limit values of toxic trace elements from WHO and EC Air quality guidelines were not exceeded except for Ni. SEM/EDS analysis has been employed to individually characterize particles collected. The results of this study shows that the majority of trace metals in aerosols come from traffic emissions and traffic-induced road-dust resuspension along with industrial activities.

1. Introduction
The measurement of levels of atmospheric particulate matter (PM) is a key parameter in air quality monitoring across the world owing to the cause/effect relationship between exposure PM levels and health impacts [1, 2]. A number of epidemiological studies [3-6] have demonstrated that acute and chronic health effects are related to the inhalable PM\textsubscript{10} (particulate matter with aerodynamic diameter less than 10 \(\mu\text{m}\)) exposure in the urban environment and some data also seem to indicate possible seasonal effects of the particulate matter on human health. 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.

As a result of health and environmental impacts, PM standards have been developed, especially for the PM\textsubscript{10} (thoracic fraction) and PM\textsubscript{2.5} (particulate matter with aerodynamic diameter less than 2.5 \(\mu\text{m}\)) (or “high risk” respirable fraction). European Commission (EC) has included PM\textsubscript{10} monitoring and limit values in the Air Quality Directive in 1999 [7]. The Directive establishes an annual limit for average value of 40 \(\mu\text{g m}^{-3}\), and a daily limit value of 50 \(\mu\text{g m}^{-3}\) (not to be exceeded more than 7 times per calendar year) to be met by 2010. Although the current focus of health-related sampling of particulate matter is on PM\textsubscript{10}, recent research pointed out the great health effect of fine particles,
PM$_{2.5}$, and even PM$_{1.0}$.[8,9] and signed that the health effects associated with PM are related mostly to anthropogenic emission sources. Recently, EC also established average PM$_{2.5}$ annual limit of 20 µg m$^{-3}$[10]. In our country, limit values are still related to total suspended particles and for urban areas daily limit amounts 120 µg m$^{-3}$ and mean annual value is 70 µg m$^{-3}$[11].

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 have a crucial role. Within the European programme for monitoring and evaluation of the long-range transmission of air pollutants (EMEP), measurements of PM$_{10}$ and trace metals, as highly toxic species have been introduced and the study of the mass concentrations, physico-chemical characteristics, possible emission 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.

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. 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 is emitted from industrial metallurgical processes. Exhaust emissions from gasoline may contain variable quantities of Pb, Cu, Zn, Ni and Cd. Zinc emission is also associated with tire rubber abrasion[12].

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[3, 4, and 13]. Urban anthropogenic particles are mainly in the PM$_{2.5}$ range and its sampling diminishes the interference of natural sources and reduces the loss of potentially volatile components such as ammonia and chloride. They could remain in the air with relatively long residence time and could efficiently penetrate human lungs. A better understanding of particle size distribution and chemical composition is essential for assessing the health risks through inhalation. Li et al. [14,15] demonstrated that smaller particles caused a greater response in epithelial cells of human airways than in those exposed to particles of different sizes. In addition to the PM mass limit values, also based on health impact criteria, recent EU standards set target (Cd, As, Ni) and limit (Pb) values for metals and PAH[7, 16]. Environmental technologies may have to be adopted in specific industrial spots to reach the target values.

Although particulate matter (PM), above all PM$_{10}$ or PM$_{2.5}$ is of great concern for public health, no systematic studies have been performed in Belgrade until recently. The studies on the quality of air in urban atmosphere related to suspended particles PM$_{10}$ and PM$_{2.5}$, 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 systematically sampling, measurements and analysis of interaction of the specific pollutants – PM$_{10}$ and PM$_{2.5}$ and trace metals in the ground level[17-23].

In this paper some of the results of the long-term project of the pollution monitoring concerning suspended particle mass and trace metal concentrations in ambient air of the Belgrade urban areas will be presented including physical and chemical characterization. The objective of the project was to assess air quality and to identify the main sources by multivariate receptor modeling (PCA, CA), enrichment factor (EF) calculation 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. The results presented in this work, are related only to part of the integrated project “Emission and transmission of pollutants in an urban atmosphere” which also includes measurements of trace metal concentration in bulk
atmospheric deposition, soil, plant leaves; and mosses, and natural and man made radionuclides (Be-7, Cs-137, Pb-210), ground level ozone and SO$_2$ concentrations.

2. Experimental

2.1. Sites and PM sampling.
Belgrade, the capital of Serbia, is situated on the junction of two rivers - Sava and Danube, with about 2 million inhabitants (figure 1). The climate of Belgrade is moderate continental with fairly cold winters and warm summers. The prevailing wind is N-NW, but a characteristic wind “Košava” (SE-ESE) blows with an annual frequency of 26% and an average speed of 4 m s$^{-1}$. In the winter, severe air pollution in the form of aerosol smog occurs frequently in the urban area of Belgrade, particularly during meteorologically calm (wind speed < 2 m s$^{-1}$) and stable conditions. The average age of passenger cars is more than 15 years, which means that leaded gasoline (0.4 g l$^{-1}$ Pb) is still widely used. There are many very old buses and trucks on the streets, which could be the major source of ambient PM$_{10}$, as diesel vehicles emit 10-20 times more particulate matter than gasoline vehicles [24]. There are 18 large heating plants with a total capacity of 2018 MW, run on natural gas or crude oil and 59 smaller plants run only on crude oil (approximately 193 MW). Fuel used for domestic heating consists mainly of coal or crude oil.

![Figure 1](image1.png)

Figure 1 The urban area of the city of Belgrade with location of sampling sites: A) Student Square; B) Botanic Garden and C) Autokomanda

Sampling of particulate matter PM$_{10}$ and PM$_{2.5}$ started on three sites in the very urban area of Belgrade in June 2002 and continued afterwards. The first sampling point was on the roof of the Rector’s Office building of Belgrade University in Student Square (A), at a height of about 20 m, near a small city-park. The square has high traffic density and a bus terminal. As this sampling point is in the very city center, on the rooftop and the airflow is not blocked by any direction, it can be considered as representative for urban-background concentrations. The second sampling episode was run at about 6 m height in the Botanic Garden (B) about 50 m far from heavy-traffic streets. The third sampling site was the platform above the entrance steps to the Faculty of Veterinary Medicine at a height of about 4 m from the ground, 5 m away from a street with heavy traffic and close to the big Autokomanda (C) junction with the main state highway. The traffic is controlled by street lights. This point can be
considered as traffic-exposed. From time to time, samples were taken at a control suburban site in Zemun, on the right bank of the Danube River, near the Institute of Physics. During the sampling, meteorological parameters including temperature, relative humidity, rainfall, wind direction and speed were provided by the Meteorological Station of the Hydro-Meteorological Institute of the Republic of Serbia (Hs = 132 m, $\varphi = 44^\circ 48' N$ and $\lambda = 20^\circ 28' E$), located inside the central urban area, very close ($\approx 200$ m) to the Autokomanda sampling site.

Suspended particles were collected on preconditioned (48 h at 20°C and constant relative humidity around 50%) and pre-weighed Pure Teflon filters (Whatman, 47 mm diameter, 2 $\mu$m pore size) and Teflon-coated Quartz filters (Whatman, 47 mm diameter) using two MiniVol air samplers (Airmetrics Co. Inc., 5 l min$^{-1}$ flow rate) provided with PM$_{10}$ and PM$_{2.5}$ cutoff inlets and positioned at 2 m height. The sampling time was 24 h, yielding a sample volume of 7.2 m$^3$. Routine maintenance of the samplers and calibration of the flow meters were often conducted in order to ensure the sampling quality. After particle collection, the filters were sealed in plastic bags and kept in portable refrigerators, in a horizontal position during transportation back to the laboratory where they were reconditioned for another 48 h. A total of 273 (209 PM$_{10}$ and 64 PM$_{2.5}$) valid samples were taken during the 2-year period. The sampling methodology used in this study was described in detail by Rajšić et al. [18].

2.2. Analytical methods.

The samples were handled and processed in a Class 100 clean laboratory, at the Institute of Physics, Belgrade. Particulate matter mass concentration was determined by weighting of the filters using a semi-micro balance (Sartorius, R 160P), with a minimum resolution of 0.01 mg. Loaded and unloaded filters (stored in Petri dishes) were weighed after 48 hours conditioning in a desiccator, in the clean room at a relative humidity of 45-55% and a temperature of $20 \pm 2$ °C. Quality assurance was provided by simultaneous measurements of a set of three “weigh blank” filters that were interspersed within the pre- and post-weighing sessions of each set of sample filters and the mean change in “weigh blank” filter mass between weighing sessions was used to correct the sample filter mass changes.

After completion of gravimetric analysis, PM samples were digested in 0.1 mol dm$^{-3}$ HNO$_3$ on an ultrasonic bath and analyzed 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 calibration, standard solutions containing all metals of interest were prepared using Merck certified atomic absorption stock standard solutions. An extraction procedure with dilute acid was used for the evaluation of elements which can become labile depending on the acidity of the environment. This procedure gives valid information on the extractability of elements, since the soluble components in an aerosol are normally dissolved by contact with water or acidic solution in the actual environment [25].

Scanning electron microscopy (SEM) coupled with Energy-Dispersive X-ray analysis (EDX) was used for the characterization (size, size distribution, morphology and chemistry of particles) and source apportionment of atmospheric particulate matter. One PM sample per episode was analyzed with the SEM/EDX according to the EPA Guidelines [26]. Prior to analyses three small sections of the filters (5 x 5 mm) were mounted on the SEM stubs and then coated with 10 nm layer of high purity gold using vacuum evaporator (Balzers/Union FL-9496). 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. 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. The elemental composition of selected particles in the secondary electron images was deduced from an energy dispersive X-ray spectrum in the energy range of 0 – 20 keV, collected from the selected particles for a spectrum acquisition time of 100 s. 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 % [22].
2.3. Source identification and source apportionment

Mass concentration and elemental composition data were analyzed using principal component analysis (PCA) in order to identify main source categories of PM$_{10}$ and PM$_{2.5}$. The extracted principal components were interpreted as source categories contributing to PM concentrations at the sampling site. The identification of source categories was done by examination of the profiles of the principal components, i.e., loadings of the elements and other variables on the varimax (orthogonally) rotated principal components. Factor loadings > 0.71 are typically regarded as excellent and < 0.32 as very poor [27]. In this study, all principal factors extracted from the variables with eigenvalues > 1.0 were retained, as suggested by the Kaiser criterion [28]. When PCA with VARIMAX normalized rotation was performed, each PC score contained information on all of the metal elements combined into a single number, while the loadings indicated the relative contribution each element made to that score.

Cluster analysis (CA), as a complementary analysis to PCA, was performed to classify elements of different sources further on the basis of their chemical properties. 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. In general, this form of CA is regarded as very efficient, although it tends to create small clusters. As the variables had large differences in scaling, standardization was performed before computing.

2.4. Enrichment factor

Enrichment factors (EFs) were used to differentiate between the trace elements originating from human activities and those of natural origin and to assess the degree of anthropogenic influence. There is no rule for the reference element choice and Si, Al, and Fe have been used as the most common elements for this purpose [29,30]. In this study, Fe was used as the reference element with upper continental crustal composition given by Mason [31]. EFs close to 1 point to a crustal origin, while those greater than 10 are considered to originate from an anthropogenic source.

3. Results and discussion

3.1. A first assessment of PM$_{10}$ and PM$_{2.5}$ particulate level in the ambient air of Belgrade

Daily mass concentrations of 96 PM samples (PM$_{10}$ and PM$_{2.5}$) were determined by gravimetric analysis of filters that were exposed to urban air in Belgrade during the year 2002. Statistical parameters of daily PM mass concentrations (µg m$^{-3}$) over two main seasons: the season without heating - summer period and the winter period - heating season are presented on table 1.

| Period   | N  | X$_{A}$ | S.D. | Max | Min | Median | 98thPercentile |
|----------|----|---------|------|-----|-----|--------|----------------|
| PM$_{10}$|     |         |      |     |     |        |                |
| Summer   | 22 | 56      | 37   | 164 | 12  | 54     | 158            |
| Winter   | 25 | 96      | 73   | 362 | 21  | 83     | 284            |
| Whole period | 47 | 77      | 62   | 362 | 12  | 57     | 214            |
| PM$_{2.5}$|     |         |      |     |     |        |                |
| Summer   | 17 | 35      | 16   | 78  | 3   | 36     | 68             |
| Winter   | 32 | 75      | 61   | 333 | 12  | 56     | 227            |
| Whole period | 49 | 61      | 53   | 333 | 3   | 44     | 169            |

N – Number of samples; X$_{A}$ – Arithmetic mean; S.D. – Standard arithmetic deviation;

The PM$_{10}$ mean 24-hours mass concentration value, over whole measuring period was 77 µg m$^{-3}$, almost twice as much as the annual limit in European Union (40 µg m$^{-3}$) and more than 60% of days
had mean daily concentrations above limit value of 50 µg m⁻³. Average PM₂.₅ mass concentration exceeded the EC annual limit of 20 µg m⁻³ [10] by a factor of 3.

The suspended particles concentration in Belgrade, during the summer, was not as high as expected taking into account that leaded gasoline was still in wide use in the country, as well as the presence of a number of old buses and trucks on the streets. We presumed, that during the summer, when the traffic density is reduced due to summer vacations, urban background PM level (56 µg m⁻³) for Belgrade was slightly above daily limit value according to EU Directive [7].

On average, a seasonal variation was found, as higher concentrations occurred during the winter period. Mean 24 h mass concentrations were 96 µg m⁻³ and 75 µg m⁻³ for PM₁₀ and PM₂.₅, respectively in winter period (officially from 15 October to 15 April), being almost twice as much as average mass concentration for the summer period. This 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. inversed layers, low temperature and stagnation of air masses. Higher winter PM₁₀ concentrations were also recently presented in some other studies of European cities [32 - 35]. Seasonal variation is in agreement with the results for other air pollutants relevant for traffic valuation. The concentrations of CO, NO₂, Pb, HC and HCHO have been measured at several main cross-streets in Belgrade by the Institute of Public Health of Serbia “Dr Milan Jovanović-Batut”. The concentrations of all pollutants were minimum during July and August (reduced traffic volume due to summer vacation) and maximum during the coldest winter months (November, December and January). For all pollutants, the annual mean values were above limit values.

The winter episode with simultaneous sampling of PM₁₀ and PM₂.₅ run at the Faculty of Veterinary Medicine (Autokomanda), showed that PM₁₀ and PM₂.₅ concentrations data were 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 and 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 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. For both seasons, the PM concentrations were higher when prevailing wind directions was south-westerly. 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 sulphate aerosols [36].

3.2. PM₁₀ and PM₂.₅ mass and trace metal concentrations

During the next sampling episode between June 2003 and July 2005, daily mass (µg m⁻³) and trace element (ng m⁻³) concentrations were calculated in PM₁₀ and PM₂.₅. The high mean and maximum levels of PM₁₀ and PM₂.₅ were observed; the PM₁₀ mean mass concentration during the 2-year period (68.4 µg m⁻³) exceeded the proposed EC annual limit of 40 µg m⁻³ [7]. Of more concern was the average PM₂.₅ concentration of 61.4 µg m⁻³ for the 2-year period, which was three times higher than the EC annual limit of 20 µg m⁻³ [10].

The average PM₁₀ and PM₂.₅ mass concentrations (68.4 µg m⁻³ and 61.4 µg m⁻³) in Belgrade were higher than in many European cities, although high mean PM₁₀ mass concentrations were reported in this region. Thus, Thessalonica, Greece, had mean values of 82, 78, and 84 µg m⁻³ [37] Athens mean values of 75 µg m⁻³ for PM₁₀ and 40 µg m⁻³ for PM₂.₅ [33], while mean values of 72, 60, 70 µg m⁻³
were found in Bulgaria, Hungary and Romania [38]. Our results for PM$_{10}$ and PM$_{2.5}$ concentrations are similar with those reported earlier for the present site [18-20, 23].

The results for the total mean concentrations of individual metals indicate iron as the most abundant metallic element (1462.9 ng m$^{-3}$) in the suspended particles with diameter less than 10 µm (PM$_{10}$). Zn and Al concentrations in this fraction were very high too. The highest mean concentration in fine fraction of particulate matter (PM$_{2.5}$) was 1998 ng m$^{-3}$ for Zn, followed by Al and Fe. The high Zn concentration implies that emissions from anthropogenic sources contributed significantly to its level in the particulate matter. Zinc is a reliable tracer for unleaded fuel and diesel powered motor vehicle emissions [39]. Moreover, Zn can be released, in large amounts, from wear and tear of vulcanized vehicle tires, corrosion of galvanized automobile parts or various industrial activities.

Comparison of trace element concentrations in PM from two different sites in the urban area of Belgrade, showed much higher concentrations for all elements at the Autokomanda site than at Student Square except for Cr and Cd, which were slightly elevated at Student Square. This result was expected, as the Autokomanda was traffic-exposed site, situated on the very busy road junction and the sampling device at Student Square was mounted at the roof of the five storey Rector’s Office building.

At the suburban Danube River bank site, in Zemun, near the Institute of Physics, the mean concentration levels of the anthropogenic elements Zn, Cu, Pb, V, Ni and Cd were lower than those at the two urban sites. The opposite occurred for typical crustal elements. Thus, the highest concentrations of Al and Cr were found at the Danube River bank, although Cr may also have been emitted from the oil refinery and chemical industrial complex near Pancevo, approximately 24 km northeast of Belgrade. The contents of Fe and Mn in PM$_{10}$ sampled at the Danube River bank site were also higher than those in samples collected on the roof of the Rector’s Office building in Student Square, but not higher than in samples from the traffic oriented site. This is one more indication that traffic is a significant source of these two metals.

3.3. Principal component analysis and cluster analysis

Multivariate methods, Principal Component Analysis (PCA) and Cluster Analysis (CA) were used to identify the combined effect of several measured variables. Principal Component Analysis with Varimax rotation on the dataset of selected metals and particle mass concentrations in PM$_{10}$ and PM$_{2.5}$ was performed for the source identification. Table 2 presents four rotated factor loadings with eigen values >1, embodying and explaining more than 73% of total variance for the case of PM$_{10}$. The first factor, explaining most of the variance (26%), has high loadings for Mn, Zn, Fe, Al, and Ni, 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. Therefore, this factor is interpreted as representing road dust resuspension, which includes soil dust mixed with traffic related particles. Zn could be released from wear and tear of vulcanized vehicle tires and corrosion of galvanized automobile parts [14, 15, 40]. Adriano [41] also reported that corrosion of galvanized steel is a major source of Zn emission in the surface environment. This is probably a significant source, as numerous old tracks, buses, cars and tires are present on the Belgrade streets. The second factor, with 17% of the total variance, shows high loading for fuel oil markers V and Ni. The third factor, including Cu, Cd and Pb, also accounted for 17%, while Factor 4 accounted for 13% with Cr and Pb as the main components. Factor 3 may be associated with road traffic emission. Cu and Cd are associated with diesel engines and wearing of brakes. Pb probably comes from exhaust emission, since road vehicles use leaded gasoline or diesel fuel. Factor 4 with the Pb component is most likely due to traffic exhausts. The results of CA are in good agreement with PCA and correlation study, showing that metals with common sources have a strong inter-relationship; emission of metals most associated with traffic (Zn,Cu, Fe, Mn, Pb, Al) is probably more related to suspension or resuspension of road dust, which includes soil dust mixed with traffic related particles, than direct exhaust emission [22, 42].
Table 2. Principal component analysis after Varimax rotation for the trace elements analyzed in PM$_{10}$

| a)Element | Factor 1 | Factor 2 | Factor 3 | Factor 4 |
|-----------|----------|----------|----------|----------|
| 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
PCA loadings > 0.5 are marked in bold)

Although Al and Fe are typically crustal elements, if coupled with other elements, they can indicate the presence of anthropogenic sources, such as steel production industry (Smederevo, 50 km in SE direction). Nickel is mainly associated with fossil fuel use, oil burning and emissions from industrial sources. The mean Ni concentration of 28.4 ng m$^{-3}$ in the PM$_{2.5}$ fraction was above the critical value of 20 ng m$^{-3}$ for PM$_{10}$ [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 [43].

3.4. Enrichment factor analysis
Enrichment factors (EFs) for the mean concentration of trace elements in PM$_{10}$ and PM$_{2.5}$, calculated using Fe as a reference, are presented in figure 2. The EF sequence in the Belgrade urban area for the sampling period was: Zn>Cd>Pb>Cu>V>Ni>Cr>Fe>Mn>Al. According to the degree of enrichment, the elements are grouped as follows [44]: Zn, Cd and Pb, elements with a toxic character, were highly enriched (EF>100) confirming that anthropogenic sources prevail over natural inputs for these elements; Cu was intermediately enriched (EF between 10 and 100); EFs for V and Ni were higher than 10 during the heating season and in the PM$_{2.5}$ fraction; Cr was less enriched (EF less than 10) probably attributed to both natural and anthropogenic sources. These results confirm previous findings related to the assessment of trace element pollution in the total atmospheric deposition in urban Belgrade [45].

EF values around 1 were found for Al, Mn and Fe, suggesting a mainly crustal origin, although an earlier analysis implicated an important influence of anthropogenic sources on the amounts of these metals. Because dilute acid was used for the extraction, the concentrations would be slightly underestimated for some common crustal elements, especially for the coarse particle size range [46, 47]. The highly enriched elements are generally volatile elements, primarily emitted from high-temperature processes (e.g. fossil fuel combustion and smelting), and these elements are usually associated with small and medium sized aerosol particles and can be transported to remote areas. Thus, EF for Zn was the highest (678 for PM$_{10}$ and 1320 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$_{2.5}$. 

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Figure 2 Enrichment factor values of trace elements in PM$_{10}$ and PM$_{2.5}$ sampled in Belgrade urban area from June 2003 to July 2005

3.5. SEM/EDX analysis of suspended particles

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. 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 [26].

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.

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 3-5. 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 3.
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) [48, 49]. In Belgrade urban area, this type of particles originates mostly from individual heating emissions and coal-fired power plant (Nikola Tesla A, B, Obrenovac).

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 also found (figure 4). Biological particles (pollen, bacteria, fungi, spores etc.) are recognized (by their characteristic morphology) as important constituents of the coarse particle fraction in the PM\textsubscript{10} samples, especially during summer period and an example of such a particle.

4. Conclusions

24-h atmospheric aerosol samples have been collected at three representative sites in the very urban area of Belgrade from July 2002. PM mass concentrations were determined by microbalance and trace element content was analysed by Atomic absorption spectroscopy, all in order to provide information about the annual average and daily maximum concentrations and to compare them to the corresponding EU standards. The results may be used in the future to assess the effectiveness of the implemented emission control strategy.

The annual mean PM\textsubscript{10} and PM\textsubscript{2.5} mass concentrations exceeded the European Union air quality annual standard. Chemical analysis of the metal content showed that Zn (1998 ng m\textsuperscript{-3}) was the most abundant element in PM\textsubscript{2.5}. The mean Ni concentration of 28.4 ng m\textsuperscript{-3} in the PM\textsubscript{2.5} fraction was above the critical value of 20 ng m\textsuperscript{-3} (for PM\textsubscript{10}) according EC (2003) regulations.

The meteorological study revealed some differences in concentrations, stratified by prevailing wind directions. Data evaluation showed 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 is responsible for the transport of particles originating from the thermoelectric plant complex and industrial zones surrounding Belgrade.

The Principal Component Analysis and Cluster Analysis resulted in tentative source categories for each site. Quantification of their contribution showed that the main contributors to trace metals in PM\textsubscript{10} and PM\textsubscript{2.5} generated in Belgrade are combustion sources, e.g. emissions from mobile and stationary units, with the major contribution from traffic emissions, road dust resuspension and industrial activities.

Enrichment factors (EFs) for elements in aerosols were determined to evaluate anthropogenic versus natural sources. Elements with a toxic character (Zn, Cd, Pb and Cu) were highly enriched, confirming that they originate mainly from anthropogenic sources.

Suspended particulate matter was 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\textsubscript{2.5}, as well as the presence of the mode of coarse particles in PM\textsubscript{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 confirmed 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 source identification of this study is in agreement with the majority of the reported data on this subject and shows that the majority of trace metals in aerosols come from traffic emissions and traffic-induced road-dust resuspension along with industrial activities.

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