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Assessment of Air Quality in an Urban Area of Belgrade, Serbia

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1. Introduction

Clean air is considered to be a basic requirement for human health and well being. Various chemicals are emitted into the air from both, natural and anthropogenic sources. In spite of the introduction of cleaner technologies in industry, energy production and transport, air pollution remains a major health risk and tighter emission controls are being enforced by many governments. In humans, the pulmonary deposition and adsorption of inhaled chemicals from the air can have direct consequences on health. Public health can also be indirectly affected by deposition of air pollutants in environmental media and uptake by plants and animals, resulting in chemicals entering the food chain or being present in drinking water, and thereby constituting additional sources of human exposure. Furthermore, the direct effects of air pollutants on plants, animals and soil can influence the structure and function of ecosystems, including their self-regulation abilities, thereby and thus affecting the quality of life.

According to the most recent update of the WHO (World Health Organization) air quality guidelines, many studies were published that had investigated the effects of air pollution on human health. Particulate matter pollution is nowadays one of the problems of the most concern in great cities, not only because of the adverse health effects, but also for the reducing atmospheric visibility and affect to the state of conservation of various cultural heritages (Van Grieken & Delalieux, 2004). On a global scale, particulate matter (PM) also influences directly and/or indirectly the Earth's radiation energy balance, and can subsequently impact on global climate change (IPCC, 2001).

The measurement of the levels of atmospheric particulate matter is a key parameter in air quality monitoring throughout the world regarding the cause/effect relationship between exposure PM levels and health impacts (WHO, 2002; WHO, 2003). A number of epidemiological studies (Dockery & Pope, 1994, 2006; Schwartz et al., 1996, 2001) have demonstrated that acute and chronic health effects are related to the inhalable PM_{10} (aerodynamic diameter less than 10 μm) exposure in the urban environment, and some data also seem to indicate possible seasonal effects of the particulate matter on human health. 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 of PM, more rigorous regulations are in force in the USA and European countries. PM standards, issued by European Commission (EC), have included PM_{10} monitoring and limit values in the Air Quality Directive in 1999 (EC, 1999). Directive established in the first stage, annual limit value of 40 μg m^{-3} and 24 h limit value of 50 μg m^{-3} (not to be exceeded more than 35 times in a calendar year) to be met by 2005, and in the second stage annual limit value of 20 μg m^{-3} and 24h limit value of 50 μg m^{-3} (not to be exceded more than 7 times a calendar year) to be met by 2010.

Although the current focus on health-related sampling of particulate matter is on PM_{10}, recent research pointed out more serious health effect of fine particles, $PM_{2.5}$ (aerodynamic diameter less than 2.5 μm), and even $PM_{1.0}$ (aerodynamic diameter less than 1.0 μm) (Vallius et al., 2005; Ariola et al., 2006) and signed that the health effects associated with PM are related mostly to anthropogenic emission sources. EC has also established average $PM_{2.5}$ annual limit of 20 μg m^{-3} (EN 14907, 2005) and current WHO Air Quality Guidelines set 10 μg m^{-3} as annual average and 25 μg m^{-3} as 24 h average (WHO, 2006).

Within the European Program 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. Spatial and temporal variation of atmospheric aerosol particles also 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 an understanding of particle formation, transport, transformation and deposition mechanisms, as well as, the impact of particles inhaled by a respiratory system.

The studies of the transport and mobilization of trace metals up to now have attracted attention of many researchers (Nriagy & Pacyna, 1988; Pacyna et al., 1989; Alcamo et al., 1992). Trace metals are persistent and widely dispersed in the environment and interacting with different natural components results in toxic effects on the biosphere.

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, V, Co, Ni, Se, Mo, Sn, Sb, and Hg. It also contributes to anthropogenic release of Cr, Mn, Cu, Zn, and As. High percentages of Ni, Cu, Zn, As, and Cd are emitted from industrial metallurgical processes. Exhaust emissions from gasoline may contain variable quantities of Ni, Cu, Zn, Cd, and Pb (Samara et al., 2003). Several trace metals are emitted through the abrasion of tires (Cu, Zn, Cd) and brake pads (Sb, Cu), corrosion (V, Fe, Ni, Cu, Zn, Cd) lubricating oils (V, Cu, Zn, Mo, Cd) or fuel additives (V, Zn, Cd, Pb) (Pacyna & Pacyna, 2001; Ward, 1990; Sutherlan & Tolosa, 2000). The platinum group of elements, Rh, Pd and Pt, represent a relatively new category of traffic related trace metals in the environment, specially urban one, due to their application in automobile catalytic converters since the beginning of the 1980s (Haus et al., 2007).

Most of the trace metals are emitted in particulate form (Molodovan et al., 2002) and are present in almost all aerosol size fractions, but mainly accumulated in the smaller particles (Espinosa et al., 2001). This has a great effect on the toxicity of metals since the degree of respiratory penetration depends on particle size (Dockery and Pope, 1994, 2006; Espinosa et al., 2001). Urban anthropogenic particles are mainly in the $PM_{2.5}$ range and their 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, and cause greater response in epithelial cells of human respiratory tract (Li et al., 2002, 2003). In addition to the PM mass limit values, also based on health impact criteria, recent European Union (EU) standards set target (Ni, As, Cd) and limit (Pb) values for metals and polycyclic aromatic hydrocarbons (PAHs) (EC, 1999; Directive 2004/107). Environmental technologies may have to be adopted in specific industrial spots to reach the target values. For aimed reduction of PM_{10} or $PM_{2.5}$ levels detailed knowledge of sources and their respective contribution to the PM levels, is required.

Most trace elements in terrestrial ecosystems originate from atmospheric wet and dry deposition. From a biogeochemical perspective, the characterization of total atmospheric deposition is relevant in order to identify the variability and sources of the atmospheric pollutants (Azimi et al., 2005). Direct collection of atmospheric deposition using bulk sampling devices offers a practical approach to monitor atmospheric heavy metal deposition providing valuable information on the influences of atmospheric inputs of heavy metals on the surface environment (Morselli et al., 2003; Azimi et al., 2003). Bulk sampling has been extensively used, since the samplers are easier to operate than wet-and-dry ones. The limitation of this sampling method is mainly possible under-estimation of fluxes; advantages are integration of samples over 1 month and the possibility of large-scale application with low-cost equipment.

Studies on atmospheric contamination have frequently been limited by high cost of instrumental monitoring methods and difficulties in carrying out extensive sampling in time and space. For these reasons, there is an increasing interest in using indirect monitoring methods such as the use of organisms that may act as bioaccumulators. Biomonitoring of trace elements from atmospheric deposition can be currently evaluated by environmental biomonitors such as mosses, lichens and higher plants (Rühling & Tyler, 1971; Steinnes et al., 1992; Markert, 1993; Bargagli, 1998; Bargagli et al., 2002; Adamo et al., 2003). Native mosses and lichens have often been used in passive biomonitoring, and have several advantages as compared to higher plants. They lack a developed root system, so they rely on atmospheric wet and dry deposition for their mineral nutrition; they have a high surface/volume ratio and cation exchange capacity; unlike many other plants, they lack variability of morphology through the growing season and they have no cuticle (Tyler, 1990; Bargagli, 1998).

The heavy metals in mosses survey, first introduced in Scandinavia (Rühling & Tyler, 1968), has been repeated since 1980, at five-years intervals, with an increasing number of participating countries (http://icpvegetation.ceh.ac.uk/intro.htm; UNECE ICP Vegetation, 2003). The survey has provided data on heavy metals concentration in naturally growing mosses throughout Europe, and there is substantial database for assessment of pollution level and identification of pollution sources. The standardized procedures for obtaining moss samples included collecting the preferred moss species: *Hylocomium splendens*, *Pleurozium schreberi*, *Hypnum cupressiforme*. As previously recommended species are not widespread in arid areas of southern European countries, it is necessary to find corresponding alternate moss species for monitoring studies.

In highly polluted areas of industrial or urban environment, terrestrial plants can act as appropriate bioindicators and biomonitors. Although biomonitoring of air quality using plants has been practiced for many years, in many European countries, it has still not been applied at a satisfactory level, due to different, and even opposite results, depending, first of all, on plant species. Therefore, efforts towards setting up the large European projects to

biomonitor air quality have been made recently (Klumpp et al., 2002). Trees are very efficient at trapping atmospheric particles, and they have a special role in reducing the level of fine, "high risk" $PM_{2.5}$, with the potential to cause serious human health problems. Thus, the use of plant leaves, primarily, as accumulative biomonitors of trace metal pollution has attained great ecological importance (Markert, 1993; Bargagli, 1998; WHO, 2000; Mignorance & Rossini, 2006).

Leaves of various tree species, both evergreen and deciduous, have been tested for this purpose in urban areas (Alfani et al., 1996; Monaci et al., 2000), including a search for sensitive tree species and approval of the validity of using such leaves as biomonitors. It is well known that metal pollution leads to physiological disturbances in plants and affects the biogeochemical balance and stability of their habitats. Metal uptake in higher vascular plants takes place through their root system, additionally through the leaves and, therefore, it is difficult to distinguish whether the accumulated elements originate from the soil or from the air (Harrison & Johnston, 1987; Verma & Singh, 2006). The research of heavy metals contamination of vegetation requires the use of standard methodological procedures (Markert, 1993; Bargagli, 1998). One of the most important is the representative sampling of plant material.

Ground level ozone (O_3) and other photochemical oxidants have become pollutants of concern because elevated concentrations are known to cause detrimental effects and threaten human health (WHO, 2003; Mulholland et al., 1998), vegetation and objects. Moreover, in recent years there have been numerous reports of an association between increases in particle air pollution (PM_{10}) and ozone concentration (Meng et al., 1997; Mulholland et al., 1998; Ying & Kleeman, 2003). In order to protect human health and ecosystem, EU has set limits for ozone concentrations (Directive 2002/03/EC). The information threshold is the same as in the previous Directive being 180 μg m^{-3} (the hourly average concentration of 240 μg m^{-3}, measured over three consecutive hours is set as an alert threshold). High ozone levels are mainly observed during periods with warm and sunny weather in combination with stagnant air masses and the build-up of precursor substances, such as nitrogen oxides (NO_x), carbon monoxide (CO) and volatile organic compounds (VOCs).

Although 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 the first measurements of their mass concentrations have been initiated in Serbia in 2002, and are still in progress. The results of preliminary investigations revealed the need for the continuous and long-term systematical sampling, measurements and analysis of interaction of the specific pollutants – PM_{10}, $PM_{2.5}$ and trace metals in the ground level (Tasić et al., 2001; Rajšić et al., 2004a, b).

In 2002, the national project "Air Quality Studies in Belgrade Urban Area: Suspended Particles, Heavy Metals and Radionuclides", financed by The Ministry for Science and Environmental Protection of the Republic of Serbia, has started. At present, the project "Emission and Transmission of Pollutants in an Urban Atmosphere", is running, and includes measurements of trace and other elements (Al, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Cd, Pb, etc.) concentration in particulate matter, PM_{10} and $PM_{2.5}$, bulk atmospheric deposition, soil, plant leaves, mosses, and natural and man made radionuclides (Be-7, Cs-137, Pb-210), and ground level ozone. The objective of the project is to assess air quality and to identify

the main sources by multivariate receptor modeling (PCA, CA), enrichment factor (EF) calculation, meteorological conditions and air back trajectories analysis.

In this review, we report some of the results of the integral monitoring of air quality in Belgrade urban area in order to evaluate the impact of airborne trace metals on the pollution load for the period from 2002 to 2006. Some of the results concerning suspended particle mass and trace metal concentrations in ambient air of the Belgrade will be presented, including physical and chemical characterization, with the aim to examine elemental associations and to indicate the main sources of trace and other metals in the city. The results of this long-term project of the pollution monitoring 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. This information is crucial in environmental quality assessment, and can lead to the determination of a possible exceedance of the critical loads.

Also, the aim of our research was to set up a reliable methodological approach in sampling and analytical procedures for investigation of moss and deciduous leaves biomonitoring, and to evaluate the reliability of investigated species for biomonitoring of trace metal pollution in Belgrade urban areas. The higher plants leaves, horse chestnut (*Aesculus hippocastanum* L.) and Turkish hazel (*Corylus colurna* L.) widely spreaded in the city have been sampled and their trace metal accumulation abilities analysed. Some physical and chemical characteristics of particles deposited on leaf surfaces have been studied as well. Mosses *Brachythecium sp.* and *Eurhynchium sp.*, used in this study, more common in Serbia, were investigated for their accumulation capability.

The first data set for ozone and correlation to relevant meteorological parameters obtained in Belgrade during several sampling periods in Belgrade will be presented, and consequently, important information about the local air quality.

Meteorological conditions favorable for the build up of ozone are frequent, in Belgrade and the surrounding area, from early spring to early autumn. During this period, photochemical smog events often show different features and are difficult to assign to a particular pattern. Although ozone levels were measured in Belgrade sporadically during the early 80-ties, and each season starting from 1991, few of these data have been published and the information is scant and difficult to find (Vukmirović et al., 1987). Therefore, it would be useful to present the more complete results of our measurements, stressing the main characteristics of the photochemical episodes recorded in the Belgrade area. As there is no available data on ozone measurements from the area of the former Yugoslavia (except Slovenia and FYROM) in European Environmental Agency reports, it is important to increase the geographical coverage of the current state of knowledge with respect to ozone seasonal cycles in the troposphere over Europe.

2. Experimental Methods and Procedures

2.1 Studied Sites and Sampling

Belgrade, (H_s = 117 m, φ = 44^0 49'14''N and λ = 20^0 27' 44''E) the capital of Serbia, with about 2 million inhabitants, is situated at the confluence of the Sava and Danube rivers (Fig. 1). In the winter, severe air pollution in the form of aerosol smog occurs frequently in the urban area of Belgrade, particularly under the meteorologically calm (wind speed < 2 m s^{-1}) and stable conditions. The total number of vehicles in the year 2002 was more than 350,000, including 22,000 heavy-duty vehicles and over 1,000 city buses using diesel. The average

age of passenger cars is more than 15 years, which means that leaded gasoline (0.4 g l^{-1} Pb) is still in wide use in the country. There are many old buses and trucks on the streets and it could be the significant major source of ambient PM_{10}. There are 18 bigger heating plants with a total capacity of 2018 MW, run with natural gas or crude oil and 59 smaller plants run only with crude oil (approximately 193 MW). Fuel used for domestic heating consists mainly of coal or crude oil and natural gas in last few years.

The climate of Belgrade is moderate continental with fair cold winters and warm summers. The prevailing wind is N-NW, but characteristic wind "Košava" (SE-ESE) blows with an annual frequency of 26% and an average speed of 4 m s^{-1} (Unkašević, 1999). Fortunately, "Košava" comes from relatively unpolluted area. This wind effectively improves the horizontal dispersing and dilution of pollutants in the ground-level atmosphere of Belgrade city.
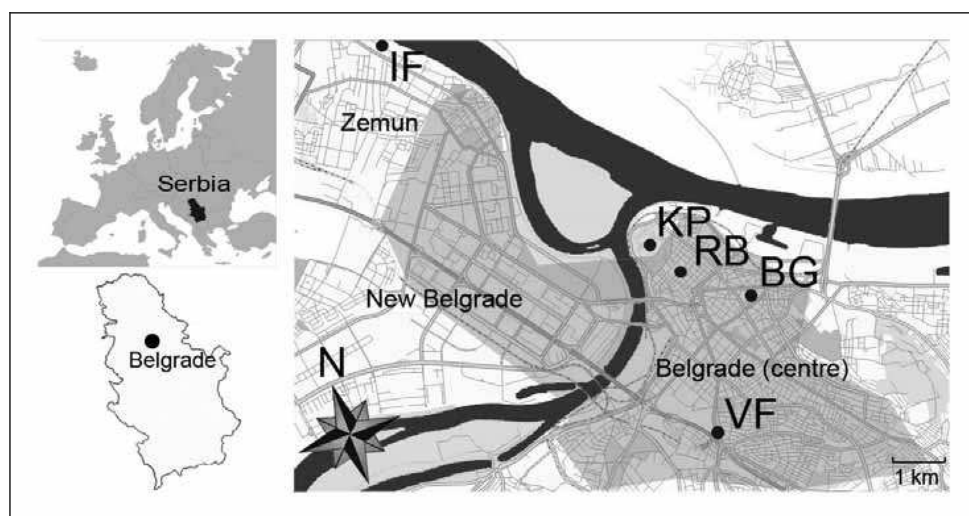

Fig. 1. Location of the sampling sites in Belgrade urban area: Rector's Office building (RB); Botanic Garden (BG); Autokomanda (VF); Institute of Physics- Zemun (IF); Kalemegdan Park (KP)

2.1.1 Particulate Matter

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 has continued afterwards. The first sampling point was on the roof of the Rector's Office building of Belgrade University on Student Square (RB), 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 where the airflow is not blocked by any direction, it can be considered as representative for urban-background concentrations. The second sampling location was at about 6 m height in the Botanic Garden (BG) 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 (VF) 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 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 (IF). 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 (H_s = 132 m, φ = 44°48′ N and λ = 20° 28′ E), located inside the central urban area, very close (≈200 m) to the Autokomanda (VF) 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 μm 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 m³. 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. The sampling methodology used in this study was described in detail by Rajšić et al. (2004a).

2.1.2 Total Atmospheric Deposition

The total atmospheric deposition (TD) collection was performed using an open polyethylene cylinder (29 cm inner diameter and 40 cm height) fixed in a basket on a pole 2 m above the ground to avoid the collection of re-suspended dust from the surface. The devices collected both dry deposition and precipitation continuously for 4 - week periods from June 2002 to December 2006 Rector's Office building, Botanic Garden (BG) and Autokomanda (VF) (Fig. 1). The collection bottles were filled before each sampling period with 20 ml of 10% HNO_3 (Suprapure, Merck).

2.1.3 Biomonitoring

Deciduous leaves for trace metal deposition and accumulation analyses were sampled from horse chestnut (*Aesculus hippocastanum* L.) and Turkish hazel (*Corylus colurna* L.) trees in the Belgrade urban area at three locations, BG, RB and VF (Fig.1). Leaf samples for the metal accumulation study were collected at the beginning and the end of the seasonal vegetation cycles. Ten leaves growing at 2 m height were cut off with Teflon coated stainless steel scissors. Measurements were performed at the single leaf level. Each leaf was placed horizontally in a polycarbonate Petri dish and transferred to the laboratory. Sampling and handling of all plant material were carried out using polyethylene gloves and bags.

Collection of native moss, *Brachythecium sp.* (*B. rutabulum* and *B. salebrosum*) and *Eurhynchium sp.* (*E. hians* and *E. striatum*), for passive biomonitoring of atmospheric trace and other elements pollution was performed according to standardized procedure (UNECE ICP Vegetation, 2003). Mosses were collected at two parks in Belgrade, IF and KP (Fig. 1), within a 30 x 30 m area, at least 100 m away from main roads, and 50 m from smaller roads and houses. The samples were taken at least 5 m from the base of any tree so as not to be directly exposed to throughfall precipitation. In laboratory, the samples were carefully cleaned from all dead material and attached litter, then only green and green-brown moss upper parts up to two/three-years old were analyzed. The samples were dried for 48 h at 35°C to constant weight prior to analysis of elements content.

2.1.4 Ozone

The tropospheric ozone concentrations were measured using UV photometric O_3 analyzer Model 108-AH Dasibi Environmental Corporation, at the same points in Belgrade urban ares as suspended particles, total atmospheric deposition and plant leaves in 2002. In June, September and October, the measurements were conducted at 20 m above the ground, on the roof of Belgrade University Rector's Office Building (RB), Student Square, Belgrade. In July, the measurements were conducted at 3 m above the ground in Botanic Garden (BG). In July, November and December, the measurements were performed at the height of 3 m on the platform above the entrance stairs to the Faculty of Veterinary Medicine (VF).

2.2 Analytical Procedures

2.2.1 Mass Concentrations

Daily PM 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 ± 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.

2.2.2 Trace Metal Analysis

Atomic absorption spectroscopy (AAS)

The elemental composition (Al, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Cd, and Pb) of the aerosol samples and total atmospheric deposition, was measured by the atomic absorption spectroscopy method (AAS). After completion of gravimetric analysis, PM samples were digested in 0.1 N HNO_3 on an ultrasonic bath. 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 (Kyotani & Iwatsuki, 2002). Depending on concentration levels, samples were analyzed for a set of elements by flame (FAAS) (Perkin Elmer AA 200) and graphite furnace atomic absorption spectrometry (GFAAS) using the transversely-heated graphite atomizer (THGA; Perkin Elmer AA 600) with Zeeman-effect background correction. The THGA provided a uniform temperature distribution over the entire tube length, rapid heating and an integrated L'vov platform, which gave an improved signal/interference ratio and high analytical sensitivity. Analyte injection (20 μl) and the atomization were done in five steps controlled by the appropriate software and auto-sampler.

Total atmospheric deposition samples were evaporated to dryness, digested with 50 ml 0.1 N HNO_3 on ultrasonic bath, the digested solution was filtered through 0.45 μm porosity Sartorius membranes and analyzed using a flame and graphite furnace atomic absorption spectrometer. Laboratory blanks were analyzed in the same manner as field samples and the heavy metal concentration values were below the detection limit values for all analyzed

metals. Data treatment included the calculation of Al, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Cd, and Pb monthly deposition fluxes.

For calibration, standard solutions containing all metals of interest were prepared using Merck certified atomic absorption stock standard solutions containing 1000 mg l^{-1} metal in 0.5 N HNO_3 and Milli-Q quality deionized water, with no matrix modifier addition. Detection limits for the trace elements were 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, 2 ng ml^{-1} for Al, and 0.5 ng ml^{-1} for As. Standard practices for the handling of trace metal samples were implemented. For quality assurance, NIST 2783 standard reference material was used.

Differential pulse anodic stripping voltammetry (DPASV)
Leaf samples were transferred to a Class 100 clean room under the specific conditions required for analysis of low concentrations of trace metals (Vukmirović et al., 1997). Leaves were rinsed in double distilled water, and the samples were then dried at 105 °C to constant weight. Ashing was carried out for 6 hours at 450 – 500 °C, with a gradual temperature increase of 50 °C per hour to eliminate organic matter without losing some constituents from the samples by volatilization. The ash was dissolved in 0.1 N HNO_3 prior to analysis. All chemicals and standard solutions employed were of ultra pure quality. An electrochemical method, differential pulse anodic stripping voltammetry with a hanging mercury drop electrode (DPASV) was used for determination of Cu, Zn, Cd and Pb contents in a single leaf. Measurements were performed with an EDT, ECP 140 Polarograph and the analytical technique was described in detail previously (Vukmirović et al., 1997; Tomašević et al., 2004). The detection limits (ng ml^{-1}) were 0.5, 1.0, 0.1 and 1.0 for Cu, Zn, Cd and Pb, respectively.

Instrumental neutron activation analysis (INAA)
Heavy metal and other element concentrations in the native moss samples were determined by instrumental neutron activation analysis (INAA). INAA was performed at the Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research (FLNP JINR), Dubna, Russian Federation (Frontasyeva & Pavlov, 2000). The moss was analyzed on 36 elements. Approximately 0.3 g of well homogenized moss was taken for analyzing by INAA and most element concentrations were determined with detection limits within the range of 0.01 - 10 µg g^{-1}. The short-term irradiation (2 min) was used for short-lived radionuclides (Mg, Al, Cl, K, Ca, Ti, V, Mn, I, and Dy). The long irradiation (100 h) was used to determine elements associated with long-lived radionuclides (Na, Sc, Cr, Fe, Co, Ni, Zn, As, Se, Br, Rb, Sr, Mo, Sb, Cs, Ba, La, Ce, Sm, Tb, Hf, Ta, W, Hg, Th, and U). Gamma-ray spectra were measured four times using a high-purity Ge detector after decay periods of 5 and 10 min following the short irradiation and after three and 20 days following the long irradiation, respectively. The low temperature during irradiation of samples (60 – 70 °C) provides determination of elements present in the samples in volatile form.

To provide quality control, content of elements yielding short- and long-lived isotopes in moss samples was determined using certified reference materials issued by the International Atomic Energy Agency (IAEA): lichen (IAEA-336), cabbage (IAEA-359) and standard reference material SRM-1575 (pine needles) from the National Institute of Standards and Technology (US NIST). For the short irradiation, the three reference materials were irradiated together with 10 experimental samples. In the case of long irradiation, the three reference materials were packed and irradiated together with 7 – 9 samples in each transport container.

2.2.3 Scanning Electron Microscopy

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 suspended atmospheric particulate matter and particles deposited on leaves.

One PM sample per sampling episode was analyzed with the SEM/EDX (JOEL JSM-5300 SEM) according to the US-EPA Guidelines (2002). Prior to analyses three small sections of the filters (5 mm 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 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 up to 20 keV, collected from the selected particles for a spectrum acquisition time of 100 s. The elements observed were: C, N, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Cd, and Pb, with detection limit of 1 wt % (Tasić et al., 2006).

An SEM Philips XL30 apparatus equipped with a thin-window EDAX DX4 system for energy dispersive X-ray microanalysis was used to analyze the particles deposited on the leaf samples. Leaf samples were dried in air in the clean room. To minimize charge build-up on the samples from exposure to the SEM electron beam the samples were coated with (10 – 15) nm layer of high purity carbon using vacuum evaporator (Balzers/Union FL-9496) prior to analyses. The SEM observations were carried out at magnifications up to 2000X while the electron beam energy was fixed at 20 KeV, and the working distance in most cases was about 10 mm and probe current was 100 pA. Particles were observed by backscattered electron images. Three different leaf discs of the adaxial and abaxial surfaces for both tree species were examined in the same way. Ten photomicrographs were randomly taken of each 0.03 mm^2 area at 624X magnification and about 1800 particles per species were assessed to their morphology and about 900 for X-ray spectra analysis. For each tree species about 0.025% of the original leaf surface was examined.

An energy dispersive X-ray spectrum (EDS) was collected from the selected particles in the range up to 15 keV for a preset time (live time) of 10 s to 20 s. The total X-ray count rate was between 1000 and 2000 counts s^{-1}. The relative elemental composition of the particles, were computed directly with EDAX software, using the "ZAF" (atomic number, absorption, fluorescence) correction. As the particles deposited on leaves have complex shapes, quite different from an ideal flat sample, there may be over- or underestimation of the actual atomic concentration, but this does not prevent identification of the most important particle types. Periodical checks of the X-ray by peak identification were conducted. EDX Spectrometer gain calibration was accomplished using a gold/copper standard since X-ray lines from these two elements span almost the entire spectral range of the detector.

2.3.4 Multivariate Receptor Modelling

Principal component analysis (PCA) and cluster analysis (CA) were used to identify the possible emission sources of trace elements and correlations among them in suspended particulate matter and total atmospheric deposits. The extracted principal components were interpreted as source categories contributing to PM concentrations at the sampling site and total deposition as well. 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 (Nowak, 1998). In this study, all principal factors extracted from the variables with eigenvalues > 1.0 were retained, according to the Kaiser criterion (Kaiser, 1960). When PCA with Varimax normalized rotation was performed, each PC score contained information on the metal elements, 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.

2.3.5 Enrichment Factor

Enrichment factor (EF) analysis was used to differentiate between the elements originating from human activities and those of natural origin and to assess the degree of anthropogenic influence. By convention, the average elemental concentration of the natural crust is used instead of the continental crust composition of the specific area, as detailed data for different areas are not easily available. 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 (Manoli et al., 2002; Gao et al., 2002). In this study, Al was used as the reference element with upper continental crustal composition given by Mason (1966). EF represents the ratio of the fraction of the element E with respect to reference element R in the samples (aerosols, atmospheric deposition, moss…) $(E/R)_{sample}$ to the fraction of E with respect to the same R in the crust $(E/R)_{crust}$:

$$EF = \frac{(E/R)_{sample}}{(E/R)_{crust}} \tag{1}$$

According to the degree of enrichment the elements may be grouped as follows: highly enriched $(EF > 100)$; intermediately enriched $(10 < EF < 100)$ and less enriched $(EF < 10)$ (Berg et al., 1994; Wang et al., 2005). If the EF approaches unity, the crustal material is likely the predominant source for element; if $EF > 1$, the element has a significant fraction contributed by non-crustal sources.

2.3.6 Air Back Trajectories

The analysis of air back trajectories for high PM concentrations episodes, in Belgrade, has been performed. Theoretical and experimental evidence was based on numerical weather prediction model and trajectory model so-called Eta model. The model used for simulation and air back trajectory calculation in this study is a regional weather prediction primitive equation model for synoptic and meso-scale processes (Mesinger et al., 1984, 1988, Janjić et al., 1990, 1994). In this study model with 3.2 km horizontal resolution and 32 layers in the vertical was used. The boundary conditions were updated every 6 hours obtained from European Centre for Medium-Range Weather Forecast (ECMWF). Construction of three-dimensional atmospheric trajectories provides a valuable diagnostic tool for illustrating and studying three-dimensional flow fields and associated transports. Trajectories are calculated from simulated wind fields, with both horizontal and vertical wind components derived from the Eta model.

Trajectories can be calculated forwards and backwards in time. Air back trajectories are calculated by specifying final parcel locations and time, and then tracing the parcels with decreasing time to ascertain their origins. The model has been used for research in entire Serbia region and boundary regions of the other countries in the neighborhood.

3. Results and Discussion

3.1 Particulate Matter

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. 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 62% of days had mean daily concentrations above limit value of 50 µg m^{-3}. Average PM$_{2.5}$ mass concentration exceeded the EC annual limit of 20 µg m^{-3} (EN 14907, 2005) by a factor of 3 (Rajšić et al., 2004; Tasić et al., 2005).

PM$_{10}$ and PM$_{2.5}$ mass and trace metal concentrations

During the next sampling episode, between June 2003 and July 2005, daily mass (µg m^{-3}) and trace and other element (ng m^{-3}) concentrations were calculated in PM$_{10}$ and PM$_{2.5}$ and already presented in detail (Rajšić et al., 2007; Todorovic et al., 2007). A total of 273 (209 PM$_{10}$ and 64 PM$_{2.5}$) valid samples were taken during the 2-year period. The high mean and maximum levels of PM$_{10}$ and PM$_{2.5}$ were observed; the PM$_{10}$ mean mass concentration during the 2-year period (68.4 µg m^{-3}) exceeded the proposed EC annual limit of 40 µg m^{-3} (EC, 1999). Of more concern was the average PM$_{2.5}$ 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} (ES 14907, 2005)

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 PM$_{10}$. Zinc and Al concentrations in this fraction were very high, amounting to 1389.2 ng m^{-3} and 873.8 ng m^{-3}, respectively. The highest mean concentration in PM$_{2.5}$ was for Zn (1998.0 ng m^{-3}), followed by Al (1180.3 ng m^{-3}) and Fe (1081.2 ng m^{-3}). Zinc is reliable tracer of unleaded fuel and diesel oil powered motor vehicle emissions (Monaci et al., 2000) and besides, it could be released in large amounts from tired friction or various industrial activities. Concerning Cu, a heavy metal characterized by its toxicity, relatively high mean values of 71.3 ng m^{-3} in PM$_{10}$ 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. Aluminum concentration was higher in PM$_{2.5}$ than in PM$_{10}$. 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 PM$_{10}$ (Directive 2004/107/EC). Mean concentrations of V (36.6 ng m^{-3}), Mn (20.8 ng m^{-3}), Cd (1.4 ng m^{-3}), and Pb (46.5 ng m^{-3}), did not exceed the current air quality guideline values (WHO, 2002). The seasonal variations of the trace metals in PM$_{10}$ and PM$_{2.5}$ were also analyzed. 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 Cr, Cu, and Cd, which suggests that some local industrial source of these elements is more influential during the summer.

3.2 Total Atmospheric Deposition

A total of 141 atmospheric deposits was collected monthly from June 2002 to Decembar 2006 in three sites in the urban area of Belgrade - RB, BG and VF (Fig. 1) and trace and other metal (Al, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Cd, and Pb) monthly fluxes calculated. Table 1 presents average daily atmospheric deposition of heavy metals (μg m^{-2} day^{-1}) in the Belgrade urban area for all sampling sites for the period of 2003 to 2006.

	Al	V	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Pb
RB	807.13	40.20	1.91	64.08	1723.19	23.92	113.03	117.65	1.59	0.58	55.67
BG	976.60	49.66	2.32	78.95	2062.74	29.07	61.84	138.24	9.78	0.58	62.35
VF	1071.59	58.89	2.77	88.84	2549.86	38.64	97.22	148.19	40.43	0.70	74.18

Table 1. Average daily atmospheric deposition of heavy metals (μg m^{-2} day^{-1}) in the Belgrade urban area for 2003 – 2006

Besides Fe and Al, the most abundant trace metal in bulk deposition was Zn, followed in order of abundance by V, Mn, Ni, Cu, Pb, As, Cr and Cd. Cu and Zn have multiple anthropogenic sources, including high temperature combustion processes and the most probable source of Cu and Zn enrichment are vehicle-related particles. The impact of human activities could be seen on several metals like Zn, Cu, Pb, Cd, Mn, Al, Cr, and Fe. This influnce was more obvious for Cu, Cd and Pb which have only anthropogenic sources, while other four metals originate from many natural sources as well (Pacyna & Pacyna, 2001).

As expected, the TD values were highest at Autokomanda site (VF) for almost all metals except Cu. High Zn and Cu fluxes in total deposition samples could also be related to roof covering of Zn metal sheets nearby and could point to the presence of point sources, which are clearly site specific. High deposition of Cu in samples at Rector's Office building (RB) comparing to other locations indicates the possible local source influence.

Seasonal variation for element concentrations in bulk deposition have been analysed. Maximum concentrations of V (Fig. 2) and Ni were in winter periods, while seasonal variations of the other elements were not pronounced.
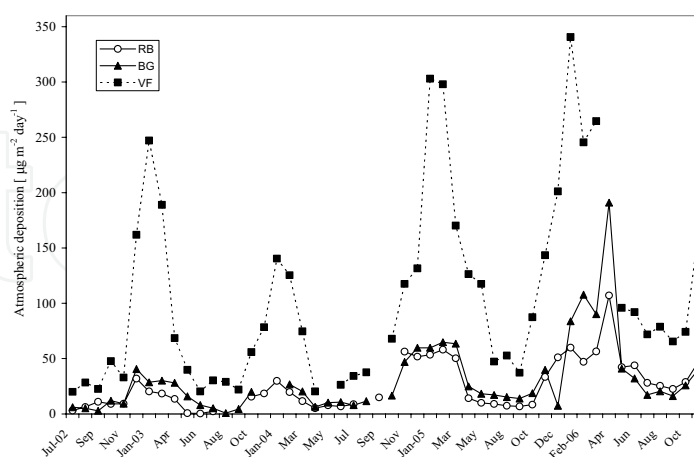

Fig. 2. Seasonal variation for V concentrations in total atmospheric deposits in Belgrade urban area for the period July 2002 - November 2006

3.3 Biomonitoring

3.3.1 Higher plants

The level of trace metals, particularly Pb, accumulated in the leaves of *A. hippocastanum* showed a high correspondence to their increased atmospheric concentrations, indicating this plant species as suitable biomonitor for trace element atmospheric pollution (Tomašević et al., 2004)

The results, presented on Fig. 3, illustrate this correspondence in two successive experimental years with different traffic and industrial emissions. Trace metal concentrations of Cu, Zn, Cd and Pb in the leaves from *A. hippocastanum* and *C. colurna* were analyzed at the beginning and in the end of the vegetation periods. Concentrations of Cd (0.02 to 0.06 $\mu g \, g^{-1}$) were below the detection limit in most of the samples. The increased atmospheric trace metal concentrations in the Belgrade down-town area affected their amounts found in the investigated deciduous tree leaves. While the average accumulations of trace metals in *C. colurna* were very similar for both experimental years, the levels found in *A. hippocastanum* leaves were considerably higher in September 1997 as compared to September 1996.
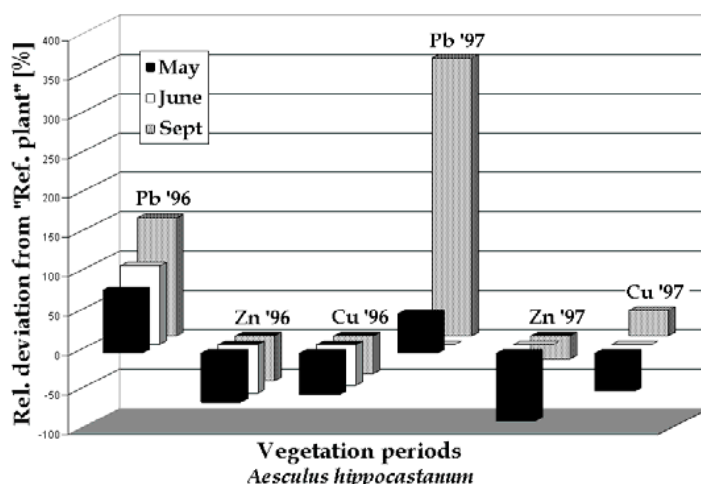

Fig. 3. Chemical fingerprints of *Aesculus hippocastanum* after normalization against the "Reference plant" system for comparison (Markert, 1992)

Similarly, over the same time interval, higher concentrations of the investigated trace metals were also found in the water-soluble fraction of deposits on leaves of *A. hippocastanum* in comparison to *C. colurna* (Tomašević et al., 2005).

Fig. 3 shows "the chemical fingerprints" of *A. hippocastanum* obtained for the second experimental year as normalized against the "reference plant" system for comparison (Markert, 1992). In both years, Pb concentrations were much higher than the "reference plant" value, and markedly increased in the second experimental year. As the chemical fingerprint may be assumed to represent the background concentrations, it offers some advantages for a quick assessment of the pollution level and allows comparison between different species and vegetation types, such as mosses, herbaceous plants and trees (Markert, 1992; Djingova et al., 1994).

Metal uptake in higher plants takes place through the roots and somewhat via the leaves, which makes it difficult to distinguish whether the accumulated elements in leaves originate from the soil or from the air (Markert, 1993; Bargagli, 1998; WHO, 2000). Pb in leaves is considered to originate mainly from atmospheric deposition (Tjell, 1979; Harrison& Johnston, 1987), while the soil contributes to Cu and Zn in leaves (Kim&Fergusson, 1994; Palmieri et al., 2005). As there were hardly any other emission sources during the investigated vegetation seasons, the results obtained here may suggest that the Pb found in the leaves mainly originated from traffic emissions. Unfortunately, leaded gasoline is still the prevailing traffic fuel in Belgrade, and many diesel engine vehicles are old and not maintained well. In the second experimental year Zn concentrations increased in *A. hippocastanum* leaves, while no increase occurred in the leaves of *C. colurna*. This result also implies a species-specific element accumulation. Moreover, the highest Pb concentrations in leaves also occurred in *A. hippocastanum* among a group of urban deciduous tree species in Istanbul (Baycu et al., 2006).

3.3.2 Moss

The element concentrations in both investigated moss genera, *Brachythecium sp.* and *Eurhynchium sp.*, were at a similar level (Table 2). For a majority of the 36 determined elements, the difference between the moss contents in the two genera was within the range of specific experimental error, except for Co, Ta, Ce, Sm, Tb, Th, and U which concentrations were close to the detection limits of used INAA, and hence it would not be reasonable to compare such data (Aničić et al., 2007). The previous result suggests that both moss species, found in sufficient quantity for sampling in the urban area of Belgrade, could be combined for biomonitoring purposes.

Especially interesting for evaluation, as carcinogenic and toxic elements (EEA, 2005), have been the obtained moss concentrations of V, Cr, Ni and As. The median values of these elements in native moss samples from this study were presented in relation to some other corresponding data (UNECE ICP Vegetation, 2003) as shown in Fig. 4.

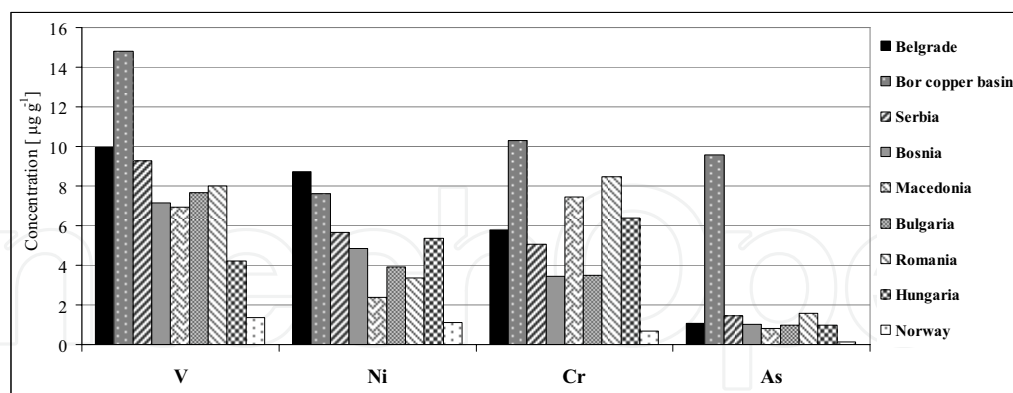

Fig. 4. Median concentrations (μg g^{-1}) of V, Cr, Ni and As in moss from Belgrade area and some European countries

Such comparison gave an insight into a level of heavy metal and other element air pollution in Belgrade urban area in relation to the highest polluted industrial area in Serbia (Bor copper basin), base-level moss content (data from Norway) and the concentration levels in

adjacent countries. In general, the concentrations of V, Cr, Ni, and As obtained for the Belgrade urban area correlated to the results from the neighbouring countries where fossil fuel is still a major energy source resulting in higher heavy metal and other element air pollution. However, the moss content for the above-mentioned elements was up to 10 fold higher than background levels (Norway).

Element	Zemun		Kalemegdan Park	
	Brach.sp.	*Eurhin.sp.*	*Brach.sp.*	*Eurhin.sp.*
Na	545	757	313	307
Mg	16950	22760	10173	8290
Al	5000	6685	2147	1940
Cl	642	565	817	332
K	10705	10637	9760	7264
Ca	12590	14937	18647	12340
Sc	0.90	1.0	0.27	0.33
Ti	329	539	137	160
V	10.0	14	9.9	9.5
Cr	7.0	9.2	4.5	4.5
Mn	90	114	56	57
Fe	3000	3504	1057	1295
Co	0.80	1.3	0.42	0.68
Ni	8.2	13	6.8	9.2
Zn	34	37	41	40
As	0.95	1.6	1.0	1.1
Se	0.06	0.09	0.12	0.14
Br	1.8	2.5	2.9	3.7
Rb	8.1	11	6.7	7.7
Sr	29	36	50	42
Mo	0.52	0.59	1.2	0.75
Sb	0.18	0.22	0.29	0.35
I	0.19	0.26	0.30	0.31
Cs	0.39	0.59	0.22	0.22
Ba	44	64	33	28
La	3.0	3.7	1.1	1.5
Ce	3.9	7.0	1.7	3.1
Sm	0.40	0.77	0.20	0.25
Tb	0.05	0.09	0.02	0.03
Dy	0.81	1.2	0.42	0.38
Hf	0.42	0.78	0.22	0.24
Ta	0.05	0.10	0.02	0.03
W	0.32	0.29	0.16	0.19
Hg	0.48	0.43	0.18	0.38
Th	0.62	1.1	0.27	0.34
U	0.07	0.14	0.23	0.10

Table 2. The element concentrations ($\mu g\ g^{-1}$) in *Brachythecium sp.* and *Eurhynchium sp.* at Zemun and Kalemegdan Park

3.4 Factor Analysis

Principal Component Analysis (PCA) 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 3 presents four rotated factor loadings with eigenvalues >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 (Li et al., 2002, 2003; D`Alessandro, 2003). Adriano (2001) 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.

		PM$_{10}$				PM$_{2.5}$			Total atmospheric deposition		
	Fac 1	Fac 2	Fac 3	Fac 4	Fac 1	Fac 2	Fac 3	Fac 4	Fac 1	Fac 2	Fac 3
Pb	-0.07	0.04	0.41	**0.72**	0.27	**0.85**	-0.05	0.06	0.51	0.31	**0.56**
Cu	0.01	0.13	**0.86**	0.02	-0.1	0.14	0.46	**0.78**	-0.08	0.1	**-0.74**
Zn	**0.78**	0.09	-0.12	0.01	**0.85**	0.17	0.25	-0.24	**0.96**	-0.08	-0.02
Mn	**0.84**	0.16	0.08	0.27	**0.8**	0.22	0.27	0.03	**0.76**	0.27	0.32
Fe	**0.77**	-0.03	0.04	-0.13	**0.78**	0.16	-0.09	0.16	**0.75**	0.42	0.11
Cd	-0.08	-0.11	**0.79**	0.03	0.1	-0.25	-0.36	**0.79**	**0.64**	0.48	0.02
Ni	0.32	**0.85**	0.19	-0.01	0.06	0.1	**0.88**	0.08	0.25	**0.84**	-0.11
V	0.02	**0.94**	-0.13	-0.05	0.3	-0.15	**0.71**	-0.11	0.26	**0.86**	0.22
Al	**0.74**	0.23	-0.14	0.22	**0.84**	0.09	0.08	-0.01	**0.71**	0.49	0.13
Cr	0.24	-0.11	-0.2	**0.81**	0.16	**0.91**	0.05	-0.15	-0.01	0.71	0.57
As	-	-	-	-	-	-	-	-	0.42	0.66	-0.33
%Variance	26.1	17.4	16.8	13.2	29	17.8	17.7	13.5	32.3	29.3	13.4

PCA loadings > 0.5 are marked in bold

Table 3. Principal component analysis after Varimax rotation for the trace elements analyzed in PM$_{10}$, PM$_{2.5}$ and total atmospheric deposition

PCA analysis and the following Varimax rotation were conducted on element concentrations dataset in total deposits. Three factor loadings explaining 75% of total variance are presented in Table 3. The first factor has high loadings for most of the elements and represents resuspended road dust, which includes soil dust mixed with traffic related particles. Factor 2 has high loading for Ni, V, As and Cr emitted from fossil fuel combustion processes and Factor 3 has high loadings for Pb and Cu. Cu shows the most independent behavior as it is almost on the third factor with negative loading indicating its specific source.

The results of CA for the variables, trace elements in PM, were obtained as dendograms displaying four main clusters. In the dendogram for PM$_{10}$ (Fig. 5a) 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 PM_{10} 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. 5b) points to several groups connected to each other at some 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. 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.

The results of cluster analysis on trace metals in PM_{10}, $PM_{2.5}$ and total atmospheric deposition (Fig. 5c) 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 to direct exhaust emission (Vukmirović et al., 1997; Rajšić et al., 2006).
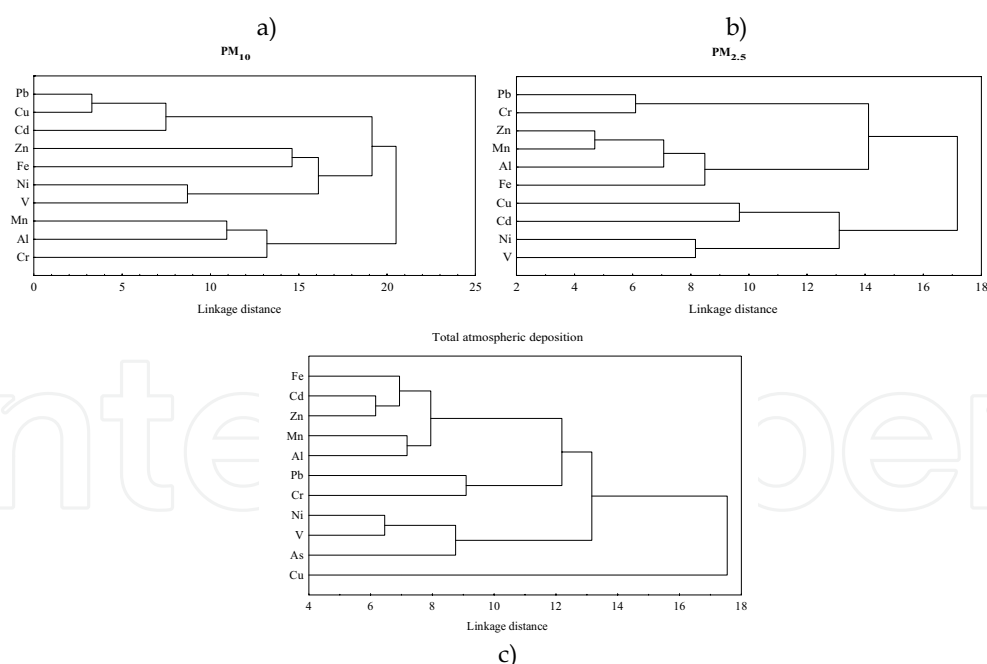

Fig. 5. Dendogram resulting from Ward's method of hierarchical cluster analysis of the trace elements in PM_{10} (a); $PM_{2.5}$ (b) and total atmospheric deposition (c)

3.5 Enrichment Factor

Enrichment factors (EFs) for the mean concentration of trace elements in suspended particles, PM_{10} and $PM_{2.5}$, total atmospheric deposition and moss samples were calculated according to the earth's crustal mean abundances of the elements given by Mason (1966) and using Al as a reference element and presented in Fig. 6.

The EF sequence related to particulate matter in the Belgrade urban area for the sampling period was: Zn > Cd > Pb > V > N > Cu > Cr > Mn > F e> Al. The highly enriched elements, primarily emitted from high-temperature processes (e.g. fossil fuel combustion and smelting), are usually associated with small and medium sized aerosol particles, and can be transported to remote areas.According to the degree of enrichment, the elements are grouped as follows (Wang et al, 2005): 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. EF values higher than 1 were found for 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 (Pakkanen et al., 1993, 2003).

For total atmospheric deposition, the calculated enrichment factors for trace elements show the same pattern as in the particulate matter. Additionally, As (484) and Cu (155) were highly enriched.
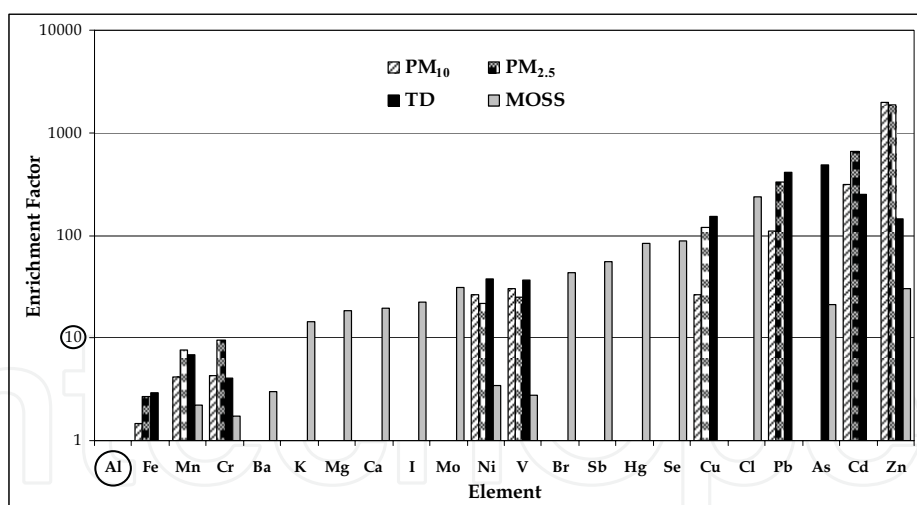

Fig. 6. Enrichment factor (EF) of elements in PM_{10}, $PM_{2.5}$, total atmospheric deposition and moss

High EFs for K, Mg, Ca, As, I, Zn, Mo, Br, Sb, Se, Hg and Cl (from 14 to 238) in moss samples were calculated. The highest EFs in moss samples were observed for Cl, Hg and Se which are important tracers for coal combustion (Watson et al., 2001). The fuel used in the complex of coal-fired power plants, 20 km SW from Belgrade, as well as for local domestic heating in Belgrade, is mainly lignite-brown coal (high in As) or crude oil. These fuels are

significant sources of the enriched elements at studied sites (Rajšić et. al., 2004). Elements such as Br, Sb, As, Mo and Zn are considered as indicators of emission from fossil fuel combustion processes, including vehicle exhausts (Arditsoglou & Samara, 2005; Pacyna & Pacyna, 2001). Kalemegdan Park is surrounded with heavy traffic roads, with trucks very frequently present. Leaded gasoline and diesel fuel (still widely used in Belgrade) contain a large amount of Br and Mo (Pacyna & Pacyna, 2001).

Tire and brake lining wear as well as other metallic parts of vehicles might be a significant source of Sb (Arditsoglou & Samara, 2005). Concentrations of the enriched elements from this study were in accordance with some previous investigations of air quality of the urban Belgrade in the vicinity of Kalemegdan Park (Tomašević et al., 2004; 2005; Vukmirović,et al. , 1997).

3.6 Correlation Factors

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 (SO_2) 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 PM_{10} and $PM_{2.5}$ were calculated, and presented in Table 4. As products of fossil fuel combustion, CO, NO, NO_2, and SO_2 were the most closely correlated (r = 0.70 to 0.95). The highest correlations among the trace elements in PM_{10} were between V and Ni (r = 0.69) (elements associated with oil combustion), Al and Mn, elements of mostly crustal origin, as well as Zn - Mn and Fe - Mn (emission from traffic and possibly steel production).

Copper was most correlated to Cd, which could have originated from brake linings and coal combustion in stationary sources, or some local industry. The mass concentration of PM_{10} was mainly correlated to the concentrations of gases related to combustion processes and, among the trace elements, to V as a product of fossil fuel combustion.

Higher correlation was found during the winter, with the most significant correlation coefficient between V and Ni (r = 0.72), while for Pb - Cu the correlation coefficient was 0.56. Pb was also significantly correlated with gases, Cd and Cr. Copper was more closely associated with Pb, than with Cd and gases, which are good indicators of combustion-related sources. These correlations support the recent finding that Cu is one of the metals most closely related to vehicle circulation in urban areas. Zinc was more correlated with Cr (r = 0.65) than with Mn, Al, Fe and Ni.

Generally, mass concentrations of $PM_{2.5}$ were positively correlated with the pollution gases, CO (r = 0.80), NO (r = 0.74), NO_2 (r = 0.70) and SO_2 (r = 0.65) as well as V (r = 0.40). The correlation of NO_2 with particle mass was more prominent than for SO_2, showing that particles from traffic emissions predominated. Lead was most closely connected to Cr, Zn to Mn and Al.

Regarding correlations between metal concentrations and wind speed, only Cu and Cd in $PM_{2.5}$ were significantly negatively correlated with wind speed, suggesting that Cu and Cd are mostly from local sources. Vanadium and Ni were strong negatively correlated with temperature. This result supports the presumption that those elements originate from combustion of fossil fuels in heating units. The absence of good correlations between Pb and most meteorological parameters (temperature, relative humidity and wind speed) suggests that those factors may not be influential enough to control the Pb levels.

The analysis of the correlation coefficients between all metal fluxes (Table 5) in total deposition (TD) have shown the similar connections as in the case of PM (Fe - Mn=0.61, V -

Ni=0.68, As - Ni=0.65; Zn - Fe=0.57, Ni - Cd=0.58). As in the case of PM$_{10}$, high correlation between V and Ni was obtained indicating the origin in oil combustion processes.

	PM$_{10}$	P$_a$	T$_{max}$	T	RH	W$_{av}$	Pb	Cu	Zn	Mn	Fe	Cd	Ni	V	Al	Cr	NO	NO$_2$	SO$_2$	CO
PM$_{10}$	1.00	**0.27**	**-0.28**	**-0.30**	0.00	**-0.26**	0.15	0.19	0.11	**0.35**	**0.25**	-0.02	**0.36**	**0.44**	0.15	-0.11	**0.58**	**0.39**	**0.56**	**0.61**
P		1.00	**-0.30**	**-0.31**	0.00	**-0.34**	-0.02	-0.03	0.05	0.12	**0.16**	0.01	0.05	0.09	0.00	**-0.20**	0.18	0.07	**0.25**	0.12
T$_{max}$			1.00	**0.99**	**-0.50**	-0.12	0.05	0.09	**-0.25**	-0.02	0.01	0.01	**-0.45**	**-0.54**	**-0.21**	0.19	-0.07	**0.32**	**-0.30**	0.02
T				1.00	**-0.45**	-0.14	0.03	0.10	**-0.27**	-0.05	0.00	0.00	**-0.46**	**-0.55**	**-0.23**	0.19	-0.09	**0.29**	**-0.32**	0.00
RH					1.00	**-0.17**	-0.04	0.08	-0.10	**-0.21**	**-0.21**	0.10	**0.25**	**0.34**	-0.03	-0.07	0.10	**-0.34**	0.03	0.07
W$_s$						1.00	-0.07	-0.14	**0.18**	-0.12	-0.09	-0.05	-0.01	-0.11	0.02	0.02	**-0.24**	**-0.24**	-0.06	**-0.25**
Pb							1.00	**0.28**	-0.02	**0.16**	-0.01	**0.25**	0.04	-0.03	0.00	**0.25**	**0.17**	**0.28**	0.12	0.12
Cu								1.00	-0.13	0.12	0.02	**0.45**	**0.29**	-0.04	-0.07	-0.09	0.13	0.14	0.07	0.11
Zn									1.00	**0.56**	**0.41**	-0.09	**0.31**	0.11	**0.54**	**0.16**	**-0.22**	**-0.19**	-0.10	**-0.15**
Mn										1.00	**0.55**	-0.05	**0.37**	**0.15**	**0.66**	**0.35**	-0.02	0.02	0.01	0.12
Fe											1.00	-0.12	**0.24**	0.05	**0.36**	0.10	0.01	0.01	0.01	0.03
Cd												1.00	0.02	**-0.14**	-0.10	-0.08	-0.02	-0.07	0.01	-0.05
Ni													1.00	**0.69**	**0.35**	0.01	0.07	-0.07	**0.16**	0.08
V														1.00	**0.22**	-0.12	**0.19**	-0.03	**0.30**	**0.18**
Al															1.00	**0.30**	**-0.15**	**-0.18**	-0.08	-0.03
Cr																1.00	-0.14	0.10	-0.07	0.01
NO																	1.00	**0.73**	**0.83**	**0.94**
NO$_2$																		1.00	**0.70**	**0.67**
SO$_2$																			1.00	**0.71**
CO																				1.00

a)

	PM$_{2.5}$	P$_a$	T$_{max}$	T$_{av}$	RH	W$_{av}$	Pb	Cu	Zn	Mn	Fe	Cd	Ni	V	Al	Cr	NO	NO$_2$	SO$_2$	CO
PM$_{2.5}$	1.00	0.01	-0.29	-0.30	0.06	-0.17	0.19	0.20	-0.17	-0.03	-0.16	-0.14	**0.26**	**0.40**	-0.16	-0.17	**0.74**	**0.70**	**0.65**	**0.80**
P		1.00	-0.16	-0.15	-0.04	-0.20	-0.25	-0.06	**-0.35**	**-0.28**	-0.17	**0.34**	-0.13	-0.15	**-0.37**	**-0.33**	0.14	0.14	0.22	0.04
T$_{max}$			1.00	**0.99**	**-0.68**	0.08	-0.12	-0.13	-0.07	-0.19	0.07	**-0.28**	**-0.29**	**-0.55**	-0.20	0.14	-0.02	0.08	-0.23	-0.02
T$_{av}$				1.00	**-0.65**	0.05	-0.14	-0.11	-0.09	-0.21	0.08	-0.25	**-0.28**	**-0.56**	-0.20	0.13	-0.04	0.06	-0.25	-0.04
RH					1.00	-0.26	0.08	0.18	-0.05	0.00	**0.27**	**0.27**	**0.37**	0.21	-0.18	0.01	-0.20	0.02	-0.02	
W$_{av}$						1.00	0.14	**-0.36**	0.03	-0.01	-0.11	**-0.34**	-0.01	-0.19	0.02	**0.28**	-0.19	-0.15	-0.07	-0.17
Pb							1.00	0.04	0.15	**0.25**	0.08	-0.12	0.04	0.10	0.20	**0.56**	0.12	0.14	0.13	0.16
Cu								1.00	0.04	0.08	0.04	0.20	**0.49**	0.16	0.01	0.08	0.13	0.06	0.18	0.14
Zn									1.00	**0.82**	**0.48**	0.12	0.08	0.00	**0.66**	**0.37**	**-0.31**	-0.18	-0.24	-0.19
Mn										1.00	**0.37**	-0.05	0.17	0.23	**0.50**	**0.34**	**-0.25**	-0.06	-0.14	-0.15
Fe											1.00	**0.29**	-0.13	-0.17	**0.43**	0.22	-0.17	-0.11	-0.19	-0.08
Cd												1.00	-0.24	-0.21	0.14	-0.01	-0.22	**-0.36**	-0.08	-0.15
Ni													1.00	**0.50**	0.02	-0.03	0.01	0.07	-0.01	0.02
V														1.00	0.07	**-0.26**	0.04	0.05	0.07	0.08
Al															1.00	0.17	-0.24	-0.20	-0.22	-0.14
Cr																1.00	-0.15	-0.05	-0.07	-0.14
NO																	1.00	**0.90**	**0.85**	**0.95**
NO$_2$																		1.00	**0.86**	**0.86**
SO$_2$																			1.00	**0.80**
CO																				1.00

b)

P$_a$ - atmospheric pressure; T$_{max}$ - maximal temperature; T - temperature; RH-relative humidity; W$_s$ – daily wind speed

Correlation coefficients significant at 0.05 level are marked in bold

Table 4. Pearson's correlation coefficients between meteorological parameters, combustion-related gases, mass and trace element concentrations in PM$_{10}$ (a) and PM$_{2.5}$ (b)

	Fe	Cd	Pb	Cu	Ni	Zn	Cr	Mn	Al	V	As
Fe	1.00	**0.49**	**0.44**	-0.18	**0.57**	**0.57**	**0.45**	**0.61**	**0.78**	**0.63**	**0.58**
Cd		1.00	**0.39**	0.15	**0.58**	**0.33**	**0.30**	**0.41**	**0.51**	**0.57**	**0.48**
Pb			1.00	-0.05	**0.29**	0.08	**0.20**	**0.34**	**0.46**	**0.41**	**0.21**
Cu				1.00	0.01	-0.15	**-0.20**	**-0.19**	-0.12	-0.07	0.11
Ni					1.00	0.15	**0.28**	**0.32**	**0.65**	**0.68**	**0.65**
Zn						1.00	**0.26**	**0.59**	**0.54**	0.17	**0.35**
Cr							1.00	**0.58**	**0.45**	**0.55**	**0.25**
Mn								1.00	**0.65**	**0.40**	**0.40**
Al									1.00	**0.61**	**0.50**
V										1.00	**0.57**
As											1.00

Correlation coefficients significant at 0.05 level are marked in bold

Table 5. Pearson's correlation coefficients of trace element concentrations in total
atmospheric deposition

3.7 Air Back Trajectories

During the period of June 2002 to December 2004 the PM_{10} and $PM_{2.5}$ mass concentrations in Belgrade urban area had high average values (83 and 75 µg m^{-3}), and 72% of PM_{10} samples exceeded the level of 50 µg m^{-3}. To make an identification of possible pollution sources and assess the influence of meteorological parameters on PM mass concentrations, air back trajectories for high PM concentrations episodes were analyzed (Mijić et al., 2006). Three selected, sixty hours backward trajectories, starting at 12 00 UTC, are shown on Fig. 7.

Fig. 7a shows backward trajectories calculated for 21/12/2002., when the highest mass concentration occurred (362 µg m^{-3}). This case was characterized by anticyclone (1030 mb) at the surface and very slow flow caused by small gradient of the pressure field. Wind varied from north at higher levels, over western and southwestern at low levels (contribution from the complex of coal power plant in Obrenovac).

The episode for 2/4/2005 (Fig. 7b) was characterized with trajectories which at all levels show very weak flow changing from north-eastern at higher levels to eastern at lower levels (Pančevo). Synoptic situation was characterized by ridge of high pressure (1020 - 1025 mb) from the north, with weak pressure gradients caused by eastern flow in our region.

On Fig. 7c, trajectories corresponding to 27/11/2005 are placed from south-western direction at highest levels to south-eastern direction at lowest levels (Smederevo). They are presented for the last 12-20 h only, because the flow is strong at all levels, and particles quickly leave domain. Synoptic situation: A cyclone is placed on the west of the domain, caused southern magnified flow in the region of interest. Calm wind conditions were found to have an increment effect on particle concentrations and were also associated with the appearance of persistent episodic events. All cases analysed in this study were characterized by very slow flow field caused by small gradient of the pressure field. At the surface layer high pressure was placed over observed region.

The main sources of particulate matter were of local origin: traffic emission, and individual heating emissions. When the air masses were coming from the SW direction, the contribution from the power plants in Obrenovac was also evident, from NE-E contribution of Pančevo-rafinery and chemical industry, and from SE direction influence of Smederevo-steel industry. Episodes of high mass PM concentrations were observed in Belgrade throughout the year, although, they were more prominent during winter period. The prevalence of stagnant or week flow regimes favors the suspension and accumulation of particles produced locally, resulting at the elevation of PM levels.
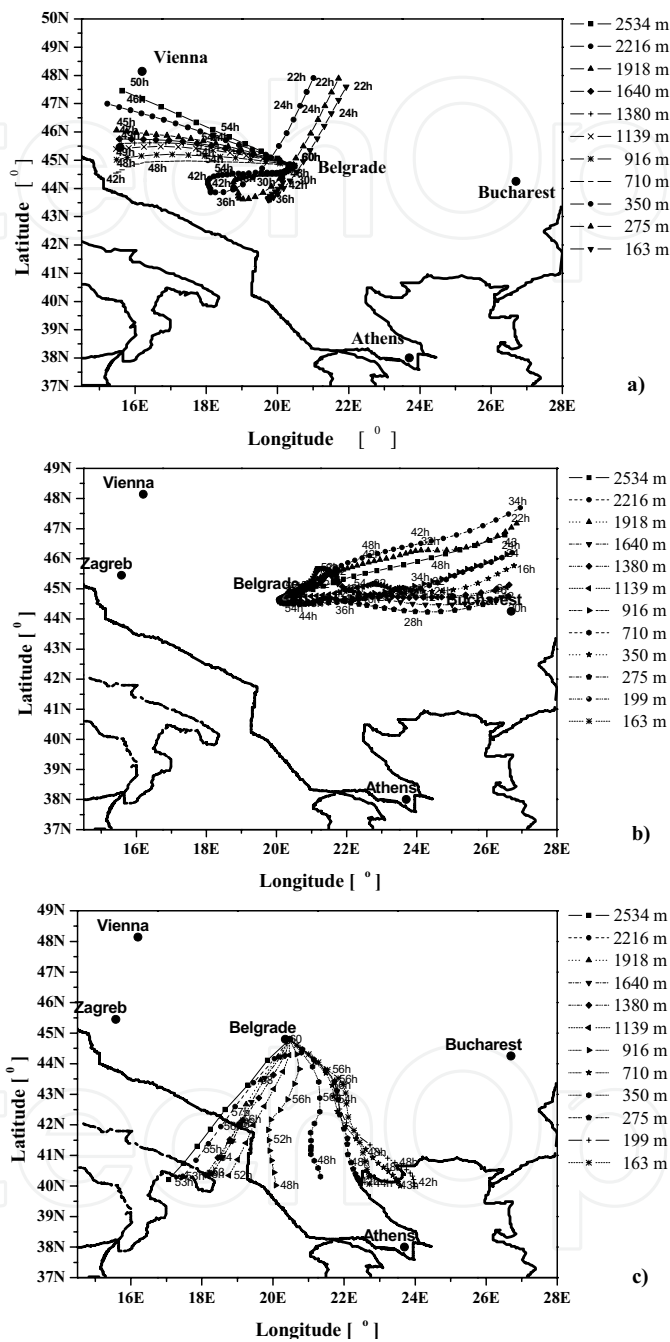
Fig 7. Air mass backward trajectories for the high PM concentrations episodes on: a) 21/12/2002; b) 02/04/2005 and c) 27/11/2005

3.8 Scanning Electron Microscopy

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. Classification of the present particles was based on the morphology (McCrone & Delly, 1973) 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 (2002). 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 Fig. 8 - 9. *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 microanalyses show traces of 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. 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) (Chen et al., 2006; Conner et al., 2001). In Belgrade urban area, this type of particles originates mostly from individual heating units.
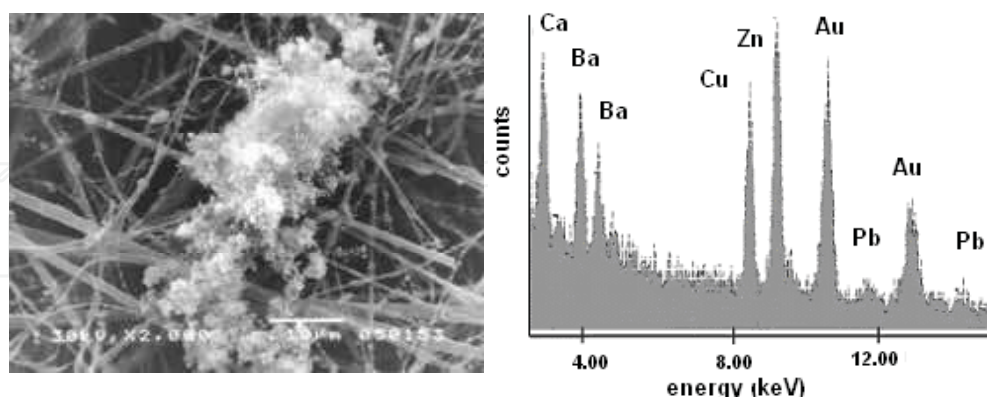

Fig. 8. High resolution SEM image and X-ray microanalysis spectrum of fly ash particles agglomerate from fossil fuel combustion process emissions and coal-fired power plant ("Nikola Tesla" A, B, Obrenovac)
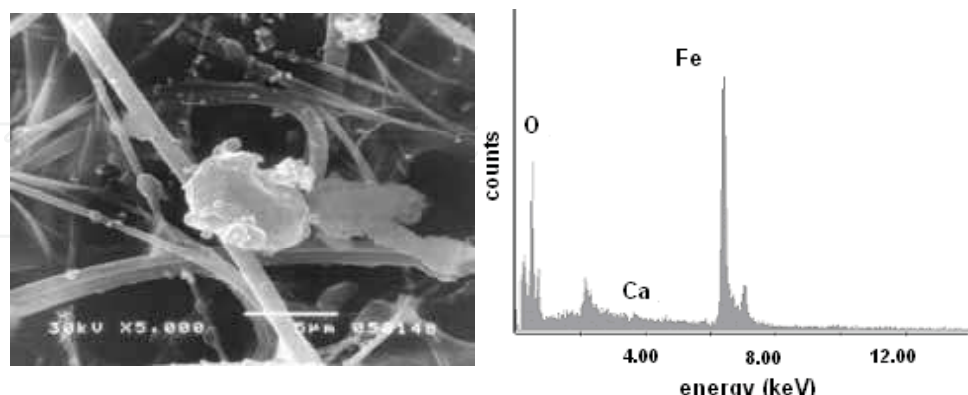
Fig. 9. Coarse Fe rich particle from the $PM_{2.5}$ sample, November 2003 and X-ray
        microanalysis spectrum

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 (Fig. 9). Biological particles (pollen, bacteria, fungi, spores, etc.) are recognized (by their characteristic morphology) as important constituents of the coarse particle fraction in the PM_{10} samples, especially during summer period.

Scanning electron photomicrographs of particles deposited on leaf surfaces showed a general appearance of adaxial and abaxial surfaces (Fig.10) of hypostomatic leaves of *A. hippocastanum* and *C. colurna* sampled in a dry period, at the end of the vegetation seasons (Tomašević et al., 2005). Approximately, 10 - 15% the leaf surface was covered with deposited particles. A greater density of particles was observed on *A. hippocastanum* than on *C. colurna*. This could be explained by different epidermal characteristic such as surface roughness, which was more prominent in *A. hippocastanum* than for *C. colurna*. Particles were present at a higher density on the adaxial leaf surfaces of both tree species. They were not homogeneously distributed and mean particle density approximately varied from 5 000 to 20 000 mm^{-2}.

Particles were present in a wide range of diameters up to 50 μm, but the analyses of the particle size distribution for both species showed that 50 - 60% of the analyzed particles were of a diameter less than 2 μm (fine particles) mainly originating from anthropogenic acitivities.
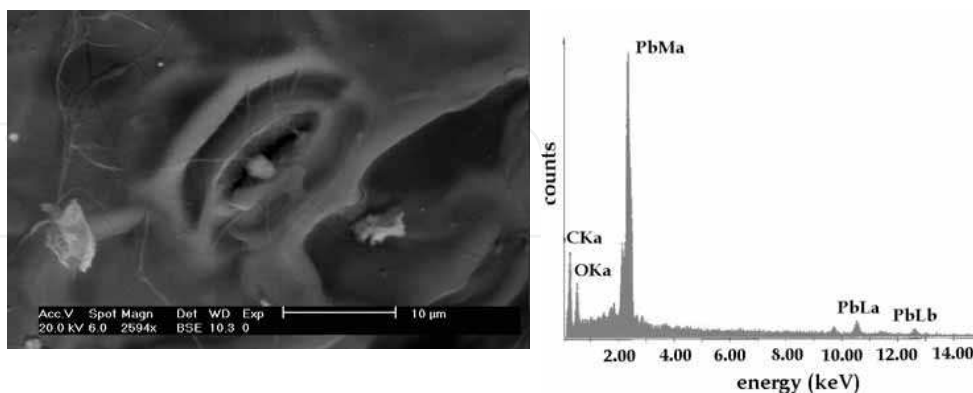
Fig. 10. Scanning electron micrograph of a stomatal area of leaf surface of *A. hippocastanum* and EDX-spectrum of a lead-rich fine particle in the stomatal opening

The chemical composition of the particles deposited on both plant species suggested that the most abundant particles were: soot (C) and soil dust with characteristic matrix elements (Si, Al, Fe, Mg, N, S, Ca, K, Cl); fuel oil particles rich in Al, Si, Ca, Ni, Fe, V and Pb; coal ash particles containing C, Al, Si, K, Ca; and industrial particles such as Fe, Zn, Ni, Cu or Pb-rich. Among the particles containing trace metals, the most abundant were particles in aggregates form, where Pb is the major element associated with lower concentrations of S, Fe, Cd, Cu, As and Zn.

3.9 Ozone

Twenty four–hour fluctuations of O_3 concentrations are recorded at all measuring sites. The obtained results mainly indicate usual afternoon maxima and night and early morning minima. The differences between maximal and minimal concentrations of O_3 are more marked during warmer periods when main daily temperatures are increased, which are correlated with maximal O_3 concentrations. At all measuring sites, ozone concentrations were for at least 1 h equal or higher than 90 ppbv what exceeds the EU threshold (EU Directive 92/72/EEC on air pollution by ozone) requiring public anouncement.

In the Fig. 11, daily changes of ozone concentrations recorded at the location BG during July 2002 are presented indicating cyclic dependence of afternoon maxima and night and early morning minima.

In Fig. 12 maximal daily O_3 concentrations recorded during measurements at the measuring point BG are presented together with mean daily air temperatures showing a tendency towards increasing ozone as the temperature increases.

Our data indicated that temperature did not play an important role in the ozone variation when high values of ozone concentration were reached (> 100 ppbv). This may be easily seen from the lack of correlation between average or maximum temperature and maximal ozone concentration (Fig. 11).
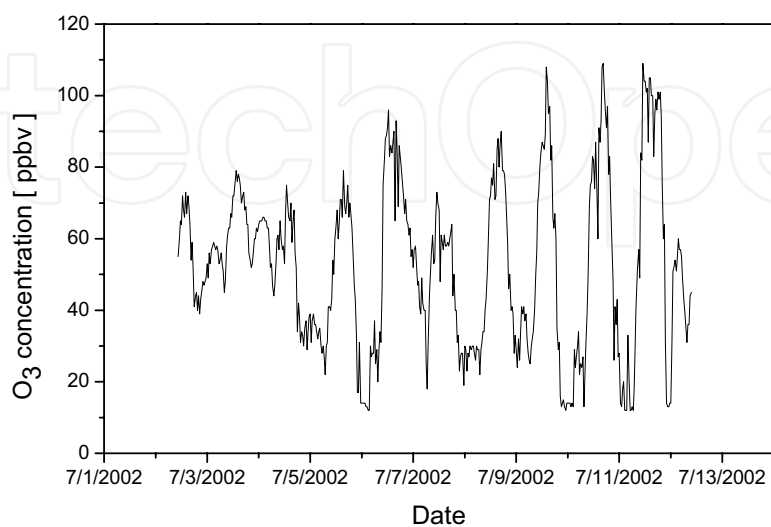
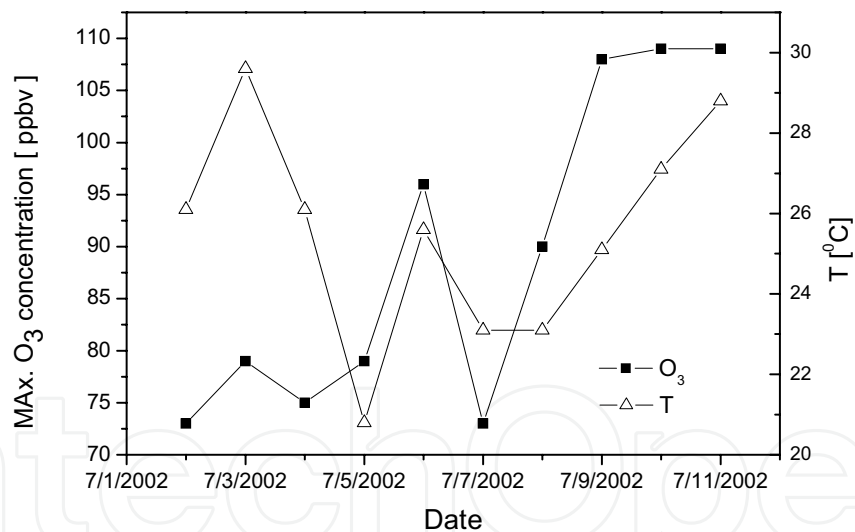Fig. 11. Daily cycles of ozone; measuring point BG, July 2002

Fig. 12. Maximal ozone concentrations and mean daily temperatures; measuring point BG, July 2002

During the days when the daily maximum ozone concentration was greater than, or equal to 100 ppbv, the surface wind speed was less than, or equal to 1 m s^{-1}. This could imply that the surface wind speed plays an important role in the processes that control variation in ozone concentration and indicates that the highest ozone concentrations are reached when the wind speed decreases.

The mean daily relative humidity during O_3 measurements at the measuring point BG did not change much and it amounted approximately to 60%. It is important to mention that in the first three days of O_3 measurements, highest values of mean daily wind speed of 4 ms^{-1} were registered, while in the subsequent four days they reached 1.5 m s^{-1} on average. During the period when maximal O_3 concentrations were recorded, average wind speed was lowest and it amounted to 1.0 m s^{-1}, mainly from the north direction. The results of O_3 concentration measurements, obtained at the points RB and VF are to a high degree in accordance with the results obtained at the point BG.

Lower values of O_3 concentrations were recorded in September and October 2002, at the measuring point RB. Mean values of maximal O_3 concentrations varied between 59 ppbv and 36 ppbv.

4. Conclusion

Air quality monitoring is used to determine the air pollution levels in urban environments and concentration measurements can be compared with the national and international guideline values. This review presents an attempt to assess air quality in Belgrade urban area and identify the possible pollution sources. An integrated monitoring approach has been applied related to the urban Belgrade locations with the aim to estimate the level of specific pollutants: particulate matter, trace metals and ozone. The measurements included the PM_{10} and $PM_{2.5}$ mass and trace metals concentrations, total atmospheric deposition fluxes, as well as, biomonitoring of deposition and accumulation of trace elements.

The obtained results gave us the first impression of concentration level, characterization and sources of inhalable particulates with aerodynamic diameter less than 10 μm in Belgrade ambient air. The PM_{10} and $PM_{2.5}$ values had high average values, compared to EU standard and results for other European cities. The highest mean metal concentration in $PM_{2.5}$ was for Zn followed by Al and Fe. The mean Ni concentration of in the $PM_{2.5}$ fraction was above the target value for PM_{10} issued by EU. Mean concentrations of Pb, Cd, V, and Mn did not exceed the current WHO air quality guideline values.

Strong seasonal modulation existed and lower summer average decreased the annual average concentrations. The explanation for the seasonal pattern could be possibly 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. temperature inversion layers, low temperature and stagnation of air masses. During the exceptional high pollution days, both in the summer and winter, high production of secondary aerosols occurred, as can be seen from increase of $PM_{2.5}$ in respect to PM_{10}. This was a result of high relevance for health aspects, as the fine particles were those of highest negative impact on health and had the longest residence time in the atmosphere.

Episodes of high mass PM concentrations were observed in Belgrade throughout the year, although, they were more prominent during winter period. Air back trajectories analysis showed that the prevalence of stagnant or week flow regimes (calm conditions) favors the suspension and accumulation of particles produced locally, resulting at the elevation of suspended particles levels. The appearance of stronger W, SE and NE flows was responsible for the particles transported from the thermoelectric plants, refineries, chemical and steel industry.

Most of traditional studies on atmospheric pollution have been limited by problem of high cost and the difficulty of carrying out extensive sampling, in terms of both time and space. There is, thus, an increasing interest in using indirect monitoring methods such as analysis of bioaccumulators.

In this study, higher plants and mosses were as biomonitors of atmospheric pollution in urban area. Variability in trace metal concentrations in deposits was estimated in *Aesculus hippocastanum* and *Corylus colurna* leaves. The method of analysis at the level of single leaves was chosen in order to assess more precisely the contribution of atmospheric deposition to trace metal accumulation. It has been shown that the effect of elevated air pollution can be reflected in the amount of deposits on leaves, and in trace metal concentrations in deposits, especially on *A. hippocastanum* leaves. Analyses of some trace metal contents (Cu, Zn, Cd, and Pb) in single leaves pointed to a high correspondence with the level of atmospheric pollution measured by instrumental monitoring.

Physical and chemical characterisation of deposits, both on filters and leaf surfaces, also indicated anthropogenic origin of particles.

The comparison of accumulation abilities of two moss genera, *Brachythecium sp.* and *Eurhynchium sp.*, showed that they could alternately be used for biomonitoring purposes in urban areas due to very close levels of the measured trace elements. The obtained data for moss collected in urban area of Belgrade are in accordance to some instrumental monitoring data for the same area.

The moss concentrations of some cancerogenic and toxic elements such as V, Cr, Ni, and As, obtained in this study, were up to 10 fold higher than moss-background levels (Norway) and correlated with results from the adjacent countries (Bosnia, Hungaria, Romania, Bulgaria, etc.) where coal is still widely used as an energy source.

High values of enrichment factors for the trace elements (Mo, Ni, V, Br, Sb, Hg, Se, Cu, Cl, Pb, As, Cd, Zn) characteristic for fossil fuel combustion were calculated for both the total atmospheric deposition and moss samples.

Ozone concentration measurements showed that in the area of Belgrade during summer of 2002, moderate to high ozone concentrations were measured and lasted long enough to represent a risk for human health and vegetation. This was accompanied with manifestations of all usual characteristics of O_3 photochemical cycle with marked influence of transport on high level of O_3 concentrations during the night. The results of ozone measurements confirmed the dependence of O_3 concentration on meteorological parameters. Ozone concentrations equal to or higher than 90 ppbv were registered at low wind speeds of about 1.5 m s^{-1} mostly from the N which indicates that the O_3 was produced at the very site of measurement.

In this work we demonstrated how to identify the sources of atmospheric trace metals by trace metal analysis, multivariate receptor modelling, air back trajectories, meteorological analysis, and biomonitoring. The complete analysis showed that the main sources of air pollution in the city of Belgrade are combustion processes, e.g. emissions from mobile and stationary units, with the major contribution from traffic and resuspended road dust. Monitoring ambient air quality also provides important input data for epidemiological studies, which are crucial in establishing associations between health outcomes and concentrations of ambient air pollution. Due to measured high PM mass concentrations, it is obvious, that it would be very difficult to meet the EU standards, by 2010. There are some necessary measures to start with: switch to unleaded gasoline, replace old cars and substitute coal by gas, light heating oil or district heating.

Urban areas are often considered as "anthropogenic deserts" in sense of plant species recommended for biomonitoring purposes. Therefore, active biomonitoring with transplanted moss (or lichen) can be applied to assess urban air pollution. "Moss bags" technique has been developed having a number of advantages: well-defined exposure time; known background concentrations of elements in the moss; flexibility in site selection and number of sampling sites to be chosen; uniformity of entrapment surface, etc.

With the aim of more comprehensive insight in air quality in urban area at Belgrade, the further investigations will include indoor measuremens, $PM_{1.0}$, volatile organic compounds (VOCs), active moss biomonitoring, etc.

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http://www.intechopen.com/books/environmental_technologies/assessment_of_air_quality_in_an_urban_area
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