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SCINTIFIC PAPER

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PRELIMINARY ANALYSIS OF LEVELS OF ARSENIC AND OTHER METALIC ELEMENTS IN PM_{10} SAMPLED NEAR COPPER SMELTER BOR (SERBIA)*

In this paper, the levels of twenty one elements (Ag, Al, As, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, S, Se, Sr and Zn) in PM_{10} are presented, as well as SO_2 concentration, measured at the sampling site in an urban area of the town of Bor (40,000 inhabitants) in eastern Serbia. The sampling site was located in a densely populated city center about 0.65 km away from one of the largest copper mines and copper smelters in Europe. For the first time PM_{10} was collected using the European standard sampler, during a preliminary campaign in duration of 7 days in early spring 2009. PM_{10} were sampled on PTFE membrane filters and element concentrations were quantified by GF AAS and ICP AES. Concentration levels and correlations within trace elements, PM_{10} and SO_2 indicated that industrial activities underpinned with meteorological conditions of low wind speed (calm) are the main factors that influence air pollution in a densely populated area. It was evident that both PM_{10} mass concentration and SO_2 concentration once exceeded the daily limit values during a measuring period of seven days. Strong relationship was found between PM_{10} and Mn, Mg, Ca and B daily average concentrations. On the other hand, SO_2 correlated strongly with As, Pb, Cd, Cu and S daily average concentrations. These results confirm the relationship between emissions of SO_2 from the Copper Smelter Bor and calm meteorological conditions (wind speed less than 0.5 m/sec) with the concentration levels of carcinogenic substances of arsenic, lead and cadmium in ambient air.

Key words: copper smelter; air pollution; SO_2; PM_{10}; carcinogenic substances; trace elements; arsenic.

The Copper Smelter Complex Bor (RTB Bor) is the largest pollution source in the region of eastern Serbia with emissions of over 200000 t of sulfur dioxide and 300 t of arsenic per year. More than a century of mining activities has left obvious consequences: dead rivers, damaged and destroyed agricultural soils with an average of 11000 t of waste per citizen [1] and higher level of toxic substances in air. The waste substances from the mining industry leak into the soil of the surrounding villages and rivers, ending up in the Danube river [1]. The Bor settlement has been established around 1800 and obtained town status in 1947. One of the largest copper mines as well as copper smelters in Europe is located next to Bor with 40,000 inhabitants and 20,000 in settlements in the surrounding area. Inhabitants in this area have been exposed to toxic substances over a century, since 1904 when a French company opened the mine and began operations. Taking into account the published research studies about element content of inhalable and respirable particulate matter as well as gaseous pollution in towns and settlements that are suited in area near copper smelters and similar industrial plants [2-6], data about the composition of atmospheric aerosols in town Bor and settlements near the Copper Smelter Bor are still poor and incomplete [1,7-9]. Exposure to toxic pollutants causes a range of human disorders and ecological damage. Knowledge of the element composition of PM_{10} (particulate matter with diameter less than 10 μm) emitted from copper smelter processes is of great importance from the

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health point of view, as many potentially toxic trace elements may be contented. It is therefore vital that emissions are strictly limited and controlled. Of particular importance is the evidence of inhalable particulates that carry higher concentrations of carcinogenic substances that may be released during the copper smelting processes as substances that contain inorganic arsenic, chromium (VI), cadmium, nickel and lead. According to International Agency for Research on Cancer-IARC classifications [10] substances as: inorganic arsenic, cadmium and cadmium compounds, chromium (VI) and nickel compound are classified as carcinogens to humans (group 1); lead compounds are classified as probably carcinogenic to humans, (group 2A); while lead and nickel metallic and alloys are recently nominated as possibly carcinogenic for humans (group 2B). Furthermore, the single element or ratio between elements could be used as a fingerprint of a special source emitting other hazardous species that are less stable and more difficult to measure.

Inorganic arsenic is found naturally in soil and many kinds of rock, especially minerals that contain copper and lead [11]. It is a component of more than 245 minerals [12]. Arsenic is released into the environment from a variety of natural and anthropogenic sources [5]. On a global level the most important source of emission of arsenic into the atmosphere is the burning of fossil fuels as well as waste incineration. However, one of the main anthropogenic sources is copper smelting, where arsenic goes up the stack and is emitted in air as fine dust [11]. Emissions from the Copper Smelter Bor mainly consist of particulate matter (PM) and sulfur oxides (SO_x). Fugitive emissions are generated during material handling operations. Copper and iron oxides are the primary constituents of the particulate matter, but arsenic, antimony, cadmium, lead, mercury, and zinc, may be also present as oxides, along with metallic sulfates and sulfuric acid mist.

Ore melted in the Copper Smelter Plant in Bor is of chalcopyrite-pyrite type with increased content of arsenic which is found in a form of FeAsS and Cu_3AsS_4. The oxidation, roasting and melting of such mineral forms result in increased heavy metal oxides and SO_2 which in certain quantities contaminate the environment. The outdated technology for copper production (pyrometallurgy) in the Copper Smelter Bor is the main source of arsenic in the air.

Typical concentrations of arsenic are 1-10 ng/m^3 and up to 30 ng/m^3 in rural and urban areas, respectively [13]. Short term breathing of highly polluted air with inorganic arsenic, with concentrations higher than 100 μg/m^3, cause throat soreness and lung irritation, while longer exposure to lower concentrations can lead to skin effects, circulatory and peripheral nervous disorders [11]. The major hazard associated with inhalation of arsenic compounds is lung cancer [14]. Risk assessments have been based on studies around numerous copper smelters. Increased risk of lung cancer can be found in workers exposed to emissions in smelters, mines and chemical factories, but also population living in the vicinity of smelters, chemical arsenic factories and wastes sites with arsenic [11]. Assuming linear dose-response relationship, a safe level for exposure to inorganic arsenic cannot be recommended. For an arsenic concentration of 1 ng/m^3 in air, the estimated lifetime risk is 1.5×10^{-3} and for arsenic concentration of 6.6 ng/m^3 the excess lifetime risk is 1:100000 [13]. The mean annual concentration for arsenic of 6 ng m^{-3} (target value) is proposed for PM_{10} by the European Commission for 2012 [17].

EXPERIMENTAL

The sampling site and surrounding area of Bor and the Copper Smelter Complex is noted on the map of the Bor municipality (Figure 1). The meteorological data that has been collected at a station near the sampling site over several decades show that the prevailing winds condition is calm with the frequency of more 50-60%. Otherwise, the prevailing winds are predominantly from west-northwest. Table 2 shows the wind conditions in the last decade. During rainy periods, the typical east or southeast winds are of more concern. Light and variable winds are likely to cause very high localized concentrations of pollutants.

The results presented in this paper cover the preliminary campaign performed from March 24 to April 1, 2009, at location Museum (location M1 at Figure 1). For the first time, particulate matter was sampled with a European reference low volume sampler LVS3 (Sven/Leckel LVS3) with inlet for PM_{10} fraction (flow rate of 2.3 m^3/h). All PM_{10} samples were collected on Teflon membrane filters (Cronus PTFE membrane filter, 0.45 μm) from the same batch. The sampler was mounted on an open terrace of Museum at 10 m above the ground. Daily (24 h) measurements were done, according to the sampling reference method defined by the EU Directive 1999/30/EC [16]. The reference method for the sampling and measurement of PM_{10} is described in EN 12341:1999, Air Quality – Determination of the PM_{10} fraction of suspended particulate matter - Reference method and field test procedure to demonstrate reference equivalence of mea-

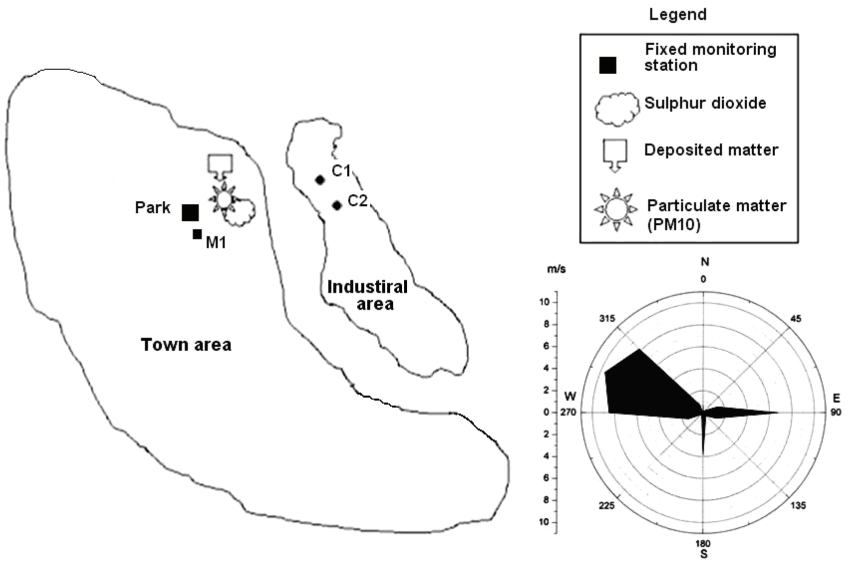

Figure 1. Map of the Bor municipality area with measuring point (M1) and Copper Smelter Bor main smokestacks (C1, C2) together with winds rose (1998-2009).

Table 1. Average wind speed and wind direction (%) in Bor, 1998-2009

Year	Calm	N	NNE	NE	ENE	E	ESE	SE	SSE	S	SSW	SW	WSW	W	WNW	NW	NNW
1998	56.6	0.2	0.2	0.8	7.5	3.9	0.3	0.3	0.2	3.3	0.7	0.1	1.0	7.0	6.9	10.0	1.0
1999	61.2	2.2	0.0	0.1	5.2	3.2	0.5	0.3	0.1	2.7	0.7	0.3	0.5	3.4	6.4	9.7	1.4
2000	75.7	0.5	0.1	0.1	3.1	2.0	0.0	0.1	0.2	2.0	0.7	0.2	0.5	2.4	6.2	5.5	0.8
2001	66.1	0.2	0.1	0.4	3.3	2.6	0.2	0.2	0.2	3.3	0.1	0.4	0.2	3.1	6.4		
2002	58.0	0.8	0.7	0.6	3.1	8.5	0.5	0.2	.4	4.0	0.4	0.6	1.7	7.4	8.4	4.4	0.3
2003	62.3	0.2	0.2	0.1	2.3	7.0	0.4	0.3	0.3	1.8	0.3	0.3	0.8	6.5	9.4	6.5	1.3
2004	51.7	0.9	0.2	0.3	1.5	7.6	0.9	0.4	0.4	4.7	0.8	0.4	1.2	6.1	11.2	10.7	1.0
2005	54.3	1.5	0.2	0.3	1.5	8.1	1.2	0.3	0.4	3.9	0.3	0.1	1.4	7.7	9.4	7.1	0.7
2006	53.6	0.7	0.1	0.3	1.4	6.8	1.3	0.4	0.6	3.9	0.3	0.2	1.4	8.5	9.6	8.2	0.8
2007	49.8	0.4	0.7	0.2	2.3	7.9	1.3	0.5	0.6	5.4	1.5	0.4	1.4	8.6	10.7	7.8	1.1
2008	50.9	0.6	0.2	0.1	3.0	7.6	1.3	0.6	0.6	4.1	2.2	0.5	1.4	10.4	9.2	5.5	1.8
2009	58.2	0.4	0.3	0.6	3.2	7.8	1.7	0.4	0.7	0.7	3.4	0.9	0.2	1.2	9.3	6.4	3.9
Average	58.2	0.7	0.2	0.3	3.1	6.1	0.8	0.3	0.4	3.3	0.7	0.4	1.0	6.0	8.6	7.4	1.3

surement methods [17]. The filters were changed at 9 a.m. every day.

Measuring point 1 - Museum was situated downwind of easterly prevailing wind from Copper Smelter Complex. The site is located 650 m west from the Copper Smelter Plant fence line. A dense population (15,000 inhabitants) settlement is situated directly downwind from the Copper Smelter Plant. A large effect on the local environment is often noted at this location - burning eyes, sore throat, and taste of sulfur dioxide. This location was selected as to represent typical and important ambient air quality situation near a copper smelter.

During the preliminary campaign in Bor, the concentrations of twenty six elements (Ag, Al, As, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, Pb, S, Sb, Se, Sr, V and Zn) in PM_{10} were quantified by Graphite Furnace Atomic Absorption Spectrometry - GF AAS (PerkinElmer 1100B Model) and Atomic Emission Spectrometry with Inductively Coupled Plasma - ICP AES (Spectro Ciros Vision model). The metals have been chosen based on their toxicity and their possible metallurgical origin. The ICP AES is a fast, sensitive, accurate and less expensive technique since it could measure concentrations of several metals simultaneously. As more sensitive, GF AAS was used for the determination of carcinogenic elements such as arsenic, cadmium and lead presented in PM_{10}.

Before and after exposure, filters were preconditioned and weighed three times following the procedure proposed in EN12341. After preconditioning in a clean room Class 100 (duration 48 h, $t = 20\pm1$ °C, $RH = 50\pm5\%$) certified weights of 100 and 200 mg and teflon filters before and after collecting PM_{10} on a daily basis were weighed using a Precisa XR 125 SB semi-micro balance with a minimum 0.01 mg mass resolution. PM_{10} mass concentrations on a daily basis were calculated using an average of three values of weight of the loaded and the unloaded Teflon filters.

The loaded filters, after gravimetric measurements, were prepared for chemical analyses following the procedure from CEN/TC 264 N779 [19]. The filters were dissolved with an acidic mixture HNO_3 (concentrated) 30% H_2O_2/H_2O (3/2/5) using analytical grade reagents (Merck) and double distilled water (MiliQ, 18.2 MΩ). After that, samples were digested in closed 100 ml Teflon vessels in a CEM Mars 5 microwave accelerated reaction system with a two-stage programmed temperature progress up to 200 °C.

Urban particulate matter Standard Reference Material 1648a (National Institute of Standard and Technology, MD, USA) was analyzed for quality control and verification of the applied procedures for microwave digestion and multi-elemental trace analysis using ICP AES and GF AAS.

RESULTS AND DISCUSSION

The results of the analysis of NIST 1648a Urban Particulate by the ICP AES and GF AAS compared with corresponding certified values are shown in Table 2. The table shows recovery and limit detection values (DL) and confirms that the results for almost all trace elements of interest agree with NIST certified values and differences between repeated tests are not significant. As it can be seen, recoveries for major of trace elements are between 90 and 110%. Recovery for Sn is less than 120% and for Sr over 80%. Significant deviation from certified values, recovery test less than 80%, was found for Na, Mg, Sb, Cr and Ti.

Table 3 summarizes the concentrations of twenty-one elements found in seven PM_{10} samples collected during the preliminary campaign. The contents of mercury, bismuth, vanadium, cobalt and antimony were below the detection limit.

Additionally, the average daily concentrations of SO_2 (μg/m^3) for the sampling period are given in Table 3. Due to a certain negative effect of SO_2 in the atmosphere, the European Union limits its mass contents: the limit per hour for protection of human health is 350 μg/m^3, not to be exceeded more than 24 times per calendar year; the daily limit for protection of hu-

Table 2. Results of ISP AES analysis of the NIST 1648a standard referent urban dust material

Element	Certified value, mg/kg	Observed value, mg/kg	Recovery, %	Detection limit, ppm
As	115.5±3.9	113.4±10.0	98.2	3
Cd	73.7±2.3	71.6±5.6	97.2	0.05
Ce	54.6±2.2	54.9±5.4	100.5	0.5
Co	17.93±0.68	17.34±3.78	96.7	0.2
Cu	610±70	550±22	90.2	0.02
Mn	790±44	718±5	90.9	0.005
Ni	81.1±6.8	81.3±8.0	100.2	0.5
Sb	45.4±1.4	52.0±19.6	114.5	5
Sr	215±17	176±1	81.9	0.04
V	127±11	116.4±5.1	91.7	0.2
Na	4240±40	1745±65	41.2	2
Zn	4800±270	3994±128	83.2	0.2
Cr	402±13	134±24	33.4	0.3
Ti	4021±86	1194±75	29.7	1
Se	28.4±1.1	40.5±10.8	142.6	9
Ag	6.0±0.3	2.9±0.9	48.6	0.08
Al	3.43±0.13	3.09±0.20	90.1	0.4
Ca	5.84±0.19	5.98±0.30	102.4	2
Fe	3.92±0.21	3.59±0.16	91.6	2
Pb	0.655±0.055	0.600±0.092	91.6	2
S	5.51±0.36	5.30±0.10	96.2	3
K	1.056±0.049	0.500±0.012	47.4	6
Mg	0.813±0.012	0.636±0.014	78.3	0.1

Table 3. Daily average PM_{10} and SO_2 concentrations (μg/m^3), element composition (ng/m^3), target values and meteorological para-meters for the sampling period

Elements/ parameters	Unit	Date							Target value [16,20,22]
		March						April	
		24	25	26	27	30	31	01	
As	ng/m^3	2.4	4.3	10.8	4.0	149	48.7	11.6	6 ng/m^3
Pb		24.9	44.9	146.7	64.8	226.4	83.8	63.1	500 ng/m^3
Mn		< 1	4	3	3	10	13	< 1	
Ni		< 1	< 1	< 1	22	3	< 1	< 1	20 ng/m^3
Cu		60	86	309	119	522	325	158	
Cr		< 1	< 1	< 1	1	3	5	2	
Fe		68	316	511	298	896	997	402	
Al		164	206	309	193	610	593	167	
Ag		< 1	7	12	< 1	< 1	< 1	< 1	
Se		< 50	< 50	96	< 50	80	< 50	86	
Zn		46	19	69	73	233	168	35	
Na		< 1	78	119	254	148	169	42	
K		46	95	135	183	208	293	87	
Mg		27	61	73	54	146	210	29	
Ca		245	689	640	640	918	2694	89	
Sr		< 1	< 1	2	< 1	6	5	< 1	
Ba		< 1	18	2	< 1	15	23	< 1	
B		16	4	12	17	10	42	10	
S		399	755	1860	771	3350	1650	1250	
Mo		5	4	< 1	< 1	7	2	< 1	
Cd		0.18	0.59	0.82	1.04	22.6	10.3	2.0	5 ng/m^3
PM_{10}	μg/m^3	15	26	35	24	50	293	24	
SO_2		11.0	18.7	24.2	19.2	185	52.4	91.8	
t / °C	-	6.4	1.4	3.0	6.2	13.4	14.6	10.3	
Wind direction	-	SSW	W	silence	silence	silence	silence	silence	

man health is 125 μg/m^3, not to be exceeded more than three times per calendar year; and the annual limit for protection of ecosystems is 20μg/m^3 [16,19]. According to the EU Directives, the prescribed daily limit of 125 μg/m^3 of SO_2 was exceeded in one case during the preliminary campaign. Since the beginning of 2004, continuous measurements of SO_2 concentrations have been started. Sulfur dioxide concentrations exceed daily limit values at this measuring point more than a hundred times per calendar year [7].

Average daily PM_{10} mass concentrations varied between 15 and 293 μg/m^3 for the period of the preliminary sampling campaign (Table 3). The daily limit of 50 μg/m^3 prescribed by EU Directives was once equal and once was exceeded (293 μg/m^3) in the measured period. The contributions of measured elements in PM_{10} vary from 2.5 to 15.1%.

In this study, it can be shown that approximately 57 (4 days), 29 (2 days) and 14% (1 day) of the daily average of arsenic, cadmium and nickel concentrations exceeded the annual mean target values proposed by EU Directive respectively during the seven days sampling period. Daily average SO_2 concentrations, PM10 mass concentration and concentrations of some significant metals in PM_{10}, collected during preliminary campaign in Bor are presented in Figure 2.

The target values for air pollutants, such as arsenic, cadmium and nickel, notified in the EU legislation and in the current legislation of the Republic of Serbia are the same. It could be emphasized that in the previous period in the Republic of Serbia, arsenic, cadmium, nickel and lead were measured in total suspended particle (TSP) in the framework of basic and urban monitoring networks [20], while the sampling and assessment of the elements content in PM_{10} has been involved since 2004 [15]. In 2008, PM_{10} was monitored at 382 stations in EU counties that was reported and stored in Air Base. At 16 stations the detected concentrations were above target value set for 2012 [21]. Exceedance was identified in: Belgium at 8 stations; including 5 located near industrial plant in Hoboken; 4 stations in Czech Republic; and one in Austria, Germany and Poland.

Table 4 shows descriptive statistics for PM_{10} mass and SO_2 concentrations and metallic elements concentrations in PM_{10}, during the experimental period and wide range of daily average concentrations. At the beginning of the experimental period, the daily average concentrations of metals in PM_{10}, and PM_{10} and SO_2 concentrations were lower. During the first and second day the prevailing wind was SSW and W with an average wind speed of 1.9 m/s. During the next five days the meteorological conditions were calm, as it is shown in Table 3. In the second part of the

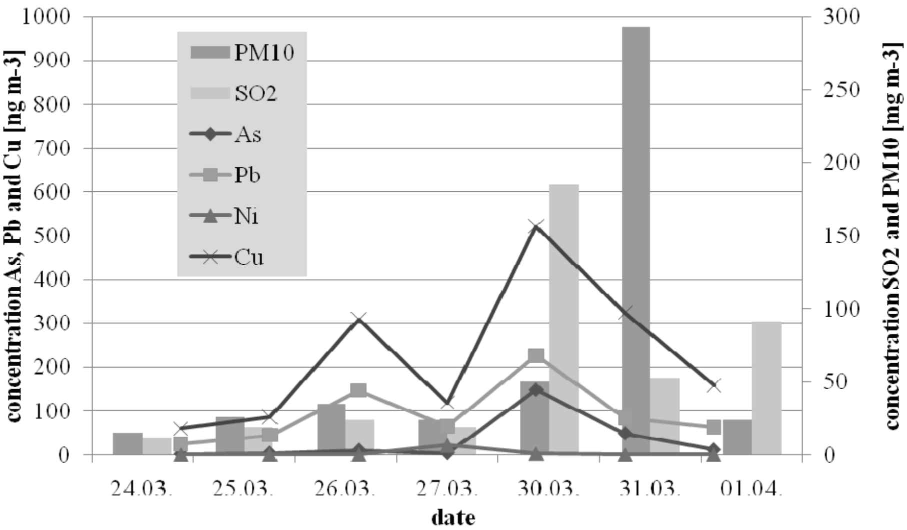

Figure 2. Daily average values of selected metals concentration in PM_{10}, and PM_{10} and SO_2 concentrations during sampling campaign, spring 2009.

Table 4. Statistical parameters for selected metallic compounds, sulfur, SO_2 and PM_{10} for preliminary sampling campaign

Element	Unit	Average	Standard deviation	Min	Max
As	ng/m^3	32.97	53.63	2.4	149
Pb		93.51	70.00	24.9	226.4
Mn		5.00	4.65	1	13
Ni		4.29	7.85	1	22
Cu		225.57	167.10	60	522
Cr		2.00	1.53	1	5
Fe		498.29	335.36	68	997
Al		320.29	198.17	164	610
Ag		3.43	4.39	1	12
Se		66.00	20.49	50	96
Zn		91.86	78.78	19	233
Na		115.86	84.69	1	254
K		149.57	84.59	46	293
Mg		85.714	67.73	27	210
Ca		845	862.56	89	2694
Sr		2.43	2.15	1	6
Ba		8.71	9.60	1	23
B		15.86	12.31	4	42
S		1433.57	992.04	399	3350
Mo		3.00	2.38	1	7
Cd		5.361	8.38	0.18	22.6
PM_{10}		66.71	100.39	15	293
SO_2	μg/m^3	57.47	62.85	11	185

campaign, concentrations of almost all metals of interest as well as SO_2 and PM_{10} concentrations were several times higher. It may be underlined that all Industrial processes were in operation in RTB Bor during the period of experiments. The preliminary sampling campaign was performed only during weekdays, with a pause during weekends.

The relationship between metals concentrations in PM_{10} and PM_{10}, and SO_2 concentrations is shown in Table 5 by Pearson's correlation coefficients. A correlation greater than 0.8 is generally described as strong, whereas a correlation between 0.25 and 0.5 is generally described as weak and less than 0.25 means that there is no linear association. In this study it is found that PM_{10} mass concentration has correlations higher than 0,8 with Mn, Cr, Mg, Ca and B, while there is weak or no association with As, Pb, Cd, Ni and SO_2 and S. It is important that the daily average SO_2 concentration had a strong correlation with the daily average concentrations of As, Pb, Cd, Cu and S. This means that the higher concentration of SO_2 is in relation with emissions of exhaust gases from the copper smelter facilities and may be a marker for higher level of carcinogenic compounds in ambient air in the city of Bor.

It is possible to compare levels of metallic compounds in PM_{10} obtained during the preliminary campaign in Bor with concentrations detected in the urban environments in the region, as well as with similar areas with copper smelting, mining or industrial activities (Table 6). The level of As in PM_{10} in Bor is similar as in the cities near copper smelters in Chile [4], much lower than in an extremely contaminated town with several mines in China [6], but it is about two times higher than in the city of Huelva (Spain) [2,3] where the copper smelter is a huge industrial complex. At Murano near Venice, a glass industrial complex, the level of As in PM_{10} was two times higher [5]. In the urban area of Belgrade, the capital of Serbia, [22] as well as in some other urban and rural areas in Europe [23] much lower concentrations were detected compared to ambient air in Bor. Levels of Pb, Cu, Se are higher in the ambient air of Bor in comparison to other industrial, urban and rural areas. The level Cd is higher than in other urban and rural areas and copper smelting industrial areas.

In order to protect the population, it is necessary to perform an integrated health risk assessment. Performing regular monitoring underpinned with measurement campaigns and element analysis of atmospheric particulate matter in the region of Bor has to be followed with health risk assessments for different air pollution scenarios.

For assessment of non-cancer health risk guidance value Reference Exposure Levels (RELs) relevant for the public exposed routinely to hazardous

Table 5. Pearson coefficient correlations between the concentrations of selected metallic compounds, sulfur, SO_2 and PM_{10} for preliminary sampling campaign (bold values: $p<0.05$; Ni, Ag, Se and Na are not included as they do not have correlation $p<0.05$ and almost all week correlations)

	As	Pb	Mn	Cu	Cr	Fe	Al	Zn	K	Mg	Ca	Sr	Ba	B	S	Mo	Cd	PM_{10}	SO_2
As	1.00																		
Pb	**0.85**	1.00																	
Mn	0.70	0.50	1.00																
Cu	**0.89**	**0.94**	0.73	1.00															
Cr	0.56	0.31	**0.89**	0.60	1.00														
Fe	0.74	0.8	**0.92**	**0.87**	**0.88**	1.00													
Al	**0.83**	0.72	**0.95**	**0.89**	**0.84**	**0.95**	1.00												
Zn	**0.92**	**0.78**	**0.86**	**0.90**	0.73	**0.86**	**0.95**	1.00											
K	0.53	0.46	**0.90**	0.66	**0.81**	**0.87**	**0.83**	**0.78**	1.00										
Mn	0.64	0.49	**0.99**	**0.73**	**0.90**	**0.93**	**0.95**	**0.83**	0.91	1.00									
Ca	0.31	0.16	**0.89**	0.44	**0.86**	**0.78**	**0.76**	0.59	0.88	**0.93**	1.00								
Sr	**0.90**	0.75	**0.92**	**0.91**	**0.81**	**0.92**	**0.99**	**0.97**	0.78	**0.90**	0.68	1.00							
Ba	0.47	0.22	**0.85**	0.42	0.70	0.70	0.71	0.53	0.62	**0.81**	**0.78**	0.66	1.00						
B	0.06	- 0.10	0.64	0.20	**0.77**	0.53	0.52	0.42	0.72	0.70	**0.86**	0.45	0.41	1.00					
S	**0.91**	**0.97**	0.63	**0.98**	0.50	**0.80**	**0.81**	**0.85**	0.54	0.61	0.28	**0.85**	0.36	0.01	1.00				
Mo	0.66	0.37	0.29	0.33	0.09	0.13	0.37	0.46	- 0.07	0.18	- 0.05	0.46	0.36	- 0.25	0.39	1.00			
Cd	**0.99**	**0.80**	**0.78**	**0.88**	0.66	**0.80**	**0.88**	**0.95**	0.62	0.72	0.43	**0.94**	0.55	0.19	**0.89**	0.61	1.00		
PM_{10}	0.22	0.05	**0.82**	0.36	0.90	0.73	0.69	0.51	0.80	**0.87**	**0.97**	0.61	0.69	**0.92**	0.20	- 0.14	0.35	1.00	
SO_2	**0.91**	**0.77**	0.47	**0.78**	0.47	0.63	0.63	0.74	0.34	0.41	0.07	0.72	0.27	- 0.12	**0.86**	0.51	**0.89**	0.05	1.00

Table 6. Examples of concentration of metals in PM10 collected at different sampling sites, copper smelter, mining, industrial processes, urban and rural area

County	Serbia						Spain				Chile		Italy	China	Switzerland	
Town/Area	Bor		Belgrade				Huelva				Toconao	Quillota	Murano	Dachang	Zurich	Payrene
References	Our results		[23]				[2,3]				[4]		[5]	[6]	[24]	
Site type	Urban-industrial copper smelter far 0.65 km		Urban background/traffic				Copper smelter far about 2 km				Urban Industrial, Copper smelter far for several km		Industrial glass	Urban Industrial mines	City center-kerb-side	Rural
Year	2009 Spring		2007 Spring		2007 Autmn		2001		2002		2000 May-October	1999-2000 one year	2003 March-April	-	1998-1999 one year	
Samples	*N* = 7		*N* = 7		*N* = 5		*N* = 25		*N* = 25		*N* = 39	*N* = 91	*N* = 45	-	*N* = 59	*N* = 17
	Ave	Max	Ave	Max	Ave	Max	Ave	Max	Ave	Max	Ave	Max	Ave	Max	Ave	Ave
As	32	149	0.45	0.84	1.03	2.17	7.7	29.4	9.9	79.8	16.7	30.7	60	21800	0.68	0.53
Pb	93	226	42.88	86	74.8	212	47.4	230.6	34.3	163.1	4.2	58.5	45	11500	50	10
Mn	5	13	18.9	39.8	12.04	24.9	-	-	-	-	12.1	43.3	12	4040	17	2.8
Ni	4	22	29.92	54.4	3.48	5.1	-	-	-	-	-	2.47	8	-	3.6	1.2
Cu	225	522	15.53	34.5	9.03	23.12	81.9	216.1	124.7	378.2	13.5	73.9	10	960	75	6
Cr	2	5	4.02	8.2	5.76	13.5	-	-	-	-	5.68	6.66	17	-	-	-
Fe	498	997	924.4	2187	1167	2013	-	-	-	-	430	1089	443	-	1611	89
Al	320	610			803	1606	-	-	-	-	931	1426	258	-	107	91
Se	66	96	0.24	0.25	0.55	0.99	1.9	4.5	1.9	10.8	-	-	64	-	0.57	0.16
Zn	91	233	22.53	44.4	53.2	173	64.5	197.6	43.6	218.4	16.1	54.4	111	18000	-	-
Na	115	254	-	-	-	-	-	-	-	-	569	1652	7483	-	690	298
K	149	293	280	366	315	572	-	-	-	-	578	649	575	-	312	98
Mg	85	210	150.8	232	268.4	621	-	-	-	-	378	410	315	-	76	48
Ca	845	2694	-	-	-	-	-	-	-	-	1160	860	1056	-	424	100
Sr	2	6	-	-	-	-	-	-	-	-	8.9	6.3	2	-	-	-
Ba	8	23	13.85	27.7	17.46	31.7	18.0	135.1	26.0	235.5	8.8	15.8	5	-	-	-
Mo	3	7	2.01	3.50	4.56	10.7	-	-	-	-	-	-	-	170	-	-
Cd	5	22	0.29	0.48	0.33	0.51	0.9	5.7	0.8	5.1	-	-	116	-	0.26	0.32

substances released in environment [25] have been used. Three REL types are defined:

- exposure averaging time for acute RELs is 1 h, A = acute;

- for 8-h RELs, the exposure averaging time is 8 h, which may be repeated, 8 = 8-hour;

- chronic RELs are designed to address continuous exposures for up to a lifetime: the exposure metric used is the annual average exposure, C = chronic.

Currently, there are RELs developed for 94 substances [25,26]. Table 7 presents available RELs for metallic elements and compounds of As, Cd, Ni, Cu, Mn, Hg, Se and V as well as S and SO_2 that are objects of this study.

Figure 3 shows the annual average values of As in TSP in the vicinity of measuring point M1 for the period 1996-2008. Samples have been collected, analyzed and presented as monthly average and calculated as annual average for the purpose of regular monitoring by Mining and Metallurgy Institute Bor [7]. In 2002, it was identified that the annual average concentration of As in TSP was more than 300 ng/m^3. In the period between 2003 and 2008 there were detected annual average concentrations of As in TSP between 20 and 50 ng/m^3, which is still very high.

Although in the process of copper smelting As is adsorbed primarily on fine particulate matter, the distribution of metals in different particulate fractions in ambient air in Bor needs to be defined. A recently published paper for ambient air sampling at similar sampling site shows that AS in PM_{10} contain 83% of As in $PM_{2.5}$ [2], but there are no data about the ratio of metals in PM_{10} and TSP in areas located nearby copper smelters. Analysis of data from preliminary campaign and comparison with available RELs confirm

Table 7. Non-cancer health effects reference exposure level (REL) for selected metals, sulfates and sulfur dioxide [25-27]

Substance	REL type	Inhalation REL g/m^3	Oral REL g/kg BW-day	Hazard Index Target Organs
Arsenic and inorganic arsenic compounds (including arsine)	A	0.20		Development (teratogenicity); cardiovascular system; nervous system
	8	0.015		Development; cardiovascular system; nervous system; lung; skin
	C	0.015	0.0035	Development; cardiovascular system; nervous system; lung; skin
	C	0.02	0.5	Kidney; respiratory system
Cadmium an d compounds	C	0.02	0.5	Kidney; respiratory system
Copper and compounds	A	100		Respiratory system
Manganese and manganese compounds	8	0.17		Nervous system
	C	0.09		Nervous system
Inorganic Mercury &inorganic mercury compounds	A	0.6		Nervous system, development
	8	0.06		Nervous system, kidney, development
	C	0.03]	0.16	Nervous system, kidney, development
Nickel and compounds (except nickel oxide for chronic exposures)	A	1.1		Respiratory, immune systems
	8	0.08		Respiratory, immune systems
	C	0.015	50	Respiratory system; hematopoietic system
Nickel oxide	C	0.06	50	Respiratory system; hematopoietic system
Selenium and selenium compounds (other than hydrogen selenide)	C	20	5	Alimentary system; cardiovascular system; nervous system
Vanadium pentoxide	A	30		Respiratory system
Sulfur dioxide	A	660		Respiratory system
Sulfates	A	120		Respiratory system

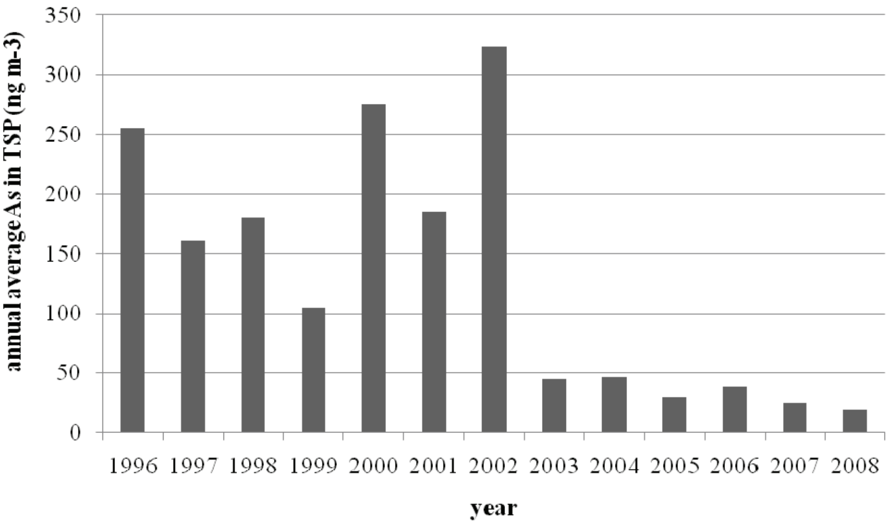

Figure 3. The annual average values of As in the vicinity of measuring point M1 for the period 1996-2008

that the concentration of arsenic in airborne particulate matter was at the level that requests corrective actions to be introduced, as in the period of two consecutive days 24 h daily average concentrations were above 8-h REL, 15 ng/m^3, for arsenic and inorganic arsenic compounds [27]. In the case of Bor it would be of great importance to define the relations between As in particulate matter fractions with SO_2 for typical scenarios of meteorological conditions such as temperature inversions and calm conditions together with the Copper Smelter Bor in full operation.

CONCLUSIONS

According to the data reported in this paper, the Bor Municipality area is considered to be one of the most polluted regions in Serbia and Europe with arsenic detected in PM_{10}. This work confirms the importance of metallic elements specification studies due to the presence of higher concentrations of toxic substances in airborne particulate matter in the densely populated area in Bor. The presence of carcinogenic substances such as inorganic arsenic in ambient air in Bor is related to an anthropogenic origin, primary smelting operations which can impact urban and rural area nearby industrial complex. Local Industrial activities coupled with meteorological conditions are responsible for high As, Pb, Cd, Cu and other metallic elements concentrations in PM_{10} in Bor. It is confirmed that the higher level of As in PM_{10} is in strong relation with the higher level of SO_2 in ambient air. During the preliminary campaign, higher levels of SO_2, inorganic arsenic and other hazardous heavy metals corresponded to calm meteorological conditions of low wind speed. Monitoring data should be performed, analyzed and reviewed at regular intervals and compared with standards as well as reference exposure values as the most appropriate corrective actions for protecting human health can be taken. Besides the sampling and analysis of PM_{10}, smaller particles ($PM_{2.5}$, PM_{10}) that are more harmful should be sampled and the content of metallic element identified in. It was feasible to determine relations between As in particulate matter fractions with SO_2 for typical scenarios of calm meteorological conditions such as temperature inversions during smelting and mining processes.

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NAUČNI RAD

PRELIMINARNA ANALIZA ARSENA I DRUGIH METALNIH ELEMENATA U PM_{10} UZORKOVANIH U BLIZINI TOPIONICE BAKRA U BORU (SRBIJA)

U ovom radu prikazane su koncentracije dvadeset jednog elementa (Ag, Al, As, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, S, Se, Sr i Zn) u PM_{10} i SO_2 uzorkovanih na mernom mestu u urbanom području grada Bora (40.000 stanovnika) u istočnoj Srbiji. Merno mesto je bilo postavljeno u gusto naseljenom centru grada udaljenom oko 0,65 km od jednog od najvećih rudnika i topionica bakra u Evropi. Za vreme preliminarne kampanje, koja je trajala 7 dana u rano proleće 2009. godine, po prvi put su u Boru uzorkovane PM_{10} korišćenjem standardnog evropskog uzorkivača. PM_{10} su prikupljane na PTFE membranskim filterima, a sardžaj metalnih elemenata je odredjivan sa GF AAS i ICP AES. Nivo koncentracija i korelacije izmedju utvrdjenih tragova elemenata, PM_{10} i SO_2 indiciraju da industrijske aktivnosti potpomognute sa meteorološkim uslovima kada duva vetar male brzine (tišina), predstavljaju glavne faktore koji utiču na aerozagadjenje u gusto naseljenim područjima grada Bora. Evidentno je da su i PM_{10} and SO_2 prekoračili po jednom granične vrednosti tokom kampanje uzorkovanja u trajanju od sedam dana. Utvrdjena su visoke korelacije između srednjih dnevnih koncentracija PM_{10} i Mn, Mg Ca i B prisutnih u PM_{10}. Sa druge strane, utvrđene su visoke korelacije izmedju srednjih dnevnih koncentracija SO_2 i As, Pb, Cd, Cu i S prisutnih PM_{10}. Ovi rezultati potvrđuju relacije izmedju emisije SO_2 iz topionice bakra i metorolških uslova kada je tišina (brzina vetra manja od 0,5 m/s) sa nivom kancerogenih materija arsena, olova i kadmijuma u ambijentnom vazduhu.

Ključne reči: topionica bakra; aerozagadjenje; SO_2; PM10; kancerogene supstance; tragovi elemenata; arsen.