

## Air-suspended particles of air in the urban zone of Lazarevac town (Serbia): An environmental aspect

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### Key words:

*Suspended particles, major elements, minor elements, Kolubara basin, Lazarevac.*

**Abstract.** Composite monthly samples of airborne particles collected at the measuring station in Lazarevac (Kolubara basin, Serbia) during nine consecutive months were chemically characterized in this study. The concentrations of certain minor elements in the PM<sub>10</sub> particles exceed a part of the elements that contain values higher than the maximum allowed concentrations. The most concerning are the As and Co concentrations, two very toxic elements that can cause cancer-related sicknesses through eventual inhalation.

This report connects the chemical composition of the suspended air particles (potential pollutants) with their source and provides an estimate of the air quality in the investigated area for a particular timeframe of several consecutive months. The results indicated that air quality in Lazarevac area was rather low, affected by the excessive As and Co concentrations. The main source of the measured air pollution was an increased level of ash. The resulting ash-dominating pollution implies the necessity of the use of proper air filters in the nearby thermo-electric power plants, and sustainable use of coal in domestic households. In addition, the pollution can be moderated by careful use of coal as a solid fuel in individual local households. The results additionally provide a solid base for the future comparative studies of the local and regional air quality.

**Апстракт.** Композитни месечни узорци ваздуха сакупљани су током девет месеци на мерној станици Лазаревац (Колубарски басен, Србија). Узорци суспендованих честица (PM<sub>10</sub>) су анализирани на хемијски састав. Концентрације одређених микроелемената у PM<sub>10</sub> честицама показују који елементи садрже вредности изнад максималне дозвољене концентрације. У забрињавајуће повишеним концентрацијама су As и Co који су два јако токсична елемента која инхалацијом могу изазвати канцерогена обољења.

У овом раду су повезани хемијски састав честица са њиховим изворима који дају процену квалитета ваздуха у узоркованом подручју у одређеном временском интервалу. Резултати узорковања током испитиваног временског интервала показују лош квалитет ваздуха на подручју Лазареваца који је узрокован повишеним концентрацијама As и Co. Између осталих, као главни извор загађења ваздуха је повишен садржај пепела

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**Кључне речи:**

*Суспендоване честице, макро компоненте, микрокомпоненте, Колубарски басен, Лазаревац.*

у ваздуху. Доминантно загађење пепелом указује на потребе инсталације ваздушних филтера на термоелектрани, као и смањено коришћење угља као чврстог горива у локалним домаћинствима. Након ових и претходних истраживања квалитета ваздуха инсталирани су филтери на локалну термоелектрану. Но, без обзира на уградњу филтера, резултати истраживања су веома добра основа и могу послужити за будуће компаративне као и корелативне студије о квалитету ваздуха на истраживаном простору.

**Introduction**

The tropospheric air contains a certain amount of aerosol particles often found in solid- or fluid states. Beside natural aerosols, the Earth’s atmosphere contains a considerable quantity of so-called industrial aerosols that might have a negative effect on local flora and fauna, and importantly represent a serious danger for human health.

Particulate matter (PM), as a criteria air pollutant, is a complex mixture of chemical agents in particles, ranging from nanometer-sized molecular clusters to coarse dust particles being large enough to not to be inhaled into the lungs with aerodynamic diameter >10 µm. Particle composition is known to affect health risk (commonly attributed to the combustion products which include mechanically generated dust), in particular those airborne particles which size goes below 2,5 µ including those decreasing below 10 µm – have been associated with excess mortality and morbidity in numerous epidemiological studies (LIPPMAN, 2012).

The main sources of coarse suspended matter (PM<sub>10</sub>), both in urban and rural areas are: power plants, vehicles and traffic, furnace combustion (wood and coal), mechanically-generated- and wind-raised dust (construction site dust, landfill site-produced dust, dust from agricultural area, street dust), fires, smelters.

There is a widely accepted hypothesis that chemical components of particles and their capacity to carry potentially toxic substances are the key risk factors affecting human health. However, it is not fully understood which of these particles are the decisive influencers on human health (WANG et al., 2005). Thus, suspended particles can often be found

in concentrations considerably above the natural background levels (in particular anthropogenic processes in urban areas) affecting local human population (*e.g.*, exposure to metallic particles; BAEZ et al., 2007).

Coal combustion in thermo-electric power plants encompasses exclusively combustion of organic portion of coal whereas inorganic components usually do not burn. Nevertheless, the combustion can induce a series of physicochemical transformations of inorganic components of coal, which ultimately remain in the ash. Combustion-transformed inorganic parts remain in the ash being a by-product of the main coal (organic matter) combustion. These inorganic elements show various distribution patterns among combustion-derived mineral fractions (POPOVIĆ & DJORDJEVIĆ, 2005). This provide a possibility to differentiate the bottom ash (residue) and “fly ash”.

By the decrease in ash particle size, the concentrations of As, Cu, Mo, Pb and Zn increase (POPOVIĆ et al., 2001), with appearance of Se and Cr (SHAH et al., 2008). In case that quartz is more abundant in the fly ash, pyrite and carbonates make a more significant part of contribution the bottom ash (POPOVIĆ et al., 2001).

Along with smoke gases, fly ash and electro-filter ash may reach local air bypassing the installed electro filters; such air can be enriched with metal particles and carry up to 85% of the total amount of ash in thermo-electric power plants. In Serbia, 6–7 t of ash is produced per year (solemnly local power plants), and is mostly deposited near thermo-electric power plants. Just a small quantity is used in the cement industry (BAŠČAREVIĆ et al., 2006). Suspended ash and mineral dust particles (less than 10 µm in size), in addition to their quantity and quality may

cause a deterioration of human health (FUBINI & AREÁN, 1999; JENG et al., 2010; CATALANO et al., 2012). If particles with toxic elements are inhaled, there is a risk of being transferred directly to the bloodstream through the lungs. Consequently, the monitoring of heavy metal content in suspended particles is of a great importance.

Owing to their toxicity or carcinogenicity, 10 metals are listed among 188 hazardous air pollutant substances, including following compounds (YUE et al., 2007): As ( $0.03 \mu\text{g}/\text{m}^3$ ), Be ( $0.02 \mu\text{g}/\text{m}^3$ ), Cd ( $0.02 \mu\text{g}/\text{m}^3$ ), Cr<sup>6+</sup> ( $0.008\text{--}0.1 \mu\text{g}/\text{m}^3$ ), Co ( $0.1 \mu\text{g}/\text{m}^3$ ), Pb ( $1.5 \mu\text{g}/\text{m}^3$ ), Ni ( $0.1\text{--}0.2 \mu\text{g}/\text{m}^3$ ), Mn ( $0.05 \mu\text{g}/\text{m}^3$ ), Hg ( $0.09 \mu\text{g}/\text{m}^3$ ) and Se ( $0.08\text{--}20.0 \mu\text{g}/\text{m}^3$ ).

Combustion of various types of coals in thermo-electric power plants, industrial boilers, and household furnaces represents a primary source of Sb, Se, Tl, Be, Ni and V. In addition, industrial coal combustion contributes to the releasing of As, Cr, Cu, Mn and Zn in atmosphere. Combined with coal combustion products in individual households the metal-enriched aerosol may additionally cause an increase of Hg, Mo, Se, As, Cr, Mn, Ti. The wood combustion, however, cause an increased concentration of V, Ni and Sn (BLOCK & DAMS, 1975; VUKMIROVIĆ, 1997; TASIĆ et al., 2006). According to the authors, these elements have documented a negative impact on the public health and the environment. At last, a presence of Ni and Mn is dominantly associated with a combustion of oil-using furnaces and ferroalloys (BAEZ et al., 2007).

Studies of fly ash derived from combustion of coal from the Kolubara basin indicate that coal contains an incombustible, inorganic matter that through combustion process partly becomes a glassy, amorphous matter (BAŠČAREVIĆ et al., 2006). The ash content is mostly composed of quartz and aluminosilicates, with low contents of feldspars and anhydrite. Particles of fly ash are generally spherical in shape with diameters of  $0.5 \mu\text{m}$  to  $100 \mu\text{m}$  and mostly contain  $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--Fe}_2\text{O}_3\text{--CaO--MgO}$  in descending order (ĐORĐEVIĆ et al., 2005; BAŠČAREVIĆ et al., 2006). Trace elements appear in the following order:  $\text{Ni} > \text{Cr} > \text{As} > \text{B} > \text{Cu} > \text{Co} = \text{Pb} > \text{V} > \text{Zn} > \text{Mn}$  (VUKAŠINOVIĆ et al., 2009).

Street dust is an important source of heavy metal pollution, and in particular, inhalation of fine parti-

cles may result in the intake of highly toxic metals in urban areas. Street or road dust develops from dry and wet deposition, biological inputs, road surface deterioration, road paint degradation, vehicle abrading including vehicular fluid and emission of fluid-associated particles (KABADAYI & CESUR, 2010). By elevating particles from the ground and through their re-suspension, ca. 50% of total natural emissions of Cr, Ni, V, 20–30% Mo, Ni, Pb, Sb, Zn and <10% Hg and Se can be emitted back into the atmosphere (VUKMIROVIĆ, 1997). Urban dust can contain following heavy metals: Cr, Cu, Ni, V, Ba, Co, Mn and Pb, as reported by numerous authors (NORRA & STÜBEN, 2004; TANNER et al., 2008; PARK & DAM, 2010).

Increased concentrations of Cd, Pb, Se and Zn have commonly been associated with the sources deriving from road traffic and thermal sources (power plants, etc). An increase of concentrations of Ca and Fe soil-derived dust has a dominant impact on elevated concentrations of Ca and Fe whereas a proximity to industrial complexes and alloy manufacturing structures is related to Cr and Ni. Cr and Ni can also contribute to an increase of Sb and Zn (PAK & DAM, 2010). Fe and Zn in fine fractions are associated with combustion processes and vehicle emissions. Having antioxidant properties, Cu and Zn are common in additives for engine oils (MAURA DE MIRANDA et al., 2010). Pb and Ni have usually been reported as leading gasoline exhaust emission by products (JOKSIĆ et al., 2009). In addition, a mechanical abrasion of metallic surfaces may affect an increase of the levels of Ni values (JOKSIĆ et al., 2009). Ni and Mn can originate both from traffic and natural sources (KABADAYI & CESUR, 2009). High percentages of As, Cd, Cu, Ni and Zn may be emitted from metallurgical industrial plants. Emissions of exhaust gases derived from the combustion of gasoline are common in urban area. Discharged gases in urban areas often exhibit fluctuation in the quantities of Pb, Cu, Zn, Ni and Cd (PACZYNA & PACZYNA, 2001). Cd often originates from the wearing of vehicle rubber tires (BAEZ et al., 2007). By measuring concentrations of various metals in PM<sub>10</sub> aerosol particles, As, Be, Ca, Cd, Co, Cr, Fe, K, Mn, Ni, Pb, Sb, Se and Zn in PM<sub>10</sub> are confirmed in urban areas (traffic), metallurgic- and petrochemical industries. The metallurgic- and petrochemical industries have been doc-

umented as the pollution sources (KIHOUNG & DAM, 2010).

A number of studies have been conducted emphasizing the environmental pollution and impact on human health. The major part of the environmental pollution emphasizes the effect on urban areas. A study reporting the environmental quality of outskirts of a city in Japan registered the elevated concentrations of six toxic elements in a course of nine years (monitoring period; As, Be, Cr, Hg, Mn and Ni). The highest average concentrations were recorded for Mn, whereas the lowest concentrations are documented for Be (NGUYEN et al., 2010).

Investigations of the smog heavy metal concentrations (Cd, Cr, Cu, Fe, Mn, Ni and Pb) in smog in the Polish city of Zabrze (traffic-laden intersection) indicated that the concentrations of Cr, Ni, Fe and Cu were in an increase, respectively 19.7, 817.4, 16.7 and 13.1 times higher than their average ambient concentrations (PASTUSZKA et al., 2010).

The mineral composition of the investigated particles from Kolubara is represented with quartz, feldspar, clay minerals, gypsum, barite, hematite, carbonate minerals, composite particles and organic particles (coal, soot, particles from motor vehicle exhaust gases, polycyclic aromatic compounds; CVETKOVIĆ et al., 2013). The particles represent the agglomerated cluster of minerals of which silicates, aluminosilicate minerals, as well as hydroxides of Fe, Mn and Ti are dominant. Silicium dioxide in aerose-diments of the investigated area (Kolubara) dominantly appears in the form of quartz representing endangering health pollutants (introduced to the human organism through breathing).

This work is an ongoing study, a continuation of earlier investigations (CVETKOVIĆ et al., 2012, 2013) with the emphasis on testing of different potential local pollution sources (power plant Kolubara-A, furnaces, fly ash from power plant Kolubara-A, traffic pollution, brick industry, heating plant - combustion of oil fuel, metallurgical plant - Kolubara metal). We provide chemical characterization of air-suspended particulate matter, air quality and potential heavy metal contaminations. The resulting values are compared with the maximum allowed concentrations (MAC). The MAC has been used for a comparison between the national regulations (OFFICIAL

GAZETTE RS 65/2008) and the regulations of the European committee for standardization.

## Methods and material

### Sampling area and sampling

The samples of PM<sub>10</sub> particles were collected near the Upper Miocene Kolubara lignite basin at the sampling point in Lazarevac (44° 22' 57" N; 20° 15' 36" E; Fig. 1). This Neogene basin is economically one of the most important coal-bearing basins in Serbia (ŽIVOTIĆ et al., 2013) supplying the local power plants. Considering the vicinity of a coal-burning power plant represents one of the major air pollution sources in the town (in particular power plant "Kolubara A" including produced fly ash).

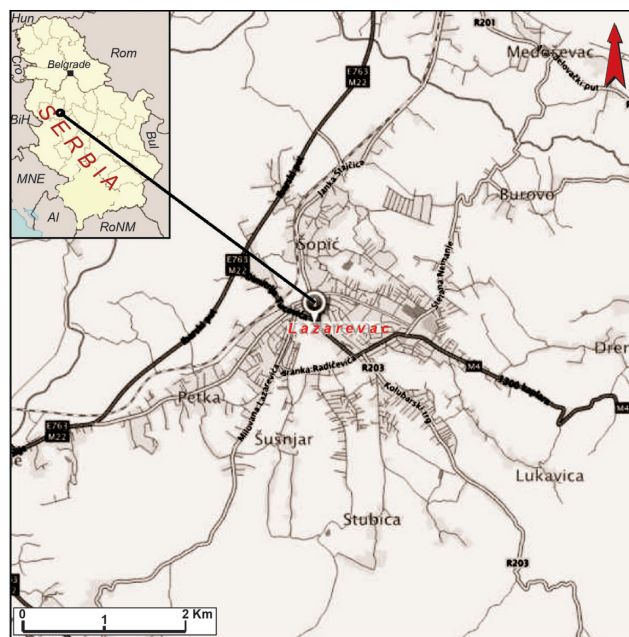


Fig. 1. Location of sampling point.

The sampling point is located in the urban area, in a local schoolyard (KOVAČEVIĆ, 2016). This chosen sampling point is interesting because it is under direct influence of various pollution sources, in particular during the wintertime. Namely, according to the earlier investigations it is reported that a quantity of the total particulate matter, carbon black and SO<sub>3</sub> was above the maximum allowed concentra-



tions per month. Moreover, this particular time-frame provides an insight into recent ecological past of this particular region.

Suspended particles had been sampled from summer (June–September 2007) to winter (October–March 2007/08). The AT-2000 device was used for sampling floating particles below 10 µm in size. This automatic device for sampling PM<sub>10</sub> was placed in an open area having a goal to collect highly representative floating particles. Using a vacuum pump, the air with suspended particles was filtered through a collector with a cellulose filter which retained the particles below 10 µm. After a 24h sampling period, the device was automatically switched off. It is to note that the efficiency of sampling of the filter paper is a function of the pressure and gas velocity. PM<sub>10</sub> mass concentrations were determined gravimetrically by using an electronic balance (10-µg precision) by measuring filter papers before and after sampling (dried at 105°C).

### **Elemental analysis**

During the procedure, the four “Blank” samples were prepared in the same manner. Two “Blank” samples were spiked with adequate aliquot of the multicomponent standard solutions of the analytes.

In order to measure concentrations of the most abundant major and minor/trace elements, the daily samples of filter-collected suspended particulate matter were amassed (or assembled, etc) into the composite monthly samples. To separate PM<sub>10</sub> particles from the cellulose filter paper, a mixture of acids was used: H<sub>2</sub>SO<sub>4</sub>:HNO<sub>3</sub>:HClO<sub>4</sub> (3:1:1), followed by a mild heating. Removal of cellulose, extraction and evaporation was followed by further decomposition of samples by using an ETHOS One microwave digestion system and a mixture of acids HNO<sub>3</sub>:HF (3:1). ICP – OES (ICap 6500 DUO, Thermo scientific, UK) was used for measurement of concentration of the metals.

### **Statistical analysis**

The statistical analysis encompasses tools for statistical data processing, which are an integral part of

the program package STATISTICA 6. In order to illustrate results, a descriptive statistics and Box-Whisker plot analysis were used. The goal of the statistical processing of data was to understand the differences of the average values of the chemical concentrations of the particles (the columns represent the measuring places, the rows the classes). As the initial hypothesis, we took a premise that the chemical concentrations of particles are normally distributed. The justification for this hypothesis is corroborated by the fact that the samples from the measuring point belong to the population that has the normal distribution.

### **Scanning electron microscopy with energy-dispersive spectrometry**

Scanning electron microscopy (SEM) analyses were carried out on an instrument JEOL JSM-6610LV microscope. This scanning electron microscope achieves high-resolution images with magnifications of 5 to 100.000 x (for magnifications used in the paper refer to Fig. 4). Microscope works in the low- and high-vacuum conditions. Tungsten filament or LaB6 crystal were used as the electron source (cathode), at accelerating voltage of 0.3–30 kV. Besides the detectors for secondary electrons (SE) and back-scattered electrons (BSE), this microscope uses energy-dispersive spectrometer (EDS) – detector X-Max large area analytical silicon drift connected with INCEA Energy 350 microanalysis system, and cathodoluminescence detector (CL). For sample preparation, a carbon tape was used, with sample adhered to one side and the other fixed to glass plate of 10 mm in size. Samples fixed in such mode were coated with gold. Semi-quantitative chemical analyses were obtained by using a 64 standard minerals and synthetic compounds.

## **Results**

### **Chemical analyses of suspended particles**

According to the standard of air quality for suspended particles (PM<sub>10</sub>; published in the OFFICIAL GAZETTE RS 65/2008), it is mandatory that the con-

centration of Cd and Mn are measured, whereas other elements (their concentration) can be compared with the literature values.

The summary of monthly concentrations of the major elements in the suspended particles sampled at the single measuring point in Lazarevac are given in Table 1. K and Al are dominant elements across the entire set of samples (collected in the period from July 2007 to February 2008). The summary of monthly concentrations of the minor elements in the samples is in Table 2.

The samples analysis indicate that the values recorded by the concentrations of Zn, Cr, Cu, Ni, Mn and Fe are below the MAC. That implies a lower probability of a toxic impact of these elements onto the public health. However, the values indicate a potential intoxication affecting local population, because even low concentrations of toxic elements in suspended particles could be inhaled over a longer period inducing health issues. At the measuring station, the concentrations of As and Co were much higher relative to the MAC value. Comparable high

daily dosages may pose a serious threat to the health of local population (Table 3).

The resulting concentrations of major- and minor components in PM<sub>10</sub> particles (Table 1 and 2) are similar to those reported in dust (NGUYEN et al., 2010) but with differences of dust analyses reported by PACYNA & PACYNA, (2001). This difference is primarily illustrated by the values of Cd, Cu, Mn, Cr, Fe, Ni, Be and As (Table 2). The increased values of the elements Ni, Cr and Be have rather similarities with the values reported by NGUYEN et al. (2010), whereas the concentrations of Fe and As are more closer to those of PACYNA & PACYNA (2001). The concentration of Mn is fully in line with the concentrations reported in both aforementioned studies. Other concentrations, of minor and major elements (see Table 1 and 2) in the most part match with the values reported within the above-mentioned studies. These elements are in the most part in accordance with the standard values from Tables 2a.

The quality control was performed by the Addition Standard Method. In order to define the accuracy

Table 1. The chemical distribution of the major elements in PM<sub>10</sub> particles (µg/m<sup>3</sup> per day).

Month	June	July	August	September	October	November	December	January	February
Element	S - 6	S - 7	S - 8	S - 9	S - 10	S - 11	S - 12	S - 13	S - 14
Al	18.54	22.79	19.26	20.16	11.02	20.68	20.31	23.87	18.77
Ca	0.33	0.58	0.34	0.25	0.20	0.25	0.41	1.43	0.24
Mg	1.19	1.59	1.38	1.25	1.06	3.07	3,20	3.65	2.97
Na	32.48	35.15	45.33	51.65	27.00	44.35	43.14	52.34	39.51
K	0.98	0.78	1.48	0.78	0.87	1.01	0.61	1.20	0.91

Table 2. The chemical distribution of trace elements in PM<sub>10</sub> particles (ng/m<sup>3</sup> per day).

Month	Samples	Fe	Ti	Zn	As	Se	Cd	Ni	Cr	Co	Be	Mn	Cu	Sb	Ba
June	S - 6	1026.08	227.61	675.10	68.04	0.93	0.78	1.35	17.90	0.21	0.129	25.58	579.78	nd	nd
July	S - 7	1540.76	288.90	818.10	140.69	3.81	1.07	3.27	26.50	0.51	0.245	36.17	915.84	nd	nd
August	S - 8	1560.77	203.84	642.00	52.61	7.47	1.32	3.50	20.85	0.46	0.177	33.69	1709.67	nd	nd
September	S - 9	1551.50	166.67	723.40	8.78	6.83	1.31	3.49	17.60	0.14	0.094	31.46	906.71	nd	nd
October	S - 10	1593.00	83.56	515.50	11.48	6.35	1.33	3.92	9.80	0.37	0.074	32.71	1402.62	1.270	nd
November	S - 11	1338.32	378.64	627.80	13.87	6.89	1.19	2.17	16.10	0.75	0.229	31.73	402.58	nd	nd
December	S - 12	1397.68	282.58	618.90	15.10	5.42	1.05	4.25	14.10	0.84	0.243	34.68	457.68	nd	nd
January	S - 13	1568.58	402.12	782.70	19.33	4.21	1.12	2.79	17.80	0.57	0.190	37.27	1044.98	nd	nd
February	S - 14	2635.52	387.04	585.70	22.41	3.46	1.09	6.12	20.90	1.39	0.273	57.48	415.72	nd	335.1

and precision, two spiked and two unspiked “Blank” samples were used. In accordance with the range of calibration curves, the final concentration of the analyses in spiked samples was 50,00  $\mu\text{g l}^{-1}$ . The “Blank” samples (spiked and unspiked) were measured at the beginning and in the middle of the measurement (after five samples of the Series). The results of the concentrations, accuracy (Recovery %) and precision (RSD %) are presented in the Table 2a. The

Table 2a. Accuracy and precision of the analytical method.

Element	Concentration ( $\mu\text{g l}^{-1}$ )	RSD (%)	Recovery (%)
Al	49.04	2.11	98.1
Ba	50.91	4.19	101.8
Cd	50.91	3.86	101.8
Co	50.10	3.49	101.2
Cr	49.50	2.13	99.0
Cu	53.37	5.25	106.3
Fe	50.60	3.57	101.2
K	62.25	10.8	119.7
Mn	51.60	1.44	103.1
Ni	51.30	3.11	102.6
Pb	52.10	6.32	104.0
Zn	52.19	4.20	104.2
Ca	76.31	5.88	134.5
Mg	51.48	1.15	102.9
Be	52.61	4.98	105.0
Se	56.30	3.98	111.2

Table 3. Values of maximum allowed concentrations for  $\text{PM}_{10}$  particles.

Element	Value	Unit	Literature
Zn	0.367	$\mu\text{g/m}^3 \text{ day}$	Directive – 2004/107/EC; Directive – 2008/50/EC Directive 2008/65/Republic of Serbia
Cd	5	$\text{ng/m}^3 \text{ day}$	Directive – 2004/107/EC; Directive – 2008/50/EC Directive 2008/65/Republic of Serbia
As	6	$\text{ng/m}^3 \text{ day}$	Directive – 2004/107/EC; Directive – 2008/50/EC
Cr	5	$\mu\text{g/m}^3 \text{ day}$	Directive 2010/75/EC
Cu	10	$\mu\text{g/m}^3 \text{ day}$	Directive 2010/75/EC
Ni	20	$\text{ng/m}^3 \text{ day}$	Directive – 2004/107/EC; Directive – 2010/75/EC
Co	0.06	$\text{ng/m}^3 \text{ day}$	Directive 2010/75/EC
Mn	150	$\text{ng/m}^3 \text{ day}$	Directive 2010/75/EC
Fe	50	$\text{ng/m}^3 \text{ day}$	Jović & JOVANOVIĆ (2004)

range of the Recovery 98.1–134.5 suggest a good accuracy in case of the minor components, but lower in case of the major components, especially Ca.

## Statistical data processing

Basic descriptive statistics of the concentrations of major- and minor elements are shown in Tables 4 and 5.

### Statistic data processing using the Box whisker plot method

The presentation of minor components in  $\text{PM}_{10}$  particles were statistically processed and presented in the diagram (Fig. 2). The diagram is used to compare the dispersion of element concentrations (in  $\text{ng/m}^3$ ). The values of element concentrations had been studied on monthly basis; these are presented in Fig. 2. Figure 2a illustrates a dominant presence of iron, with a median shifted towards the upper quartile. The presence of dispersed concentrations is for a feature typifying Fe, in particular the maximum values that have a relative uniformity throughout the sampling months. Copper is the second most abundant element. It is similar to Fe, Cu characterized by very high concentrations in the entire set of the samples analyzed. The median of the Cu concentrations has lower values in the relation to those of Fe. The concentrations of Zn are lower than the values

of the previous two elements. The median is shifted towards the lower values of the quartile, whereas the dispersion of the maximum and minimum values is lower, in particular, relative to the minimum values. A high uniformity of the throughout the months is also the main feature characterizing the Zn concentrations overall consistency throughout the sampling period. Ti differs from the previous elements, the concentrations are lower and

Table 4. Basic descriptive statistics of major element concentrations (n=9).

Element	Mean	Median	Minimum	Maximum	St. Dev.
<b>Al</b>	19.49	20.16	11.02	23.87	3.64
<b>Na</b>	41.23	43.14	27.00	52.34	8.52
<b>Mg</b>	2.15	1.59	1.06	3.65	1.04
<b>Ca</b>	0.45	0.33	0.20	1.43	0.39
<b>K</b>	0.96	0.91	0.61	1.48	0.26

the median occupies up to the central part of the quartile. The dispersion of the Ti has not been distinguished, their values are consistent with average values. In Fig. 2b, Mn is characterized by the equalized concentrations, the median takes up the space between the quartiles, and dispersion is more noticeable with reference to the higher concentrations. Concentrations of Cr are regular, having a median similar to those of Mn; it occupies the segment between the quartiles. With regard the As, the median is shifted towards the lower values, whereas a dispersion of the maximum concentrations is prominent across all minor elements.

The elements with lower concentrations and their distribution are shown in Fig. 2c. Selenium appears as a most common element. The median is positioned within the central part of the quartile, whereas the minimum values have dispersed pattern. The Cd median is shifted towards the lower quartile. A dispersion of the extreme values is negligible, thus dismissed from the interpretation. Ni has the most prominent dispersion of maximum concentrations. As for the other elements in Fig. 2c

Table 5. Basic descriptive statistics of concentrations of major elements (n=9)

Element	Mean	Median	Minimum	Maximum	St. Dev.
<b>Fe</b>	1579.13	1551.50	1026.08	2635.52	435.26
<b>Cu</b>	870.62	906.71	402.58	1709.67	451.23
<b>Zn</b>	665.47	642.00	515.50	8.810	95.84
<b>Ti</b>	269.00	282.58	83.56	402.12	109.01
<b>Se</b>	5.04	5.42	0.93	7.47	2.21
<b>Cd</b>	1.14	1.12	0.78	1.33	0.18
<b>Ni</b>	3.43	3.49	1.35	6.12	1.35
<b>Sb</b>	0.14	0.00	0.00	1.27	0.42
<b>Co</b>	0.58	0.51	0.14	1.39	0.38
<b>Mn</b>	35.64	33.69	25.58	57.48	8.85
<b>Cr</b>	17.95	17.80	9.80	26.50	4.68
<b>As</b>	39.52	19.33	8.78	140.69	43.16
<b>Be</b>	0.18	0.19	0.07	0.27	0.07

appears as a most common element. The median is positioned within the central part of the quartile, whereas the minimum values have dispersed pattern. The Cd median is shifted towards the lower quartile. A dispersion of the extreme values is negligible, thus dismissed from the interpretation. Ni has the most prominent dispersion of maximum concentrations. As for the other elements in Fig. 2c

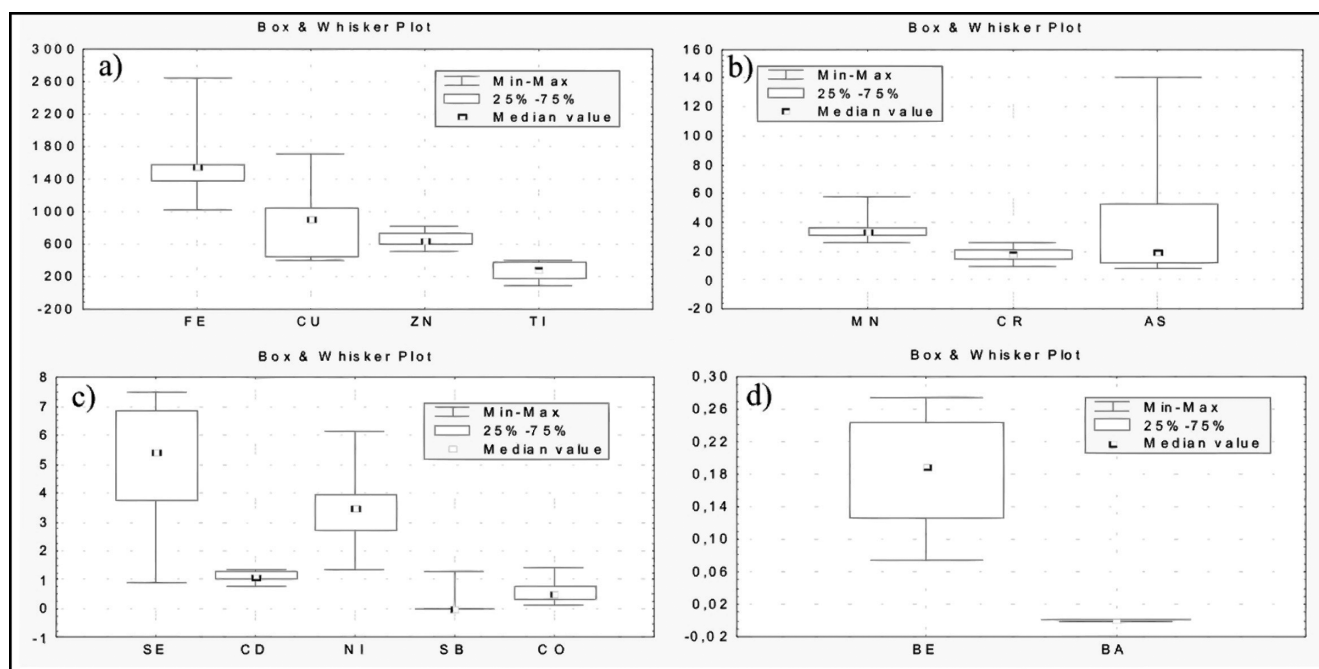


Fig. 2. Box – plot diagram of the chosen minor elements in suspended particles (in ng/m<sup>3</sup>).



the Ni is less apparent. The dominant values of the Sb concentrations are clustered around the lower quartile. The dispersion is moderate, still with minor presence of higher values. The concentrations of Co throughout the months are regular indicating the value of the meridian. The dispersion of the higher Co values is more prominent. Be is represented by the concentrations falling into a narrow range (Fig. 2d), the median is around the center of the quartile. The measured values of Be have no distinctive discrepancies (see Table 2 for details).

The major components in PM<sub>10</sub> particles are shown by the following five elements (Al, Na, K, Mg, Ca). The values are represented in  $\mu\text{g}/\text{m}^3$ . The diagram 3a exhibits a dominant distribution of K. The position of the meridian is towards the higher-level concentrations. The dispersion of the maximum concentrations is moderate. Al is the second most common element. Concerning the Al median, this value exhibits a shift towards the higher concentrations. The low dispersion is present by the lower concentrations of Al. The positions of the quartiles indicate a high consistency of Al concentrations throughout the months, being in a direct correlation with the mineral composition (unchanged presence of aluminosilicate minerals for the complete testing period). Dominant concentrations of Mg are rather balanced during the entire sampling period (corroborated by the quartile position). The dispersion of the minimum concentrations is narrow. Dominant concentrations of Ca are regular, along with a considerable dispersion of the higher values. The distribution of Ca concentrations is regular (Fig. 3b).

## The elemental mapping of the surface with suspended particles - distribution of all elements present

The determination of the distribution of all present elements in suspended particles of daily samples is performed on the sample surface of ca. 700  $\mu\text{m}$  (Fig. 4). In this manner, the spatial arrangement of all the elements is present including their participation in the sample (the denser/darker and lighter zones represent high concentration). In addition, by a comparison of the concentrations of certain elements in the same zones, we can more closely define a particular mineral phase. In addition to the area with the mapped particles, Fig. 4a exhibits the summary spectrum, whereas Fig. 4b illustrates the distribution of individual elements in the analyzed area.

## Discussion

The concentration of chemical elements in suspended particles was measured during the entire test period, and the results represent monthly element concentrations. According to the type of mutual bonding and content, all of the tested elements were divided into major elements and minor elements.

Major elements are dominant in suspended particles and are building the structures of the minerals as the elements carriers. Na and Al are the prominent leading elements in the structures of clays, feldspars and other aluminosilicates. Moreover, Al is

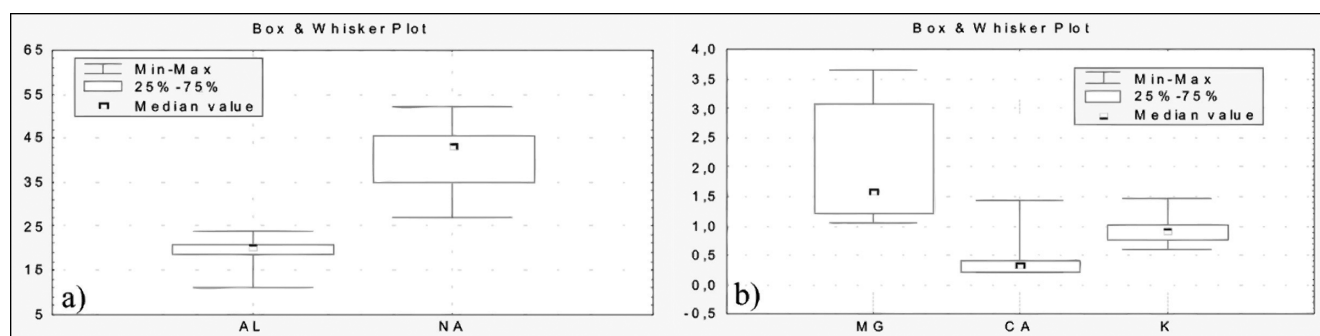
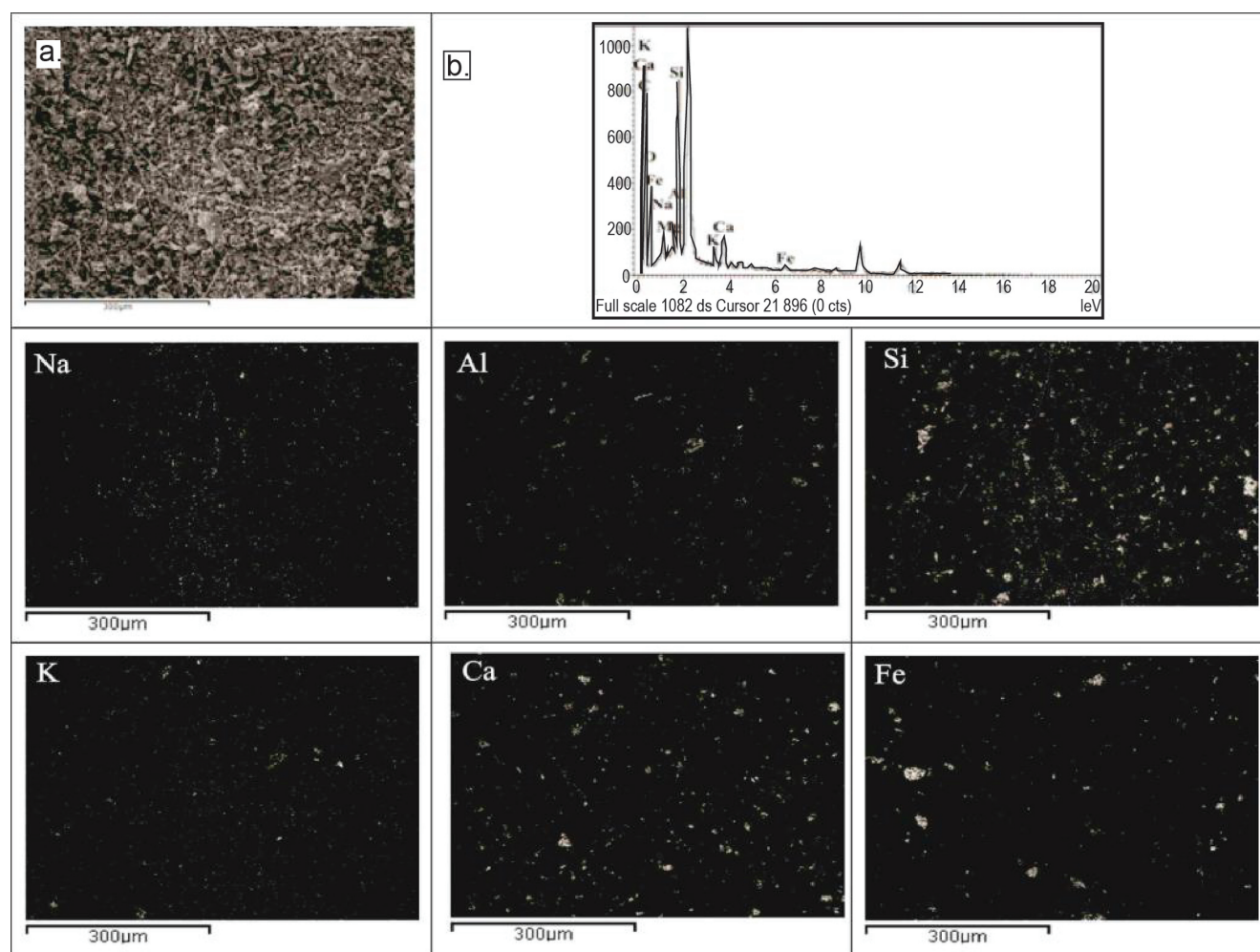


Fig. 3. Box - plot diagram of major elements in suspended particles (in  $\text{ng}/\text{m}^3$ ).



**Fig. 4. a.** Mapped suspended particles; **b.** Mapped area with EDS spectrum. Distribution of the elements present in the particles covered (Na, Al, Si, K, Ca, Fe).

a composite part of many amalgamated, complex particles, which have mostly an aluminosilicate structure. In addition to the investigations of mineralogical structures of suspended airborne particles in Lazarevac (CVETKOVIĆ et al., 2012, 2013), the similar conclusion that the presence of minor and major elements in fly ash as products of combustion has been reported by number of authors. In the six fractions of fly ash samples derived after coal combustion, many minerals are detected: calcite, anhydrite, gypsum (Ca); magnetite, hematite, Fe-spinels (Fe); clay minerals (Na, K, Al); plagioclase, K-feldspar, muscovite (Na, K, Al, Fe), glass – amorphous matter (Si, Al, Na, K) (VASSILEV et al., 2005; KRISHNAN et al., 2017).

In Fig. 3, the monthly medium content has variations according to the median that is shifted toward

higher values. This indicates that even dispersed maximum values of Na concentrations are not prominent (Table 1; S-7 and S-13). A similar distribution would be the case for Al, if the average concentration values for each month show more consistency. The average frequency is shifted almost to the boundary of the maximum concentrations. Al exhibits even the lower maximum value dispersion (Table 1; S-7 and S-13). The monthly distribution of the concentrations for Ca and Mg is relatively consistent, in particular for Ca (Fig. 3). The discrepancies in concentrations for these two elements were in December and January 2008, at the expense of the increased presence of dolomite, calcite and sulfates in samples of PM<sub>10</sub> particles (CVETKOVIĆ et al., 2012; 2013). At last, calcium has regular content through-

out the months. The values are quite regular, according to the quartiles that match the average value. Concerning the major elements, according to the diagram (Fig. 2) Fe and Ti are also present (illustrated together with the minor elements for a better visual presentation). Monthly variations are a feature characterizing Fe. The medians are shifted towards the higher concentrations. Such dispersed concentration values is the characterized the presence of Fe. The maximum value is measured in February 2008 (S-14). Concentrations of Ti are in balance for the entire testing period, indicating by the position of the medians. Dispersion of the maximum and minimum concentrations is in balance, no distinctive discrepancies.

Maximum values are measured during January 2008 (S-13). In suspended particles, Fe and Ti are in connection with hematite, magnetite or limonite and leucoxene. In addition, according to investigations of KUKIER et al. (2003) Fe oxides can be located within inclusions of silicate particles. It is noteworthy that the concentrations of these elements are elevated during the winter months, which can be explained by the presence of ash particles that may concentrate the aforementioned elements (CVETKOVIĆ et al., 2012, 2013). By observing mutual relationships, an interdependence of major elements is emphasized as their connection with a particular mineral composition. Because the suspended particles are of great importance as influencers on human health, the proper characterization of a composition of major elements has a high significance. The resulting relationship of concentrations is as expected; the entire set of the elements among themselves are a composite part of many mineral types traced in PM<sub>10</sub> particles. Aluminosilicate minerals (clays, chlorite, mica, feldspars) which are a segment of suspended particles best illustrate this relationship. In addition, metallic minerals (hematite, limonite-leucoxene) are very common. An increased level of deviations is only characteristic of calcium, which is most commonly in connection with gypsum, calcite or dolomite.

The concentration of minor elements is very important in PM<sub>10</sub> particles; at they directly influence a toxicity of inhaled dust. Toxicity of each element is characterized according to the maximum allowed concentrations (MAC), prescribed by the European

directive (2010/75/EU) and Serbian regulations (OFFICIAL GAZETTE RS; 65/08). The concentrations of the toxic elements, in PM<sub>10</sub> particles are of a great significance due to the possibility of influencing public health.

Besides major elements in coal ash, numerous minor elements are detected: lithophile (Ca, Be, Cs, Mg, Mo, rare elements, W), chalkophile or siderophile (As, Cd, Cu, Bi, Co, Fe, Mn, Ni, V), nonmetals S and B (VASSILEV et al., 2005).

The values of Zn in PM<sub>10</sub> particles represent the measured daily concentrations during entire sampling period (per month). Different monthly concentrations are measured, exposing different values for each month. The highest content is measured in the summer months. The July (S-7) in particular stands out as the month with the sunniest days. The appropriate climatic conditions enabled the distribution of Zn to the area of the Kolubara basin arrived from the Zn factory in Šabac. Among the analyzed minor elements, the contents of daily concentrations of Zn measured each month and across a year do not exceed the MAC prescribed by the European directive and Serbian regulations. Consequently, they do not pose a threat to human health (Tables 2 and 3). Zn in particles is bonded with silicate minerals, usually concentrated in ash, which characterized by using the presence of Zn in silicate phases of ash. In addition, mixed particles of silicate minerals and Fe oxides are the carriers of the concentrations of Cr, Cu, Mn, Ni and Zn (KUKIER et al., 2003).

*Arsenic (As)* is one of the most toxic elements, which once inhaled, can cause numerous sicknesses, of which cancer is the most common (ATSDR 1999; IPCS 1999). The reported monthly concentrations of As are elevated, reaching higher values during the entire measurement period. The maximum measured values of As are recorded within the summer months (June, July, August). High concentrations of As measured in the location of Lazarevac raise a warning flag, as the area has dense population. Numerous reports have analyzed the presence of As in urban dust, flying ash and coal dust. Majority of the reports are similar to the results obtained during this work (e.g., BLOCK & DAMS, 1975; GATARI et al., 2005; SENLIN et al., 2007). A few reports elaborated the impact of As<sup>3+</sup> and the less toxic As<sup>5+</sup> ash through com-

bustion (SHAH et al., 2008; TANBOONCHUY et al., 2011; CATALANO et al., 2012). As and Se found in PM<sub>10</sub> particles are in non-silicate phases (KIM & KAZONICH, 2004), whereas in coal ash, arsenic is present in a form of arsenopyrite (KIM & KAZONICH, 2004).

**Cadmium (Cd).** Concerning the toxic elements, Cd is least present in coal (in sphalerite) and urban dust (KABADAYI & CESUR, 2010; PARK & DAM, 2010). Through coal combustion, Cd is concentrated in ash, where it bonds with silicate phases (KIM & KAZONICH, 2004). Some reports indicate that Cd discharged by coal combustion occurs in submicron phases of ash (PASTUSZKA et al., 2010). Its monthly distribution at the measuring location of Lazarevac has values below the MAC, indicating that the measured concentrations of dust are not harmful to human health. However, through absorption and even lower concentrations of those allowed during an extended time period could become harmful to human health.

**Manganese (Mn)** is an element that may originate from numerous sources. The most common sources of Mn are coal dust, or the latter can be a product of fuel combustion. Its monthly distribution has variations, mostly being a function of the impact of the before-mentioned sources (NGUYEN et al., 2010; KABADAYI & CESUR, 2010; MORENO et al., 2011; AL-KHASHMAN, 2013). Concentrations of Mn from July to January 2008 are regular. Higher values are measured in February 2008, nevertheless monthly concentrations of Mn do not exceed the MAC. Concentrations of this element do not affect human health. Concerning trace element associations in the ash from the "Nikola Tesla" power plant (combustion of Kolubara's basin coal) the oxides of Fe and Mn seem to be dominant substrates of Cr and Ni (POPOVIĆ et al., 2001).

**Selenium (Se)** is one of the elements whose concentrations considerably differ through the monthly measurements. Lowermost concentrations measured are those from January and March, whereas the highest values are measured in August same year. Because coal is considered as the main source of Se, the impact of coal dust PM<sub>10</sub> particles is dominant in the summer period. After coal combustion, Se becomes concentrated in crystal, a glassy and amorphous phase of ash. The following researchers (BLOCK & DAMS, 1975; KIM & KAZONICH, 2004; SHAH et al., 2008) reached similar conclusions. The entire set of

the monthly inputs was below the MAC, concluding that Se concentrations do not affect human health.

The monthly contents of *chromium (Cr)* has considerable variations (Lazarevac measuring station). The full set of measured values of Cr are below the MAC (with very low values) of which the months June, July and August are emphasized having a considerable increase of values. Concentrations of Cr in Lazarevac are likely affected by individual household furnaces indicate that Cr is mostly concentrated in particles of ash and dust (SHAH et al., 2008; TANNER et al., 2008; NGYEN et al., 2010).

The highest measured concentrations of *copper (Cu)* were in August, October and January 2008. The entire set of measured values is below the MAC. The highest Cu contents seems not to originate from coal processing, it is rather associated with local agricultural activities (BEM et al., 2003; TANNER et al., 2008; KHAN et al., 2010; KABADAYI & CESUR, 2010).

**Cobalt (Co)** detected within suspended particles is present across the entire sampling period. The concentrations exhibit an irregular pattern. Co belongs to the group of highly toxic elements, and minimal doses of inhalation can cause serious consequences. The values measured in February 2008 contain a highest Co concentration. Increases in the concentrations across the sampling period impose a health threat to the local population at the expense of the diseases that may be induced by Co inhalation (carcinogenic, bronchial asthma, pituitary gland damage to lungs, bone marrow; KOMATINA, 2001). The results exhibit that Co often appears in inorganic sulfide particles of coal in the summer months (CLARK & SLOSS, 1992). In the winter months, Co is available in silicate semi-crystalline and crystal phases of ash (KIM & KAZONICH, 2004).

Concentrations of *nickel (Ni)* for the entire investigated period were under the Mac value, with the exception of February 2008 once the highest concentrations were registered. Despite the monthly concentrations are below the MAC, these value may affect human health. Even lower concentrations if introduced to a body over a longer period could cause change. Ni can be released in the air by numerous sources (coal, fuel, dust), and is characterized with a capability to achieve a strong connection with a considerable number of elements (PARK & DAM, 2010; NGYEN et al., 2010; KABADAYI & CESUR, 2010; AL-KHASHMAN, 2013).



The presence of *barium* (*Ba*) in  $PM_{10}$  particles is not very high. Within the sampling site, Ba is detected exclusively in February 2008 (S-14) attesting its dominance among ash particles. As Ba is not considered as a toxic element, there is no impact or evaluation on public health. Barium is detected in the finest particles in the form of barite, or as a composite part of particles released due to fireworks (combustion of the green flame) and setting off firecrackers (CONKING, 1985; MORENO et al., 2007; VECCHI et al., 2008).

The lower concentrations of *beryllium* (*Be*) are measured during the entire sampling period. Such distribution of concentrations leads to a conclusion that Be is connected with industrial dust, or is released due to fuel combustion. Globally, Be and his impact on the environment has not been sufficiently studied, thus there is no MAC value for this element. The latter is well-connected with a large number of elements due to its capability to appear in wider pallet of the pollution sources (PARK & DAM., 2010; ARKIAN et al., 2010; GARCIA et. al., 2012).

The concentration of *antimony* (*Sb*) was measured for October (S-10). The content is very low and is below the MAC for the months in which it was detected. Antimony is very rare in  $PM_{10}$  particles, and if present, it is in connection with industrial dust (BLOCK & DAMS, 1975; PARK & DAM, 2010).

The results of the mapping of the surface of suspended particles through the distribution of all present elements indicate the presence of particles of different shapes, ranging from rounded, spherical forms to irregular complex particles of different shapes that form aggregates of multiple mineral species. The main mineral phases were identified earlier by this method (CVETKOVIĆ et al., 2012; 2013; CVETKOVIĆ, 2013): from the group of silicates (quartz, alkaline feldspars, plagioclases, clay minerals, chlorite, biotite), from the sulfate group (barite, gypsum), and from the oxide group (magnetite, hematite) and calcite.

## Conclusion

The evaluation of air quality in school yard (Lazarevac) was performed by monitoring and sampling the air over nine consecutive months. The concentrations of minor elements in suspended particles

exhibited that certain elements appear in concentrations higher than the MAC. This particularly refers to As, Co sampled at the above-mentioned measuring station. The most worrying are concentrations of As (as an extremely toxic element that can cause deadly diseases through inhalation).

This study connected the chemical composition of the particles with its mineralogical composition providing an evaluation of air quality in the investigated area for a particular period. In general, air quality in the entire area during the period was is rather poor due to the exceeded values of As, Co. In order to improve the air quality, it was necessary to change or install new filters (onto a local thermoelectric power plant), what would considerably lower the ash content in the air. A bit later after the sampling period, new air filters were installed. Other sources of higher concentrations are not dependent on the technological process, making a human impact of limited influence (primarily regarding urban and coal dust). Most importantly, the results provide a solid base for the eventual comparative monitoring studies of local air quality, which is already an ongoing local environmental topic.

**Conflict of interest.** The authors report no conflicts of interest. The authors alone are responsible for the content and writing of the paper. The authors declared that they have no financial and personal relationships with other people or organizations that can inappropriately influence their work. There is no professional or other personal conflict of interest of any nature or kind in any product, service, and/or company.

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## Резиме

### Геохемија животне средине кроз анализу суспендованих честица ваздуха у урбаној средини Лазаревца (Србија)

Топографски ваздух увек садржи одређену количину аеросолних честица које се налазе у чврстом или течном стању. Поред природних аеросола, у атмосфери се налазе и значајне количине тзв. индустријских аеросола који могу негативно утицати на развој биљног и животињског света, а представљају и озбиљну опасност по здравље људи. Између осталих, силицијум диоксид се углавном налази у облику кварца и један је од најопаснијих загађивача који се удисањем може унети у људски организам.

Хемијски садржаји суспендованих честица (PM<sub>10</sub>) су мерени током целог испитиваног периода на мерном месту у Лазаревцу. Изабран локалитет због потенцијално великог броја загађивача треба да укаже на могуће концентрације тешких и других метала. Резултати представљају месечне концентрације мерног места током периода узорковања (2008 година). Добијене вредности су посматране и упоређене са максималним дозвољеним концентрацијама (МДК), како домаће тако и регулативе Европског комитета за стандардизацију.

Према стандарду за суспендоване честице објављеном у Службеном Гласнику РС за одређивање квалитета ваздуха инструментално су измерене су концентрације Cd и Mn, док су концентрације осталих елемената упоређене са стандардном литературом (табела 3). По начину везивања и садржаја сви испитивани елементи су подељени на макроелементе и микроелементе.

**Макроелементи** су доминантни у PM<sub>10</sub> честицама и директно су везани за структуре минерала као носећи елементи. Од њих су најважнији Na и Al као водећи елементи у структури глина, фелдспата и осталих алумосиликата. Такође, Al је саставни део великог броја стопљених, сложених честица који су претежно алумосиликатног састава.



Пошто су суспендоване честице врло важне јер могу директно утицати на здравље људи, одређивање састава макро елемената је од изузетног значаја. Из табеле 1 види се да су сви макроелементи у доброј међусобној зависности, са изузећем Са који је у нешто лошијем односу. Овакав однос је очекиван, јер скоро сви елементи представљају саставни део многих минералних врста које су присутне у  $PM_{10}$  честицама. То се најпре односи на алумосиликатне минерале (глине, хлорит, лискун, фелдспати) који су саставни део  $PM_{10}$  честица. Такође, врло су чести метални минерали (хематит, лимонит-леукоксен). Као што је наглашено, веће одступање једино је карактеристично за Са који је најчешће везан за гипс, калцит или доломит.

Садржаји **микроелемената** су врло важни у  $PM_{10}$  честицама јер могу директно утицати на токсичност прашине која се удише. Концентрације токсичних елемената у  $PM_{10}$  честицама су од изузетног значаја због могућег задржавања ових честица у човековом организму. Концентрације As и Co су изнад МДК вредности. Највише забрињавају концентрације As - изузетно токсичног елемента који инхалацијом може изазвати тешке болести.

Овај рад је повезао хемијски састав са минералним саставом честица и дао процену квалитета ваздуха у испитиваном подручју за дати период узорковања. Генерално посматрано квалитет ваздуха у Лазаревцу је лошег квалитета због утврђених прекорачења везаних за дати период узорковања. Да би се квалитет ваздуха побољшао неопходно је променити или уградити нове филтере на термоелектрани да би се знатно смањили садржаји пепела. Након ових и ранијих истраживања квалитета околног ваздуха, ваздушни филтери су постављени на локалну термоелектрану. Остали извори концентрација не зависе од технолошког процеса, тако да је утицај човека ограничен (првенствено се мисли на урбану и угљену прашину). Резултати истраживања ваздуха околине Лазаревца у датом временском интервалу су веома добра основа за даља испитивања квалитета ваздуха, како у локалу, тако и ширем подручју узорковања.

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