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Original scientific paper

## Physical and chemical characterization of the particulate matter suspended in aerosols from the urban area of Belgrade

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**Abstract:** Within this study, attempts were made to characterize the coarse and fine particulate aerosol fractions in urban area of Belgrade and define the inorganic chemical composition of the aerosol fractions. For this purpose, daily deposits of PM<sub>10</sub>, PM<sub>2.5</sub> and PM<sub>1</sub> aerosol fractions were collected during spring and autumn sampling periods in 2007 and analyzed for the PM mass concentrations, trace elements and secondary ions. The results obtained in the two campaigns showed average daily mass concentrations of 37 and 44 µg/m<sup>3</sup> for PM<sub>10</sub>, 22 and 23 µg/m<sup>3</sup> for PM<sub>2.5</sub> and 15 and 17 µg/m<sup>3</sup> for the finest particulate matter fraction PM<sub>1</sub> with the maximums exceeding the limit values set by the EU air quality regulations. A correlation with the gas-phase ambient air pollutants SO<sub>2</sub>, NO<sub>2</sub> and O<sub>3</sub> was found and is discussed. The concentrations of trace elements (Mg, Al, K, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sb, Ba, Tl, Pb and Th) and secondary ions (NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Na<sup>+</sup>) determined in the PM<sub>10</sub>, PM<sub>2.5</sub> and PM<sub>1</sub> aerosol fractions showed levels and distributions indicating soil and traffic-related sources as the main pollution sources. This study was conducted as the first step of PM assessment in order to point out main air pollution sources and suggest a remedy strategy specific for this region.

**Keywords:** aerosols; particulate matter; characterization; trace elements; secondary ions.

### INTRODUCTION

Particulate matter is an air pollution component directly emitted into the atmosphere through man-made and natural processes, including combustion from car-engines, households, industrial activities, road erosions, *etc.*, or formed as se-

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condary aerosols due to chemical transformations of gases mainly emitted by traffic or industry. It is a complex mixture of particles that may be solid, liquid or both, suspended in the air and consisting of organic and inorganic substances.<sup>1</sup> The coarse fraction (PM<sub>10</sub>), consisting of particles with an aerodynamic diameter of up to 10 µm, usually spends no more than a few hours suspended after emission before being removed from the atmosphere by sedimentation or precipitation processes, whereas the fine particles, of 2.5 µm diameter (PM<sub>2.5</sub>) or less (PM<sub>1</sub>), may remain in the atmosphere for days or even weeks and, consequently, be transported over long distances. Comprehensive toxicological and epidemiological studies conducted over the last decades have implicated that human exposure to such small airborne particles (PM<sub>10</sub> and less) have adverse health effects and may be a cause of a number of respiratory and cardiovascular inflammations.<sup>2</sup> During inhalation, the coarse particulate fraction usually remains in the upper part of the airways and lung but the fine particles penetrate deeper and reach the alveolar region. The chemical composition of air particulate matter fractions thus becomes very important and engrosses both scientific and public auditory.<sup>3,4</sup> The main adverse health effects were evident during episodes of extremely high levels of air pollution so that extensive air pollution control was initiated by authorities contributing to establishment and adoption of regulations for air quality improvement.<sup>5</sup> Regulations on the EU level have set objectives and limit values for ambient concentrations of PM with significant results (WHO, 2002). Their implementation in Serbia is, however, not completed so far and a new methodology for sampling and analysis is to be adopted and established within the existing air quality monitoring network.<sup>6</sup>

Since 2002, the suspended particles PM<sub>10</sub> and PM<sub>2.5</sub> in aerosols and their physical and chemical characterization were the subject of a few research projects dealing with air quality assessment in the Belgrade urban area.<sup>7-9</sup> The first air quality assessment resulted in valuable conclusions on air pollution in this area and some attempts were made to specify the emission sources using statistical methods and modeling. The main pollution sources were identified to be traffic and local heating units. These evaluations had, however, limitations due to non-referenced sampling facilities and incomplete chemical characterization of the aerosol fractions. Recently, a comprehensive study on PM<sub>10</sub>, M<sub>2.5</sub> and PM<sub>1</sub> in aerosols of the urban area of Belgrade have started within the frame of the WeBIOPATR project.<sup>10</sup> The main goal of the project is to introduce and establish standard operating procedures and quality assurance procedures in all stages of aerosol management and analysis, to use advanced analytical techniques for PM chemical characterization and finalize the research with source apportionment analysis.<sup>11</sup> The very first results of this study concerning mass concentrations measurements, elemental analyses and secondary ions determination in PM<sub>10</sub>, PM<sub>2.5</sub> and PM<sub>1</sub> aerosol fractions, collected during two sampling cam-

paigns (spring/autumn) in the urban residential area of Belgrade, will be presented and discussed in this paper. The obtained results should define mass concentration ranges of different aerosol fractions, trace elements and ions concentrations as a set of complementary data on the inorganic part of the chemical composition of PM. These data are compared with previously obtained data from the monitoring network and give some insight into the present situation in the residential area of New Belgrade concerning the particulate matter composition related to different air pollution sources.

#### EXPERIMENTAL

##### *Aerosol sampling*

The sampling campaigns were performed at the urban background residential site (Fig. 1) in Omladinskih Brigada Street (OBS), a fast developing New Belgrade area of the Serbian capital city (44°49'7" N, 20°28'5" E, 116 A) during two periods: from April 26<sup>th</sup> to May 2<sup>nd</sup> 2007 and from September 15<sup>th</sup> to September 19<sup>th</sup> 2007.

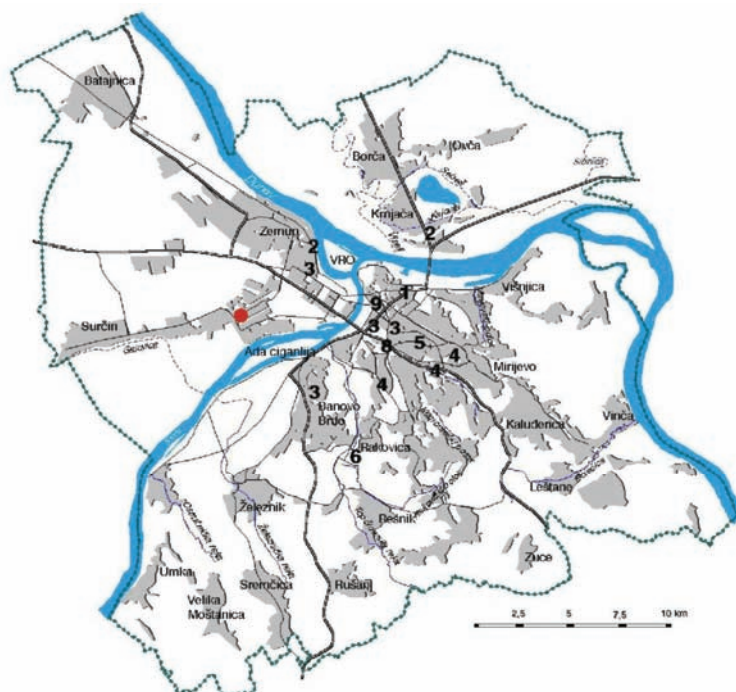


Fig. 1. Schematic position of the urban background residential sampling site OBS in Belgrade, labeled with the red point.

The aerosol sampling was conducted using three separate European reference low-volume samplers (Sven/Leckel LVS3) with inlets for collecting PM<sub>10</sub>, PM<sub>2.5</sub> and PM<sub>1</sub> fractions; all with flow rates 2.3 m<sup>3</sup> h<sup>-1</sup>. During the first campaign, the sampling devices were placed 1 m above the ground at 3 m distance to the building, with the PM heads next to each other. Their

position was changed in the next campaign, when the samplers were mounted on the 15 m high roof of the building and the inlets were pointed 2 m away from each other to allow independent aerosol collection. This position should be representative enough to enable further source apportionment analysis. The suspended particles were collected onto 47 mm Whatman QM-A double-sided quartz fiber filters, taken from the same batch and handled with special care, according to the standard operating procedure.<sup>12</sup> The PM<sub>10</sub>, PM<sub>2.5</sub> and PM<sub>1</sub> aerosol fractions were sampled on a daily basis (24 h, beginning at 7 a.m.) with one "field blank" per week, according to the sampling reference method defined by the EU Directive 1999/30/EC.<sup>13</sup>

An automatic air monitoring station with Horiba monitors: APSA-360, APNA-360, APOA-360 for SO<sub>2</sub>, NO<sub>2</sub> and O<sub>3</sub> measurements, respectively, and an Eberline FH-62I/R air particulate monitor for PM<sub>10</sub> mass concentration measurements was placed 1 m above the ground in front of the building at the OBS site, within the Belgrade municipal monitoring network. The corresponding hourly readings of SO<sub>2</sub>, NO<sub>2</sub>, O<sub>3</sub> and PM<sub>10</sub> concentrations were recalculated into average daily values and were used for comparison as considerable additional data from the same location in the same time periods.

#### *Gravimetric measurements*

Before exposure, the quartz fiber filters were pre-fired at 900 °C for 3 h to remove organic impurities<sup>14</sup> and the preconditioning procedure of both non-exposed and loaded filters was applied prior to gravimetric measurements.<sup>15</sup>

During the first (spring) sampling campaign, pre-fired quartz filters were placed in opened Petri dishes into a dessicator for 48 h in a Class 100 clean room with controlled temperature and relative humidity (20±2 °C, 50±5 %). The mass concentrations were determined as the average of two gravimetric measurements using a Sartorius 160P semi-micro balance with a minimum 0.01 mg mass resolution. Quality assurance was provided by the simultaneous measurement of a set of three blank filters that were interspersed within the pre- and post-weighing sessions of each set of sample filters and the mean change in the weight of the blank filter mass between the weighing sessions was used to correct the sample filter mass changes. This procedure was applied to both unexposed and exposed filters.

During the second (autumn) sampling campaign, the gravimetric procedure was conducted under improved conditions, according to EN 12341 for PM<sub>10</sub>.<sup>12</sup> The filters were exposed in opened Petri-slides for 48 h at 20±1 °C temperature and 50±5 % relative humidity in a Class 100 clean room with automatic temperature and pressure regulation. After preconditioning, the filters were weighed twice using a Precisa XR 125 SB micro-balance with 0.01 mg mass resolution and the mass concentrations were calculated as average values. Two pre-fired blank quartz filters were exposed in the conditioning room all the time and their mass checked after each series of eight sample measurements. Before and after each weighing session, certified test weights of 100 and 200 mg were used for accuracy control of the micro-balance. Following the gravimetric measurements, the loaded filters were stored in a cool room at 4 °C until analysis.

#### *Chemical analysis*

Once the gravimetric measurements were realized, loaded filters with PM<sub>10</sub>, PM<sub>2.5</sub> and PM<sub>1</sub> aerosol fractions were punched and areas of 6 and 3 cm<sup>2</sup> of each filter were used for trace elements analysis and secondary ions analysis, respectively. The CEN/TC 264 N779 procedure<sup>16</sup> was applied for extraction of the trace elements. The loaded quartz filters were treated with acidic mixture: HNO<sub>3</sub> (c)/30 % H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O (3/2/5) using analytical grade reagents (Merck) and distilled/deionized water (MiliQ, 18.2 MΩ). The filters were digested in closed

100 ml Teflon vessels in a Mars 5 microwave accelerated reaction system with a two-stage programmed temperature progress up to 200 °C. The concentrations of 20 elements: Mg, Al, K, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sb, Ba, Tl, Pb and Th were determined by inductively coupled plasma–mass spectrometry (ICP–MS) using an Agilent 7500 device with an Octopole Reaction System.

Quality control and verification of the applied procedures for microwave digestion and multi-elemental trace analysis using ICP MS was realized by the analysis of 2783 NIST (National Institute of Standard and Technology, MD, USA) standard reference material containing a PM<sub>2.5</sub> fraction of urban dust from a mixed industrial urban area of Vienna, collected on a polycarbonate membrane filter.

Before secondary ions analysis, the samples underwent a nano-pure water extraction for 24 h.<sup>17</sup> The aqueous extracts were further analyzed by standard ion chromatography using a Dionex DX-500 IC system to determine: NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Na<sup>+</sup> according to SOP MDL 064.<sup>18</sup>

## RESULTS AND DISCUSSION

### *Mass concentrations of PM<sub>10</sub>, PM<sub>2.5</sub> and PM<sub>1</sub> fractions*

The results of the PM<sub>10</sub>, PM<sub>2.5</sub> and PM<sub>1</sub> mass concentrations measurements in 24-hour aerosol deposits on quartz fiber filters collected in the spring and autumn sampling periods are shown in Fig. 2.

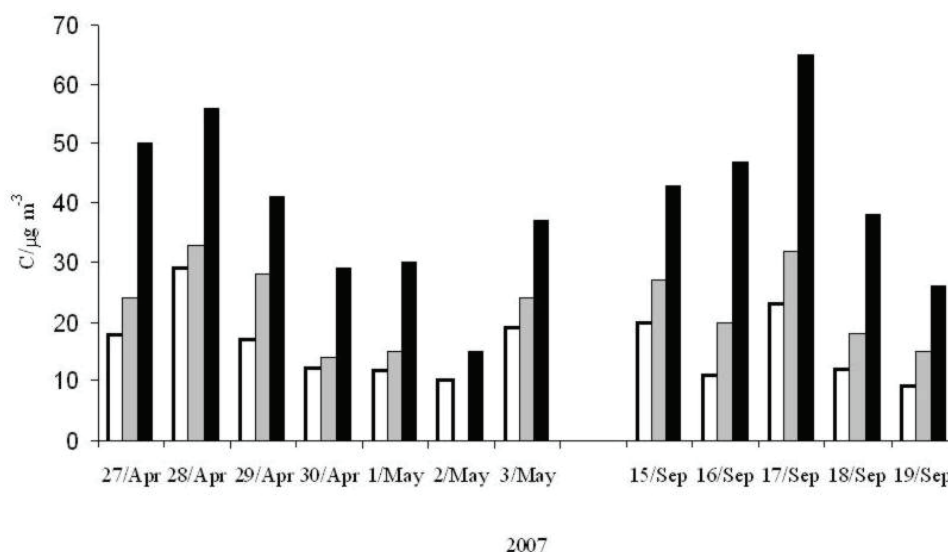


Fig. 2. Mass concentrations of the PM<sub>10</sub>, PM<sub>2.5</sub> and PM<sub>1</sub> fractions in ambient aerosol deposits collected during the spring and autumn sampling periods at the OBS sampling site.

In the graph PM<sub>10</sub>, PM<sub>2.5</sub> and PM<sub>1</sub> are presented by the black, gray and white bars, respectively.

It may be seen that all fractions follow the same trend, with noticeable working day/holiday differences. The spring sampling campaign was performed du-

ring non-working days, since the weekend was linked with holidays, except the first and last days of the sampling period. Consequently, on the 27<sup>th</sup> and 28<sup>th</sup> Apr, when the traffic frequency was very high, the PM<sub>10</sub> mass concentrations had maximum values of 50 and 56 µg/m<sup>3</sup> and the maximum mass concentrations of PM<sub>2.5</sub> and PM<sub>1</sub> were 33 and 29 µg/m<sup>3</sup>, respectively. During the autumn campaign, the PM<sub>10</sub> mass concentration had the maximum value of 65 µg/m<sup>3</sup> on Monday, 17<sup>th</sup> Sep, the first working day of the week. The corresponding PM<sub>2.5</sub> and PM<sub>1</sub> mass concentrations were also the highest in the period, with values of 32 and 23 µg/m<sup>3</sup>, respectively.

European air quality regulations stipulated that the average daily PM<sub>10</sub> mass concentrations should not exceed 50 µg/m<sup>3</sup> more than 35 times a year by 2005 and 7 times by 2010, with average annual limit values of 40 and 20 µg/m<sup>3</sup>, respectively. Monitoring of the fine particulate fraction is still not obligatory in EU,<sup>19</sup> although a recently published Directive<sup>20</sup> for PM<sub>2.5</sub> proposes 20 µg/m<sup>3</sup> as the annual average daily limit value and 35 µg/m<sup>3</sup> not to be exceeded more than 35 times a year. According to WHO, the PM<sub>10</sub> average annual mass concentrations vary widely, from 16 µg/m<sup>3</sup> in Finland and Ireland, to 50–52 µg/m<sup>3</sup> in Bulgaria and Romania in 2004, and the levels were higher during 2006 by at least 5 µg/m<sup>3</sup> in Austria, Hungary, Norway and Poland, and lower by at least 5 µg/m<sup>3</sup> in Bulgaria, Greece, Slovenia and Serbia.<sup>21</sup> These values mostly came from the air quality monitoring programs of the countries, in which 566 cities were assessed, with different QA/QC applied. If the mass concentrations values obtained within a few regional research projects are evaluated, there are observable but no remarkable differences. In urban areas from neighboring countries, the mean values of PM<sub>10</sub> mass concentrations were reported as: 75 µg/m<sup>3</sup> for Athens, Greece;<sup>22</sup> 72 µg/m<sup>3</sup> for Sophia, Bulgaria;<sup>23</sup> 51 µg/m<sup>3</sup> for Genoa, Italy;<sup>24</sup> 2001, 75 µg/m<sup>3</sup> for Bucharest, Romania.<sup>23</sup> Within earlier studies on air quality in Belgrade urban area, the mean biannual PM<sub>10</sub> and PM<sub>2.5</sub> concentration values were 68 and 61.4 µg/m<sup>3</sup> respectively.<sup>25</sup> Comparing these data, the mass concentrations values of both the coarse and fine particulate fractions obtained for Belgrade were within expectable levels for the region, with reserve concerning the considerable differences in data assessment periods and methodologies.

Concerning the particles size distribution in the mass concentrations, in the spring campaign, PM<sub>1</sub> on average counted for about 78 % of PM<sub>2.5</sub> and 47 % of PM<sub>10</sub>, while PM<sub>2.5</sub> counted 56 % of PM<sub>10</sub>. In the autumn campaign, the average PM<sub>1</sub> counted for about 66 % of PM<sub>2.5</sub> and 34 % of PM<sub>10</sub>, while PM<sub>2.5</sub> counted for 50 % of PM<sub>10</sub>. In general, a regular pattern of the distribution of the coarse and fine fractions in air particulate matter does not exist for urban background sites in Europe, in spite of a number of projects. Again, comparing to previous results for Belgrade urban areas,<sup>25</sup> there is a discrepancy in the ratios of the



fractions. Obviously, a better differentiation between two size fractions was achieved due to use of separate reference air-samplers with different inlets.

Seasonal variations of the PM<sub>10</sub>, PM<sub>2.5</sub> and PM<sub>1</sub> mass concentrations values as well as their ratios are slightly noticeable since both campaigns were performed in non-heating periods and in similar weather conditions. During the sampling periods, the mean values of temperature, relative humidity and wind speed were: 17.4 °C, 40 % and 0.8 m s<sup>-1</sup>, respectively, in the spring and 19.4 °C, 59 % and 0.2 m s<sup>-1</sup>, respectively, in the autumn campaign. There was no measurable precipitation level during both sampling periods, except for 0.1 dm<sup>3</sup> m<sup>-2</sup> on September 18<sup>th</sup>.

In general, the present results on the PM mass concentrations in the residential urban area may be reputed as a reliable indicator of still high air pollution in Belgrade City, as in previous periods of assessment, indicating the necessity of further studies and remediation.

#### *Correlations of the mass concentrations with other parameters*

During the sampling campaigns, the concentrations of SO<sub>2</sub>, NO<sub>2</sub> and O<sub>3</sub>, as well as the \*PM<sub>10</sub> mass concentration were simultaneously recorded by the automatic monitoring station situated at the OBS site within the Belgrade monitoring network. Hourly readings obtained at this station were recalculated into average daily values, which are given in Table I.

TABLE I. Average daily concentrations of SO<sub>2</sub>, NO<sub>2</sub>, O<sub>3</sub> and \*PM<sub>10</sub> obtained during the spring (26<sup>th</sup> Apr.–2<sup>nd</sup> May) and autumn (15<sup>th</sup> Sep–19<sup>th</sup> Sep) sampling campaigns at the automatic monitoring station at the OBS site

Date	$c(\text{SO}_2) / \mu\text{g m}^{-3}$	$c(\text{NO}_2) / \mu\text{g m}^{-3}$	$c(\text{O}_3) / \mu\text{g m}^{-3}$	$c(\text{PM}_{10}) / \mu\text{g m}^{-3}$
26 Apr. 2007	16.9	57.5	69	38
27. Apr. 2007	16.9	48	67.6	48
28 Apr. 2007	7.6	19.6	106.2	38
29 Apr. 2007	6.3	17.7	88.4	29
30 Apr. 2007	3.6	10.4	86.6	20
1 May 2007	4.6	18.6	86.7	21
2 May 2007	24.3	49.6	74.9	24
15 Sep. 2007	15	37	58	30
16 Sep. 2007	17	64	52	40
17 Sep. 2007	45	89	44	65
18 Sep. 2007	22	54	55	44
19 Sep. 2007	12	27	39	18

The concentrations of the ambient air gas-phase pollutants  $c(\text{SO}_2)$ , and  $c(\text{NO}_2)$ , and the mass concentration  $c(*\text{PM}_{10})$  obtained at the automatic air-monitoring station are shown in Fig. 3, together with the mass concentration  $c(\text{PM}_{10})$  obtained using the separate sampling device with a PM<sub>10</sub> inlet, for both the spring and autumn sampling periods.

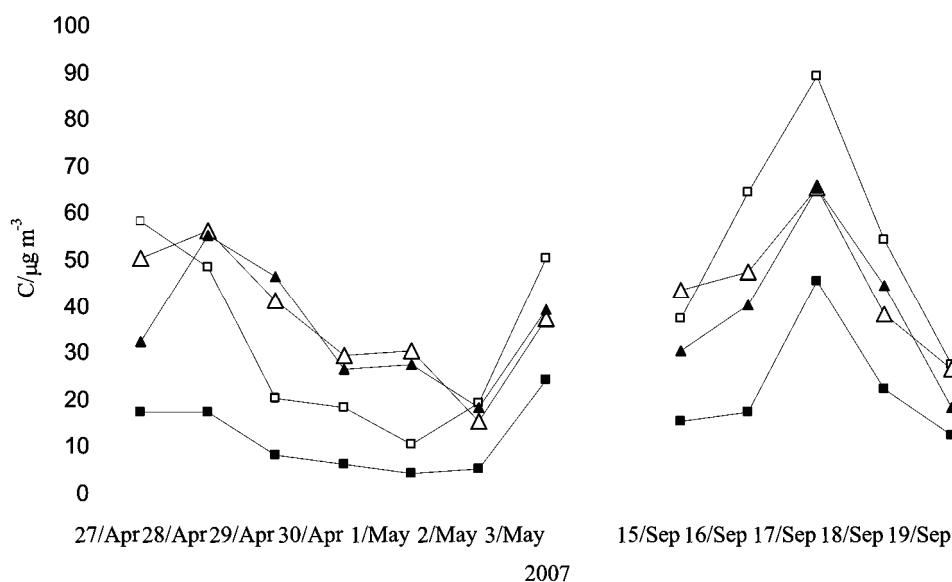


Fig. 3. Correlations between the daily concentration values of  $C(\text{PM}_{10})$  determined in this work and the  $c(\text{SO}_2)$ ,  $c(\text{NO}_2)$  and  $c(*\text{PM}_{10})$  values obtained at the automatic air-monitoring station (presented with the symbols  $\blacktriangle$ ,  $\blacksquare$ ,  $\square$  and  $\triangle$ , respectively) during the spring and autumn campaigns at the OBS sampling site.

It may be concluded that the same trends of data exist between the parameters presented in Fig. 3. Quantitatively, the correlations obtained after linear statistical analysis applied on the  $\text{PM}_{10}$  daily mass concentrations  $C(\text{PM}_{10})$  and the average daily concentrations  $c(\text{SO}_2)$ ,  $c(\text{NO}_2)$ ,  $c(\text{O}_3)$  and  $c(*\text{PM}_{10})$  are listed in Table I. The corresponding Pearson's coefficients of regression  $R^2$  for  $c(\text{SO}_2)$ ,  $c(\text{NO}_2)$  and  $c(*\text{PM}_{10})$  with respect to  $c(\text{PM}_{10})$ , were: 0.38; 0.52 and 0.76 in the spring and 0.75, 0.85 and 0.83 in the autumn sampling period, respectively. No significant correlation between the  $\text{O}_3$  and  $\text{PM}_{10}$  concentration values was obtained. In the autumn period, it was  $R^2 < 0.01$  and in the spring period, the correlation was negative with  $R^2 = 0.23$ . However, these conclusions may be taken only as indicative due to the considerable lack of data.

#### *Trace elements and ion contents in the PM fractions*

The chemical characterization of the  $\text{PM}_{10}$ ,  $\text{PM}_{2.5}$  and  $\text{PM}_1$  aerosol fractions comprised the determination of the elemental concentrations of Mg, Al, K, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sb, Ba, Tl, Pb and Th and the concentrations of the secondary ions  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NH}_3^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^+$  and  $\text{K}^+$ .

Prior to trace elements determination, the microwave acid extraction described in the previous section was applied to the aerosol deposits and the obtained extracts were further analyzed using the ICP MS technique. The utilized analyti-



cal procedure was validated by the analysis of the NIST 2783 standard reference urban dust material containing a PM<sub>2.5</sub> aerosol fraction, collected on a polycarbonate membrane filter. The results of this analysis are listed in Table II.

TABLE II. Results of the ICP–MS analysis of the NIST 2783 standard reference urban dust material containing a PM<sub>2.5</sub> fraction deposited on a polycarbonate membrane filter

Element	Certified value, ng	Observed value, ng	Recovery, %	LLD / ng
Al	23210±530	17124	74	0.1
As	11.8±1.2	6.9	58	0.03
Ba	335±50	350	104	0.034
Ca	13200±1700	9575	73	60
Co	7.7±1.2	7.6	98	1
Cr	135±25	143	106	0.04
Cu	404±42	357	88	0.025
Fe	26500±1600	25769	97	4
K	5280±520	5475	104	2.3
Mg	8620±520	7386	86	2.7
Mn	320±12	319	100	0.03
Na	1860±100	3689	198	40
Ni	68±12	44	64	0.02
Pb	317±54	346	109	0.03
Sb	71.8±2.6	3.5	5	0.025
V	48.5±6	45	93	0.03
Zn	1790±130	1574	88	0.13

The obtained recoveries in two runs were within  $\pm 15\%$  of the certified values for most of the elements. Some lower recoveries were attained for As, Ni and the crystal originating elements Cr, Al and Ca, which was already observed by other authors and usually explained by incomplete dissolution during the microwave digestion.<sup>26–28</sup> An exceptionally high recovery (198 %) was obtained for Na and an extremely low recovery (5 %) for Sb, consequently, these elements will not be further rendered. No reliable explanation for these results can be given, except that Na contamination might have occurred during the performance of the analysis. The lack of data on Na and Ca concentrations from ICP–MS analysis may partly be rectified by IC analysis of Na<sup>+</sup> and Ca<sup>+</sup>. In spite of outliers, the results of the elemental analysis NIST 2783 were satisfactory for the majority of the elements and the method may be considered as approved.

After this verification, the described analytical procedure of microwave acid extraction followed by ICP–MS analysis was applied to the aerosol samples. The mean and maximum concentration values of the trace elements determined in the PM<sub>10</sub>, PM<sub>2.5</sub> and PM<sub>1</sub> aerosol fractions from the spring and autumn periods are summarized in Table III.

TABLE III. The mean and maximum concentrations of trace elements in the PM<sub>10</sub>, PM<sub>2.5</sub> and PM<sub>1</sub> aerosol fractions in the spring and autumn sampling periods

Element	<i>c</i> / ng m <sup>-3</sup>														
	PM <sub>1</sub>			PM <sub>2.5</sub>			PM <sub>10</sub>			Spring			Autumn		
	Mean	Max	Autumn	Mean	Max	Autumn	Mean	Max	Autumn	Mean	Max	Spring	Mean	Max	Autumn
Mg	36	56.1	56	20.33	22.9	46.6	122	150.8	232	268.4	621	—	803.4	1606	—
Al	53.42	126.3	92	53.75	78.3	164.4	207	—	—	—	—	—	—	—	—
K	99.12	156.6	83	76.94	124.5	162.2	361	280	366	315.6	572	—	—	—	—
V	3.31	10.7	1.44	3.29	9.9	1.9	2.2	5.6	14.5	3.56	5.3	—	—	—	—
Cr	0.65	1.5	2.52	0.73	2.2	4.55	8.9	4.02	8.2	5.76	13.5	—	—	—	—
Mn	3.21	8.7	5.8	4.12	12	12.04	24.9	18.9	39.8	12.04	24.9	—	—	—	—
Fe	104.01	294	58.4	161.7	492	147	319	924.4	2187	1167	2013	—	—	—	—
Co	0.13	0.42	0.05	0.08	0.14	0.07	0.11	0.27	0.35	0.392	0.75	—	—	—	—
Ni	12.48	23	1.68	13.42	16.6	1.94	3.6	29.92	54.4	3.48	5.1	—	—	—	—
Cu	1.88	4.6	—	3.16	8.4	2.88	4.11	15.53	34.5	9.03	23.12	—	—	—	—
Zn	7.05	13.7	14.4	9.9	18.5	53.2	173	22.53	44.4	53.2	173	—	—	—	—
As	0.15	0.26	0.3	0.18	0.28	0.472	0.68	0.45	0.84	1.026	2.17	—	—	—	—
Se	0.15	0.24	0.32	0.16	0.26	0.438	0.63	0.24	0.35	0.556	0.99	—	—	—	—
Mo	1.58	3.35	3.76	3.49	5	4.54	6.3	2.01	3.5	4.56	10.7	—	—	—	—
Cd	0.17	0.28	0.24	0.21	0.33	0.298	0.42	0.29	0.48	0.326	0.51	—	—	—	—
Sb	0.07	0.18	0.04	0.06	0.1	0.085	0.13	0.21	0.44	0.248	0.52	—	—	—	—
Ba	0.61	1.86	3.74	1.43	4	5.2	7.8	13.85	27.7	17.46	31.7	—	—	—	—
Tl	0.02	0.04	0.032	0.03	0.05	0.03	0.057	0.04	0.07	0.04	0.051	—	—	—	—
Pb	23.42	62.6	35.2	30.05	80	57	161	42.88	86	74.8	212	—	—	—	—
Th	0.01	0.026	0.085	—	—	0.044	0.115	0.1	0.12	0.159	0.331	—	—	—	—

Additionally, the contents of  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NH}_3^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{K}^+$  in the  $\text{PM}_{10}$ ,  $\text{PM}_{2.5}$  and  $\text{PM}_1$  aerosol fractions, determined by the ion-chromatography (IC) technique described in the previous section, are given in Table IV.

TABLE IV. The mean and maximum concentrations of secondary ions in the  $\text{PM}_{10}$ ,  $\text{PM}_{2.5}$  and  $\text{PM}_1$  aerosol fractions in the spring and autumn sampling periods

Ion	$c / \mu\text{g m}^{-3}$											
	$\text{PM}_1$				$\text{PM}_{2.5}$				$\text{PM}_{10}$			
	Spring		Autumn		Spring		Autumn		Spring		Autumn	
	Mean	Max	Mean	Max	Mean	Max	Mean	Max	Mean	Max	Mean	Max
$\text{NO}_3^-$	0.52	0.42	0.77	1.48	0.67	0.67	1.11	2.09	1.00	1.18	1.88	2.87
$\text{SO}_4^{2-}$	4.03	6.46	4.59	7.36	4.16	8.10	5.20	6.61	3.98	6.00	5.20	8.03
$\text{NH}_3^+$	1.22	1.68	0.54	0.92	0.83	1.36	0.71	1.20	1.21	1.82	0.63	1.18
$\text{Na}^+$	0.61	1.77	1.22	1.79	0.90	1.88	1.09	1.56	0.33	0.42	1.03	1.67
$\text{Ca}^+$	1.21	1.40	0.20	0.22	1.64	1.89	0.21	0.24	1.23	2.11	1.69	3.67
$\text{K}^+$	0.51	1.66	0.11	0.17	0.80	1.77	0.15	0.21	0.23	0.32	0.20	0.28

Although the chemical composition of the aerosol fractions may not be accomplished by the data presented in Tables III and IV, these data indicated the main characteristics of the air pollution in this area. The crystal, soil-related elements, Fe, Mg, Al and K, had mean concentration values much higher than those of the other elements in both the coarse and fine aerosol fractions, especially in the autumn season, when resuspension processes are significant. In the total K concentration, there is usually a contribution from biomass combustion.<sup>29</sup> The anthropogenic originating elements Zn, Ni, As, Se, Mo, Cd, Ba and Pb present in the coarse aerosol fraction were higher in the autumn than in the spring, while the concentrations of V and Cu were higher in the spring season. The Zn concentrations determined in  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  were observable but not much higher than the concentrations of other trace elements, as was the case in recent assessments of the Belgrade air quality.<sup>7-9</sup> However, the concentrations of Pb, Ni and Zn were the highest among the trace elements in  $\text{PM}_1$ , that is the very fine aerosol fraction and, consequently, the most vulnerable for lungs. These elements originated mainly from traffic; Zn usually reported as a tracer for unleaded fuel and diesel powered motor vehicle emissions and Ni and Pb as lead gasoline exhaust emission products.<sup>30</sup> The EU Directive defines the Pb limit concentration value as  $500 \text{ ng/m}^3$  in  $\text{PM}_{10}$  and target values: 6, 5 and  $20 \text{ ng/m}^3$  in the  $\text{PM}_{10}$  aerosol fraction for As, Cd and Ni, respectively. Both mean and maximum concentrations of Pb, As and Cd observed in this work were below these values, except for the Ni mean  $29.9 \text{ ng/m}^3$  and maximum  $54.4 \text{ ng/m}^3$  concentrations determined in the spring period. In addition to heavy oil combustions and mechanical abrasion of metallic surfaces,<sup>31</sup> enhanced values of Ni may be caused by industrial activities.

The results showed significant concentrations of sulfates that may be associated with ammonia in the fine particles and preferably with nitrates in the PM<sub>10</sub> fraction. Sulfates, nitrates and ammonia are primarily associated with anthropogenic activities, referring to pollution from fuel or wood combustion. Moreover, nitrates usually present a coarse mode as a consequence of the reaction of HNO<sub>3</sub> with soil particles containing calcium carbonate.<sup>32,33</sup>

In general, as a result of the applied acidic and water extraction procedures and the highly sensitive measurements, the concentration values of a number of particulate matter constituents were determined with high precision and accuracy. Low-level concentrations of trace elements were easily detected in the finest particles fraction (PM<sub>1</sub>) due to the low detection limits of the employed measurement techniques. Although the obtained results may not be used to define the aerosol particulate matter composition as a whole, the results indicate that, in addition to natural sources, particulate matter from traffic might be an important source of air pollution in non-heating seasons.

#### CONCLUSIONS

A review of selected methods and means of monitoring and physical and chemical characterization of aerosol particulate matter in the urban area of Belgrade, followed by results obtained in spring and autumn sampling periods within the Project WeBIOPATR, are presented in this paper. A few conclusions may be drawn.

The mass concentration values of the PM<sub>10</sub> and PM<sub>2.5</sub> aerosol fractions obtained here are in accordance with previous results on the air quality in the Belgrade urban area and with other results in the region, showing the enhanced pollution levels in comparison with the limit values permitted by EU recommendations. Results for the finest fraction PM<sub>1</sub> were obtained for the first time in the urban area of Belgrade and they showed the same characteristics as the coarser fractions.

Correlations of the PM<sub>10</sub> mass concentrations with the concentrations of gas-phase ambient air pollutants  $c(\text{SO}_2)$ ,  $c(\text{NO}_2)$  and  $c(\text{O}_3)$  and the mass concentration  $c(*\text{PM}_{10})$  obtained by the automatic air-monitoring station the same trend of concentrations during the campaigns, except for  $c(\text{O}_3)$ .

The air particulate composition concerning the elements: Mg, Al, K, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sb, Ba, Tl, Pb and Th and the contents of secondary ions: NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NH<sub>3</sub><sup>+</sup>, Na<sup>+</sup>, Ca<sup>+</sup> and K<sup>+</sup> determined in the aerosol fractions PM<sub>10</sub>, PM<sub>2.5</sub> and PM<sub>1</sub> indicated soil and traffic related sources of pollution as dominant in the residential Belgrade urban area (OBS) in non-heating seasons.

Considering the limited numbers of aerosol samples taken into consideration, the presented results are just indicative but, from the aspect of data

quality, this evaluation enclosed all relevant internationally recommended standards and procedures.

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## ИЗВОД

ФИЗИЧКО-ХЕМИЈСКА КАРАКТЕРИЗАЦИЈА ЧЕСТИЦА СУСПЕНДОВАНИХ У  
ВАЗДУХУ УРБАНОГ ПОДРУЧЈА БЕОГРАДА

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У оквиру овог истраживања урађена је карактеризација различитих фракција ваздуха урбане средине Београда и одређен је неограничени удео у фракцијама аеросола. У ту сврху, узорковани су и анализирани дневни депозити PM<sub>10</sub>, PM<sub>2,5</sub> и PM<sub>1</sub> фракција аеросола током пролећног и јесењег периода 2007. године да би се одредиле масене концентрације и садржаји одабраних елемената и секундарних јона. Резултати добијени током ових кампања узорковања показују да су средње дневне масене концентрације: 37 и 44 µg/m<sup>3</sup> за фракцију PM<sub>10</sub>, 22 и 23 µg/m<sup>3</sup> за PM<sub>2,5</sub> и 15 и 17 µg/m<sup>3</sup> за најфинију фракцију PM<sub>1</sub>, са максималним вредностима које превазилазе граничне нивое постављене прописима ЕУ за квалитет ваздуха. Приказана је и дискутована веза ових концентрација са гасовитим загађивачима, CO<sub>2</sub>, NO<sub>2</sub> и O<sub>3</sub>. Концентрације елемената (Mg, Al, K, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sb, Ba, Tl, Pb и Th) и јона (NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> и Na<sup>+</sup>) одређених у PM<sub>10</sub>, PM<sub>2,5</sub> и PM<sub>1</sub> аеросолним фракцијама имају вредности које указују на природне изворе и саобраћај као главне изворе емитовања честица. Ова мерења су урађена као први корак при одређивању и карактеризацији честица аеросола да би се указало на главне изворе загађења и предложили одговарајући поступци ремедијације, специфични за овај регион.

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## REFERENCES

1. WHO, *Fact sheet EURO/04/05*, Berlin, Copenhagen, Rome
2. M. R. Gwinn, V. Vallyathan, *Environ. Health Perspec.* **14** (2006) 1818
3. M. R. Heal, L. R. Hibbs, R. M. Agius, I. J. Beverland, *Atmos. Environ.* **39** (2005) 1417
4. R. Reiss, E. L. Anderson, E. C. Cross, G. Hidy, D. Hoel, R. McClellan, S. Moolgavkar, *Inhal. Toxicol.* **19** (2007) 419
5. C. Buzea, I. P. Blandino, K. Robbie, *Biointerph.* **2** (2007) 17
6. M. Jovašević-Stojanović, S. Matić-Besarabić, in *Proceedings of the First International Webiopatr Workshop*, Book of extended abstracts, (2007), Belgrade, Serbia, 2007, p. 71
7. M. Tasić, S. Rajšić, V. Novaković, Z. Mijić, *Facta Universitatis* **4** (2006) 83

8. S. Rajšić, Z. Mijić, M. Tasić, M. Radenkovic, J. Joksic, *Environ. Chem. Lett.* **6** (2008) 95
9. M. Tasić, S. Rajšić, M. Tomašević, Z. Mijić, M. Aničić, V. Novaković, D. M. Marković, D. A. Marković, L. Lazić, M. Radenković, J. Joksić, *Environmental Technologies, New Developments*, E. Burcu Ozkaraova Gungor, (Ed.), I-Tech Education and Publishing, Vienna, 2008, p. 209
10. M.Jovašević, A.Bartonova, in *Proceedings of the First International Webiopatir Workshop*, Book of extended abstracts, (2007) Belgrade, Serbia, 2007, p. 10
11. C. W. Lewis, G. A. Norris, T. L. Conner, R. C. Henry, *J. Air Waste Manag. Assoc.* **53** (2003) 325
12. CEN 1998, *Air Quality. Determination of PM<sub>10</sub> Fraction of Suspended Particulate Matter. Reference Method and Field Test Particulate to Demonstrate Reference Equivalence of Measurement Methods (EN 12341)*, Brussels, 1998
13. EEC (1999), European Council Directive 1999/30/EC, *Official Journal L* **163** (1999) 41
14. *EMEP manual for sampling and chemical analysis*, Norwegian Institute for Air Research, Kjeller, 2001
15. *SOP MLD055: Standard operating procedure for the determination of PM<sub>2.5</sub> mass in ambient air by gravimetric analyses*, Northern Laboratory Branch, Monitoring and Laboratory Division, Air Resources Board, California Environmental Protection Agency, Washington D.C., 2003
16. *CEN/TC 264 N799: Ambient Air Quality – Standard method for the measurement of Pb, Cd, As and Ni in PM<sub>10</sub> fraction of suspended particulate matter*, European Committee for Standardization, Brussels, 2006
17. C. Lin, S. Chen, K. Huang, W. Lee, W. Lin, C. Liao, H. Chaung, C. Chiu, *Environ. Pollut.* **145** (2007) 562
18. *SOP MLD064: Standard operating procedure for the analysis of anions and cations in PM 2.5 speciation by ion chromatography*, Northern Laboratory Branch, Monitoring and Laboratory Division, Air Resources Board, California Environmental Protection Agency, Washington D.C., 2002
19. CEN, EN 14907, *Ambient Air Quality – Standard Gravimetric Measurement Method for the Determination of the PM<sub>2.5</sub> Mass Fraction of Suspended Particulate Matter*, European Committee for Standardization, Brussels, 2005
20. EC (European Commission), *Council Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe*, Official Journal European, 2008
21. *Exposure of children to air pollution (particulate matter) in outdoor air*, [http://www.enhis.org/object\\_document/o4741n27382.html](http://www.enhis.org/object_document/o4741n27382.html) (October 2008)
22. A. Valavanidis, K. Fiotakis, T. Vlahogianni, E. B. Bakeas, S. Triantafillaki, V. Paraskevopoulou, M. Dassenakis, *Chemosphere* **65** (2006) 760
23. D. Houthuijs, O. Breugelmans, G. Hoek, E. Vaskovi, E. Mihalikova, J. S. Pastuszka, V. Jirik, S. Sachelarescu, D. Lolova, K. Meliefste, E. Uzunova, C. Marinescu, J. Volf, F. Leeuw, H. Wiel, T. Fletcher, E. Lebret, B. Brunekreef, *Atmos. Environ.* **35** (2001) 2757
24. V. Ariola, A. D. Alessandro, F. Lucarelli, G. Marazzan, F. Mazzei, S. Nava, I. Garcia-Orellana, P. Prati, G. Valli, R. Vecchi, A. Zucchiatti, *Chemosphere* **62** (2006) 226
25. M. Tasić, S. Rajšić, V. Novaković, Z. Mijić, *J. Phys. Conf. Series* **71** (2007) 012016
26. C. Hueglin, R. Gehrig, U. Baltensperger, M. Gysel, C. Monn, H. Vonmont, *Atmos. Environ.* **39** (2005) 637
27. N. J. Pekney, C. I. Davidson, *Anal. Chim. Acta* **540** (2005) 269
28. S. Karthikeyan, U. M. Joshi, R. Balasubramanian, *Anal. Chim. Acta* **576** (2006) 23



29. E. S. Lindgren, D. Henriksson, M. Lundin, P. Therning, J. Laursen, N. Pind, *X-Ray Spectrom.* **35** (2006) 19
30. J. M. Pacyna, E. G. Pacyna, *Environ. Rev.* **9** (2001) 269
31. T. Okuda, S. Naoko, M. Katsuno, S. Tanaka, *Atmos. Environ.* **41** (2007) 7642
32. N. Galindo, J. F. Nikolas, E. Yubero, S. Caballero, C. Pastor, J. Crespo, *Atmos. Res.* **88** (2008) 305
33. M. Viana, X. Querol, A. Alastuey, *Chemosphere* **62** (2006) 947.