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ANALYSIS OF CANCEREGENIC ELEMENTS IN TOTAL ATMOSPHERIC DEPOSITION IN BOR, SERBIA

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Abstract. *In this paper the analysis of atmospheric deposition fluxes of Pb, Cd, Ni, and As in the Bor town (Serbia) is presented for the period 2011-2020. The results of measurements from the period of operation of the old smelter (2011-2015) were compared with the results of measurements during the period of operation of the new smelter (2016-2020). As a result of changes in the copper smelting technology and the better treatment of waste gases in the smelter, the average level of the total atmospheric deposition (TAD) was reduced by 63% in the period 2016-2020. The reduction of atmospheric deposition fluxes of Pb (59%), Cd (34%), and As (65%) are detected at all sampling points over the 2016-2020 period. In contrast, the fluxes of Ni were increased (211%). Also, pH values of TAD have been changed at all sampling points from acidic (5.7 pH), during the period of operation of the old smelter, to alkaline (7.7 pH) in the period of operation of the new smelter. The presence of a very strong (r>0.8) and strong (0.8>r>0.6) Pearson correlation between the atmospheric deposition fluxes of cancerogenic elements were determined at all sampling points during 2016-2020, as opposed to 2011-2015 where these correlations were weak (r<0.4).*

Key words: *total atmospheric deposition, cancerogenic elements, copper smelter*

1. INTRODUCTION

Atmospheric deposition is considered to be the major pathway for transferring the substances from the atmosphere to the terrestrial ecosystems [1]. Wet and dry depositions are important processes for removing particulate matter and other pollutants from the atmosphere. In recent years, a total atmospheric deposition (TAD) has been widely studied with the aim to examine the elemental associations in the TAD with the potential sources of heavy metal contaminants [2, 3].

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It is well known that the primary metal and metalloid constituents of the particulate matter (PM) emitted by the copper smelter are Cu and Fe oxides and other elements, such as As, Sb, Pb and Zn [4]. Cancerogenic elements, such as Pb, Cd, Ni, and As released as a part of waste gases from such industrial facilities pose serious risks to the environment and human health. Fugitive emissions from the open pits, ore waste dump, flotation tailing dumps, and from the copper smelter, together with the emissions from the point sources in the copper smelter are the main sources of PM in the Municipality of Bor, Serbia [5-7].

One of the largest copper mines in Europe is located in the Municipality of Bor, Serbia. Owing to the fact that the town was built in the near vicinity of the mine, as well as the location of the copper smelting plant and two more mines nearby, the town itself represents a serious environmental hot spot in the Republic of Serbia and Europe [5].

The technology of processing the copper concentrates in the copper smelter in Bor was obsolete and because of that, it was changed in 2016, when the new copper smelter started to operate together with the sulphuric acid factory. As a consequence of the emissions of SO_2, PM and other pollutants contained in the copper smelter waste gases were reduced to prescribed limits.

The primary goal of this research was to compare levels of cancerogenic elements Pb, Cd, Ni, and As in TAD in the periods before and after the construction of the new copper smelter in Bor. In that aim, the results of measurements in the 2011-2015 period (old smelting technology) were compared with the results for the 2016-2020 period (new smelting technology).

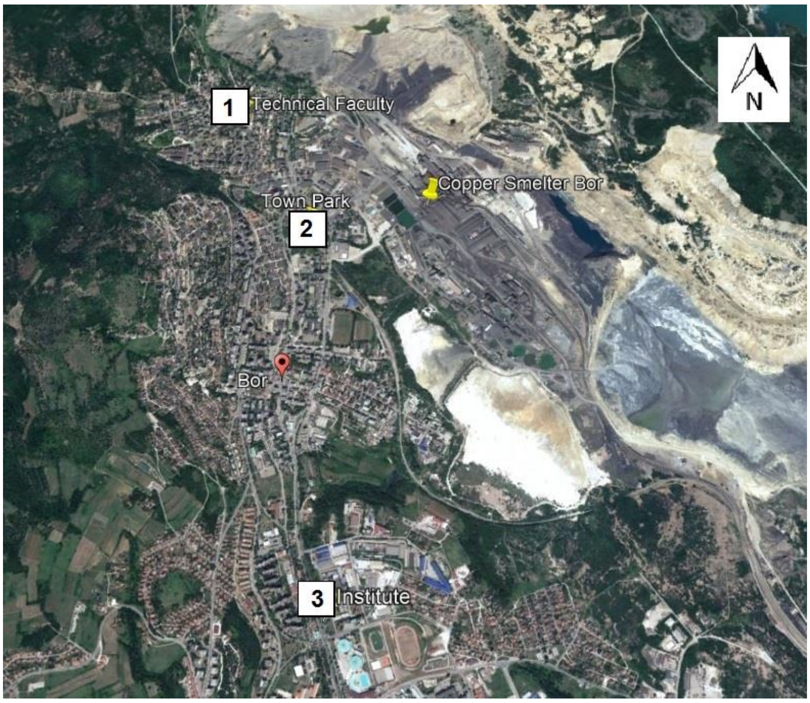

Fig. 1 Sampling locations in the Bor town urban areas relative to the copper smelter facilities (1. Technical Faculty in Bor -TF, 2. Town Park -TP, 3. Mining and Metallurgy Institute Bor - IN) [8]

2. MATERIALS AND METHODS

Results presented in this paper are obtained from the sampling campaigns conducted from January 2011 to June 2020 at three locations in the Bor town urban area (Technical Faculty in Bor - TF, Town Park - TP, and Mining and Metallurgy Institute Bor - IN) as shown in Fig. 1. The TAD samples were collected continuously for the periods of 1 month. In total, 342 monthly samples were collected, 114 samples per each sampling point. Sampling campaigns were conducted by the Mining and Metallurgy Institute Bor, Department for Chemical and Technical Testing, following the state and municipal monitoring program.

2.1. Sampling locations

The sampling point TF is located close to the Technical Faculty in Bor, about 1 km N-NW relative to the copper smelter. The sampling point TP is located close to the Town Park in Bor, about 1 km W relative to the copper smelter. The sampling point IN is located close to the Mining and Metallurgy Institute Bor, about 2 km S-SW from the copper smelter.

2.2. Sampling equipment and procedures

The analysis of TAD samples was done following the standard SRPS EN 15841 [6]. This standard specifying the general requirement for sampling equipment and different sampling strategies relative to sampling site type. A study that evaluated the sampler uncertainties of different collectors (wet only, bulk, Bergerhoff, and bulk bottle/funnel) showed that at the industrial sites and possibly at very dry rural and urban sites, it is necessary to use the Bergerhoff or bulk bottle funnel methods for the collecting of TAD [10]. Therefore, the Bergerhoff collector was used in this study. The collecting surfaces of all the collectors used in the present study were made of high-density polyethylene. The height of the sampling orifice was about 1.5 m above the surface to avoid the collection of the re-suspended dust from the surface.

3. RESULTS AND DISCUSSION

The average levels of pH of TAD and atmospheric deposition fluxes of Pb, Cd, Ni, and As are shown in Table 1. According to the data from Table 1, TAD levels at TF and TP are almost 2 times higher over the 2011-2015 period compared with TAD levels for the period 2016-2020. Such a decrease in TAD (also shown in Figure 2) is a consequence of new technology for copper smelting and the better treatment of waste gases in the smelter. Also, Pb, Cd, and As deposition fluxes were on average 59%, 34%, and 65% lower in the period 2016-2020 compared with those fluxes in the 2011-2015 period (as shown in Figures 3-5). This decrease is also a direct consequence of changes in the copper smelting technology and the better treatment of waste gases in the smelter. In contrast, in the same period, the fluxes of Ni were increased by 211%, as shown in Figure 6. This increase could be partly explained by changes in the amounts and compositions of imported copper concentrates processed in the smelter in the 2016-2020 period.

Table 1 Average pH values of TAD and deposition fluxes of Pb, Cd, Ni, and As for the periods 2011-2015 and 2016-2020

Parameter	Unit	Technology used in the copper smelter in Bor	
		Old 2011-2015	New 2016-2020
TAD-TF	$mg \cdot m^{-2} \cdot day^{-1}$	372.3	199.1
TAD-TP	$mg \cdot m^{-2} \cdot day^{-1}$	339.5	184.7
TAD-IN	$mg \cdot m^{-2} \cdot day^{-1}$	129.9	104.8
Pb-TF	$\mu g \cdot m^{-2} \cdot day^{-1}$	86.8	38.0
Pb-TP	$\mu g \cdot m^{-2} \cdot day^{-1}$	54.5	30.4
Pb-IN	$\mu g \cdot m^{-2} \cdot day^{-1}$	15.5	12.0
Cd-TF	$\mu g \cdot m^{-2} \cdot day^{-1}$	5.8	1.1
Cd-TP	$\mu g \cdot m^{-2} \cdot day^{-1}$	2.6	0.9
Cd-IN	$\mu g \cdot m^{-2} \cdot day^{-1}$	0.7	0.3
Ni-TF	$\mu g \cdot m^{-2} \cdot day^{-1}$	3.6	4.9
Ni-TP	$\mu g \cdot m^{-2} \cdot day^{-1}$	3.2	6.7
Ni-IN	$\mu g \cdot m^{-2} \cdot day^{-1}$	0.9	2.6
As-TF	$\mu g \cdot m^{-2} \cdot day^{-1}$	108.5	36.9
As-TP	$\mu g \cdot m^{-2} \cdot day^{-1}$	45.8	26.8
As-IN	$\mu g \cdot m^{-2} \cdot day^{-1}$	7.2	7.4
pH-TF	pH	5.6	7.7
pH-TP	pH	5.6	7.7
pH-IN	pH	6.0	7.7

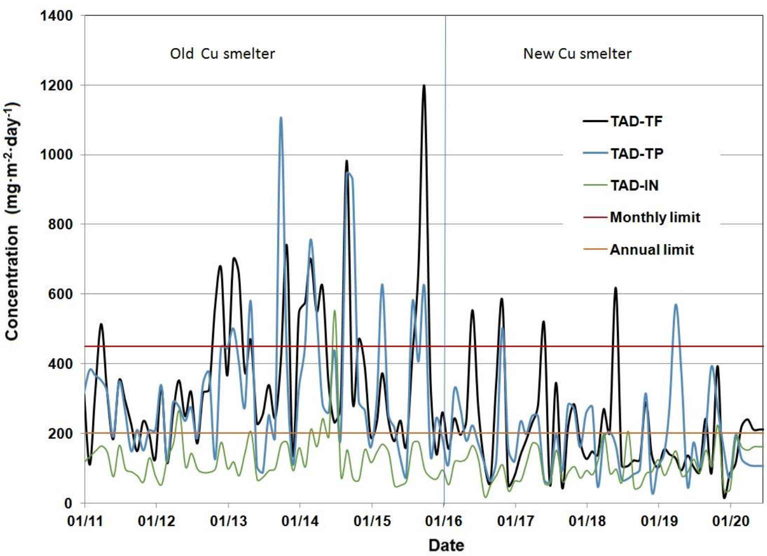

Fig. 2 TAD levels in the period 2011-2020

Also, pH values of TAD have been changed at all sampling points from acidic (5.7 pH) in the period 2011-2015 to alkaline (7.7 pH) in the period 2016-2020, as shown in Figure 7. The increase of pH in the period of operation of the new smelter is occurred due to the better treatment of waste gases in the smelter, primarily SO_2.

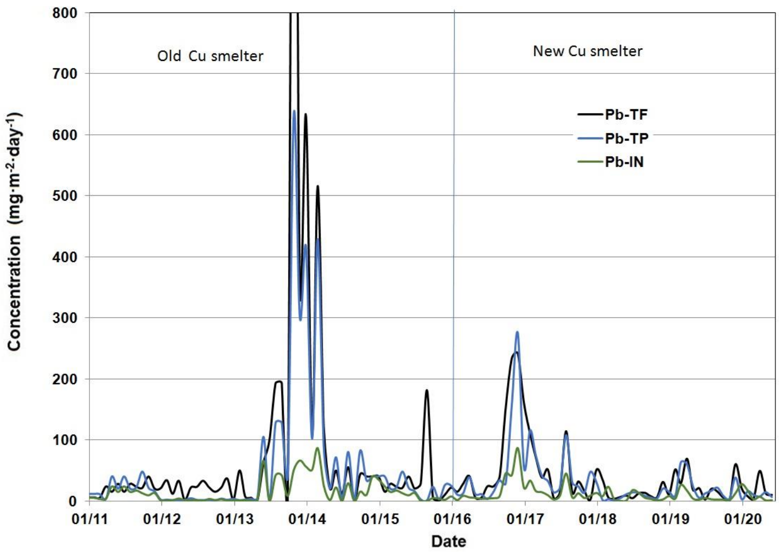

Fig. 3 Atmospheric deposition fluxes of Pb in the period 2011-2020

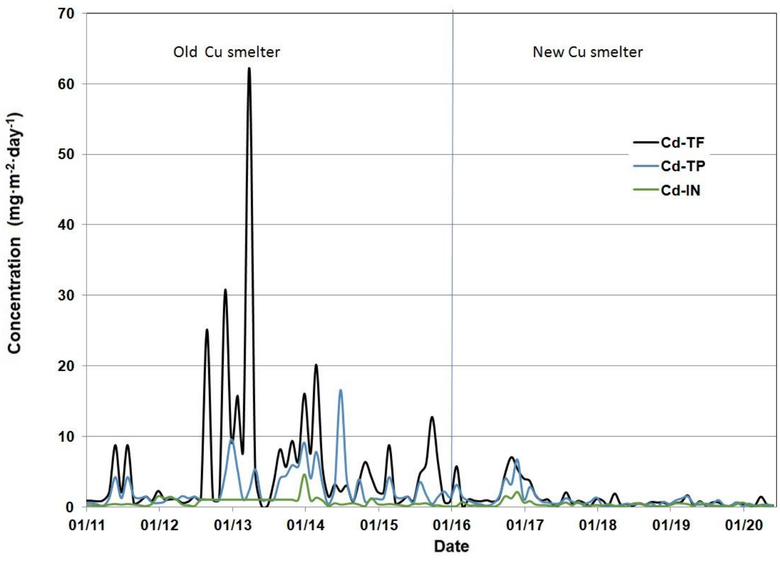

Fig. 4 Atmospheric deposition fluxes of Cd in the period 2011-2020

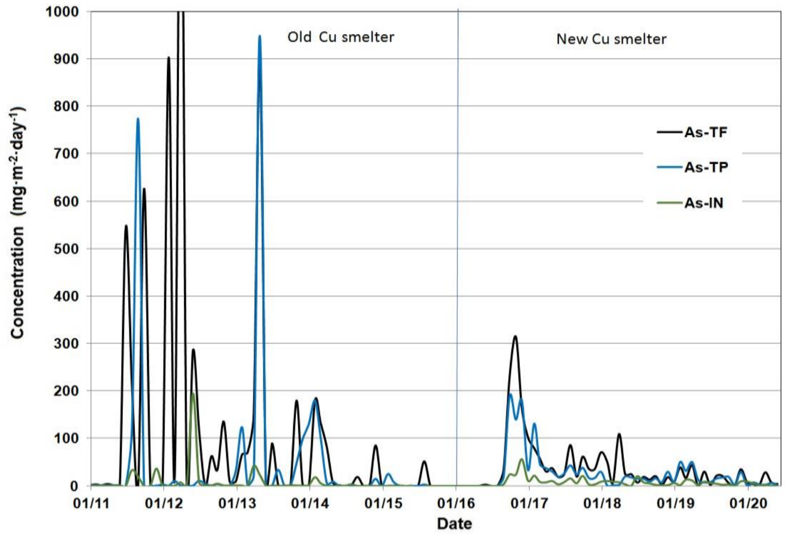

Fig. 5 Atmospheric deposition fluxes of As in the period 2011-2020

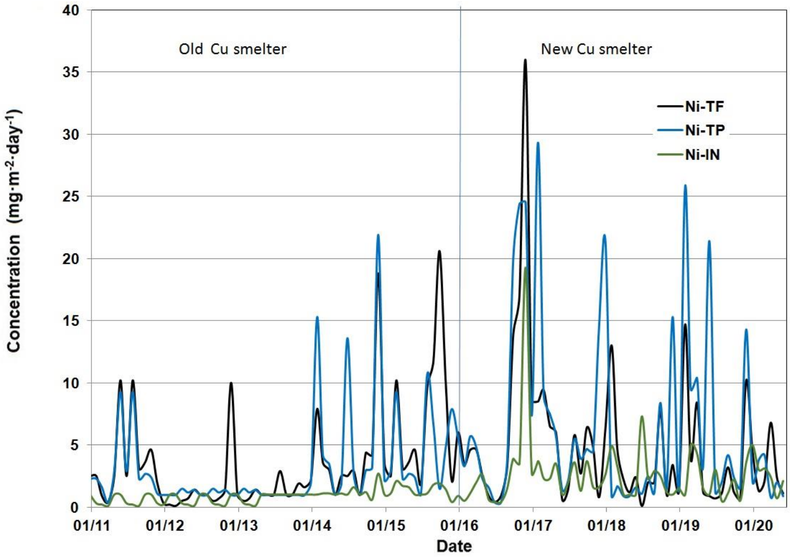

Fig. 6 Atmospheric deposition fluxes of Ni in the period 2011-2020

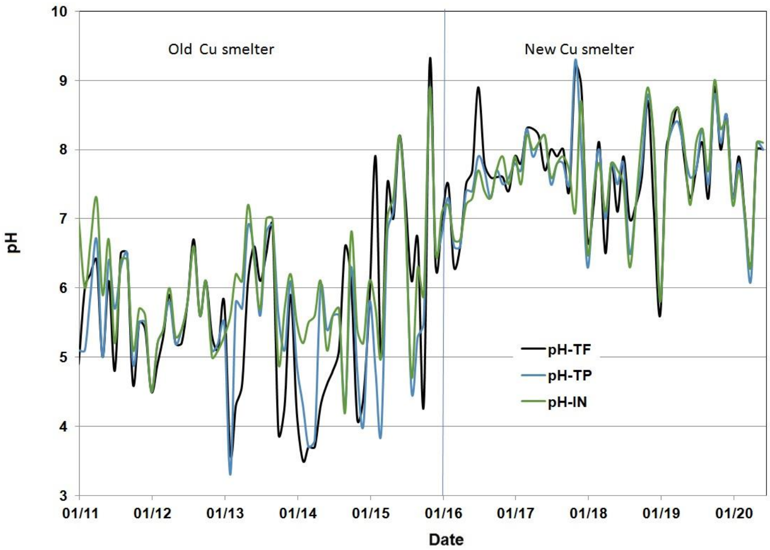

Fig. 7 Average pH of TAD in the period 2011-2020

The "Annual Report on the Air Quality in the Republic of Serbia in 2018" [11] contains the results of measurements of TAD at 53 measuring points in the Republic of Serbia. The maximum allowed annual value was exceeded in Senta (375 $mg \cdot m^{-2} \cdot day^{-1}$) and Krusevac (306 $mg \cdot m^{-2} \cdot day^{-1}$). The average TAD level at TP in 2018 (182 $mg \cdot m^{-2} \cdot day^{-1}$) occupies 17th, while the TAD level at IN (101 $mg \cdot m^{-2} \cdot day^{-1}$) occupies 48th position out of 53 positions in the mentioned report. Similarly, in 2016 according to the "Annual Report on the Air Quality in the Republic of Serbia in 2016" [12], the highest average level of TAD in 2016 was recorded in Pirot (421 $mg \cdot m^{-2} \cdot day^{-1}$), while the lowest level was recorded in Pancevo (65 $mg \cdot m^{-2} \cdot day^{-1}$). The average TAD level at TP in 2016 (202 $mg \cdot m^{-2} \cdot day^{-1}$) occupies 15th, while the TAD level at IN (92 $mg \cdot m^{-2} \cdot day^{-1}$) occupies 47th position out of 49 positions. Based on these data, it can be concluded that the levels of TAD in Bor are within the average compared to other urban areas in the Republic of Serbia.

The levels of TAD at sampling point IN were once above the monthly limit (450 $mg \cdot m^{-2} \cdot day^{-1}$), while at the TF and TP monthly limit was exceeded 16 and 11 times, respectively, in the period 2011-2015. The levels of TAD at sampling point IN were below the monthly limit, while at the TF and TP monthly limit was exceeded 4 and 2 times, respectively, in the period 2016-2020. This also points out that the emissions of waste gases from the smelter were significantly reduced over the 2016-2020 period.

The comparison of annual atmospheric deposition of cancerogenic elements (Pb, Cd, Ni, and As) determined in our study with the results obtained for some other regions are presented in Table 2. According to the data obtained in Table 2, the annual atmospheric deposition fluxes of Pb, Cd, and Ni determined in Bor, in the period 2016-2020, are comparable with those obtained for the other regions. On the contrary, the atmospheric deposition fluxes of Pb and Cd determined in Bor in 2011-2015 (sampling points TF and TP), were higher compared to those obtained for other regions. The annual atmospheric deposition fluxes of As in Bor (except for the sampling point IN) are significantly higher compared to the fluxes of As obtained for other regions.

Pearson correlation coefficients between the atmospheric deposition fluxes of Pb, Cd, Ni, and As in the periods 2011-2015 (old smelting technology) and 2016-2020 (new smelting technology) are shown in Table 3. The presence of a very strong (r>0.8) and strong (0.8>r>0.6) Pearson correlation between the atmospheric deposition fluxes of cancerogenic elements were determined at all sampling points during 2016-2020, as opposed to 2011-2015 where these correlations were weak.

Table 2 Comparison of annual atmospheric deposition fluxes of Pb, Cd, Ni, and As ($mg \cdot m^{-2} \cdot year^{-1}$) between the different regions

Location	Period	Pb	Cd	Ni	As	References
TF, Bor, Serbia	2011-2015	31.7	2.1	1.3	39.6	This study
TP, Bor, Serbia	2011-2015	19.9	0.9	1.2	16.7	This study
IN, Bor, Serbia	2011-2015	5.7	0.2	0.3	2.6	This study
TF, Bor, Serbia	2016-2020	13.9	0.4	1.8	13.5	This study
TP, Bor, Serbia	2016-2020	11.1	0.3	2.4	9.8	This study
IN, Bor, Serbia	2016-2020	4.4	0.1	0.9	2.7	This study
Belgrade, Serbia	2002-2006	21.7	0.2	11.3		[2]
Tokyo Bay, Japan	2004-2005	9.9	0.4	6.8	2.9	[13]
Seine Estuary, France	2001-2002	18.0	0.4	4.1		[14]
Paris, France	2001-2002	4.2	0.2	0.6		[14]
Pearl River delta, China	2001-2002	13.0	0.1	8.4		[15]
Lake Superior, USA	1993-1994	1.5	0.5	0.8	0.2	[16]
North Sea	1992-1994	3.7		1.2	0.3	[17]

Table 3 Pearson correlation matrix of atmospheric deposition fluxes of Pb, Cd, Ni, and As for the periods before and after the application of the new copper-smelting technology

Technology used in the copper smelter									
	Old				New				
	Pb-TF	Cd-TF	Ni-TF	As-TF		Pb-TF	Cd-TF	Ni-TF	As-TF
Pb-TF	1				Pb-TF	1			
Cd-TF	.125	1			Cd-TF	.832**	1		
Ni-TF	-.056	.085	1		Ni-TF	.832**	.650**	1	
As-TF	-.014	.036	-.116	1	As-TF	.857**	.798**	.674**	1
	Old				New				
	Pb-TP	Cd-TP	Ni-TP	As-TP		Pb-TP	Cd-TP	Ni-TP	As-TP
Pb-TP	1				Pb-TP	1			
Cd-TP	.387**	1			Cd-TP	.820**	1		
Ni-TP	.064	.336*	1		Ni-TP	.595**	.640**	1	
As-TP	.051	.152	.067	1	As-TP	.760**	.843**	.739**	1
	Old				New				
	Pb-IN	Cd-IN	Ni-IN	As-IN		Pb-IN	Cd-IN	Ni-IN	As-IN
Pb-IN	1				Pb-IN	1			
Cd-IN	.489**	1			Cd-IN	.896**	1		
Ni-IN	.398*	.118	1		Ni-IN	.821**	.736**	1	
As-IN	-.107	-.083	-.279	1	As-IN	.904**	.887**	.879**	1

** Correlation is significant at the 0.01 level (2-tailed).
* Correlation is significant at the 0.05 level (2-tailed).

4. CONCLUSIONS

In this paper the analysis of atmospheric deposition fluxes of Pb, Cd, Ni, and As in Bor town is presented for the period 2011-2020. In that aim, the results of measurements in 2011-2015 (old smelting technology) were compared with the results from 2016-2020 (new smelting technology).

The average TAD level was reduced by 63% in 2016-2020 as a result of changes in the copper smelting technology and the better treatment of waste gases. Also, Pb, Cd, and As deposition fluxes were on average 59%, 34%, and 65% lower in the period 2016-2020. In contrast, in the same period, the fluxes of Ni in TAD were increased by 211%. Also, pH values of TAD have been changed at all sampling points from acidic (5.7 pH) in 2011-2015 to alkaline (7.7 pH) in 2016-2020. In general, in the 2016-2020 period, the annual atmospheric deposition fluxes of Pb, Cd, and Ni determined in Bor, are similar compared with the fluxes reported in similar studies for other regions. In contrast, the atmospheric deposition fluxes of As are significantly higher compared to those obtained for other regions in the available literature. The presented results indicate that the level of carcinogenic elements (except Ni) in TAD decreased during the operation of the new smelter in Bor. Unfortunately, atmospheric deposition fluxes of As are still far above those in other regions of the world. This indicates that there is still an unresolved problem of arsenic emissions from the copper smelter facilities into the environment.

The presence of a very strong ($r>0.8$) and strong ($0.8>r>0.6$) Pearson correlation between the atmospheric deposition fluxes of cancerogenic elements were determined at all sampling points during the period 2016-2020, as opposed to the period 2011-2015 where these correlations were weak. This points out that they come from the same source, which is copper smelter.

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ANALIZA KANCEREOGENIH ELEMENTA U UKUPNIM TALOŽNIM MATERIJAMA U BORU, SRBIJA

U ovom radu je prikazana analiza kancerogenih elemenata (Pb, Cd, Ni i As) u ukupnim taložnim materijama (UTM) za tri merna mesta u gradu Boru, u periodu 2011-2020.god. Upoređivani su rezultati merenja iz perioda 2011-2015.god. (stara tehnologija topljenja) sa rezultatima merenja u periodu 2016-2020.god. (nova tehnologija topljenja). Kao posledica promene tehnologije topljenja bakra i boljeg tretmana otpadnih gasova u topionici, količina UTM je u periodu 2016-2020.god. smanjena u proseku za 63% u odnosu na period 2011-2015.god. Takođe, prosečna pH vrednost UTM je promenjena na svim tačkama uzorkovanja od kisele (5.7 pH) na alkalnu (7.7 pH). Smanjenje atmosferskog depozicionog fluksa Pb (59%), Cd (34%) i As (65%) primećeno je na svim tačkama uzorkovanja u periodu rada nove topionice (2016-2020). Nasprot tome, u istom periodu, prosečni atmosferski depozicioni fluks Ni je povećan (211%). Prisustvo veoma jake ($r>0.8$) i jake ($0.8>r>0.6$) Pearson-ove korelacije između kancerogenih elemenata u UTM detektovano je na svim tačkama uzorkovanja tokom perioda rada nove topionice, za razliku od perioda rada stare topionice kada su ove korelacije bile slabe ($r<0.4$).

Ključne reči: *ukupne taložne materije, kancerogeni elementi, topionica bakra*