ANALYSIS OF CANCEROGENIC ELEMENTS DETERMINED IN PM10 NEAR THE COPPER SMELTER IN BOR, SERBIA

Abstract: The concentrations of four cancerogenic elements (Pb, Cd, Ni, and As) determined in PM10 at three locations in the urban areas near the copper smelter in Bor (Serbia) were analyzed in the period from January 2017 to May 2020. The aim of this research was to examine the correlations between the selected elements and to compare them with those obtained previously. The reason for this is the fact that the new copper smelter started operating in Bor in 2016. The results presented here showed that the average content of As in PM10 was over the annual national limit at all sampling points for the total period of observation, as well the contents of Cd in PM10 at the sampling point Jugopetrol. The content of Pb in PM10 was over the annual limit only at sampling point Jugoperol. The correlations between the As-Pb, As-Cd, and Cd-Pb, at all sampling points, mostly vary from very strong (r>0.8) and strong (0.8>r>0.6) to moderate (0.6>r>0.4). Also, compared to previously obtained results, these correlations are generally stronger. Such results indicate that As, Cd, and Pb determined in PM10 mostly originate from the same source, the copper smelter in Bor. Opposite to that, correlations of Ni with other selected elements are mostly very weak (r<0.2) to moderate. This shows that Ni mostly originated from natural sources.

Keywords: air pollution, particulate matter, copper smelter, correlation, arsenic.

INTRODUCTION

The Municipality of Bor is located in Europe on the Balkan Peninsula in the eastern part of the Republic of Serbia, as shown in Figure 1. With about 50,000 inhabitants in urban and rural settlements, Bor has been the major center of copper and other precious metals mining and processing for more than a century [1].

The ore melted in the copper smelter in Bor is of the chalcopyrite-pyrite type with the increased contents of arsenic, found in the form of enargite (Cu₃AsS₄) and tennantite (Cu₆[Cu₄(Fe,Zn)₂]As₄S₁₃) [1]. The oxidation, roasting, and melting of such mineral forms result in increased heavy metal oxides and SO₂ gas which, in certain quantities, contaminate the environment [2]. The toxicity of suspended particles (PM₁₀) is related to their elemental composition, meaning that aerosols in smelter plumes enriched with metals and metalloids pose a serious risk to human health. That is the main reason why the impact of airborne particle emissions from the copper smelter in Bor has been the subject of many studies [1-5]. The Serbian Government has invested over 200 million euros in building the New Copper Smelter and Sulphuric Acid Plant in Bor that became operative in 2016. By modernization of the copper smelter, the emissions of SO₂, PM₁₀, and other pollutants in the waste gas streams were significantly reduced with the aim to bring the emissions under the prescribed limit values.

One of the goals of this research was to investigate the influence of the new smelting technology, applied in the copper smelter in Bor on the cancerogenic elements (Pb, Cd, Ni, and As) determined in PM₁₀ in urban areas in Bor. Also, the correlations between the selected elements were examined.

According to International Agency for Research on Cancer (IARC) substances like inorganic arsenic, cadmium and cadmium compounds, as well as nickel compounds 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 defined as possibly carcinogenic to humans (group 2B) [7].

People living near emission sources of inorganic arsenic, such as smelters, have a slightly higher risk of lung cancer. Typical concentrations of arsenic range from 1-10 ng/m³ in rural areas up to 30 ng/m³ in uncontaminated urban areas [8]. A large part of the anthropogenic arsenic emissions is associated with copper production [5].

Average Pb levels in the ambient air are usually below 0.15 µg/m³ in rural areas. Pb concentration in ambient air typically ranges between 0.15 and 0.5 µg/m³ in most of the European cities [9]. Pb accumulates both in soft
tissues and bones, it damages the nervous system and causes brain disorders.

Typical Cd levels in the airborne aerosol or settled dust are 0.1 - 0.4 ng/m³ in rural areas, 0.2 - 2.5 ng/m³ at the urban background and traffic-related sites, and up to 20 ng/m³ at industrial sites. Cd and Ni compounds in particulate matter mainly originate from coal and fuel oil combustion processes, metallurgical industry and road transport [9].

Typical Ni levels in the airborne aerosol or settled dust are 0.4 - 2 ng/m³ in rural areas, 1.4 - 13 ng/m³ at the urban background and traffic-related sites, and up to 50 ng/m³ near industry. In case of inhalation exposure, Ni compounds are considered human carcinogens [9].

One of the largest copper mines, as well as the copper smelter in Europe, is located in the Municipality of Bor. Mining production started in 1903 with the exploitation of the only underground mine, followed by the exploitation of three other open pits in the Bor area (Bor, V.Krivełj and Cerovo) [5]. Fugitive emissions from the open pits, ore waste heaps, flotation waste heaps, and copper smelter, together with the emissions from point sources in the copper smelter are the main sources of PM₁₀ in the Municipality of Bor (see Figure 1).

In this study, the levels of cancerogenic elements (As, Pb, Cd, and Ni) determined in PM₁₀ in the urban-industrial (Park and Institute) and suburban areas (Jugopetrol) in Bor town were analyzed. The aim of this research was to examine the correlations between the selected elements and to compare them with those obtained previously (before 2016). This is because the new copper smelter has commenced operations in Bor during 2016.

METHODOLOGY

Sampling locations and equipment

The locations of sampling points in the urban-industrial (Park and Institute) and suburban areas (Jugopetrol) in the Bor town is presented in Figure 1. The sampling point Park (P) is located downwind of the easterly prevailing wind from the copper smelter. This location is within the Town Park in Bor, about 1 km on the West, relative to the copper smelter. The sampling point Institute (IN), is located downwind of the north-northeasterly prevailing wind from the copper smelter. This location is close to the Mining and Metallurgy Institute Bor, about 2 km in the south-southwest direction relative to the copper smelter. The sampling point Jugopetrol (JP) is located downwind of the northwesterly prevailing wind from the copper smelter. This location is 2 km in the south-southeast direction relative to the copper smelter.

In this paper, we have analyzed data from the sampling campaigns conducted by the Mining and Metallurgy Institute Bor, Department for Chemical and Technical Control, in the period January 2017 to May 2020 [6].

In total, 594 samples were collected, 198 samples per each sampling point. The SVEN/LECKEL LVS3 sampler [10] with the airflow rate 55 m³/24h was used for PM₁₀ sampling. Whatman QM-A 47 mm quartz filters were used as the collection medium. Samples were collected on a daily basis (24h). The concentrations of As, Pb, Cd, and Ni were determined with Inductively Coupled Plasma Mass Spectrometry - ICP MS (Agilent model 7700). The detection limits for As, Pb, Cd, and Ni determined by the ICP MS method were 0.1, 0.5, 0.02, and 0.7 ng/m³, respectively. Sample FINE DUST (PM₁₀-LIKE) ERM-CZ 120 (Institute for Reference Materials and Measurements, Retieseweg 111, B-2440 Geel, Belgium) was analyzed for quality control and verification of the applied procedures for microwave digestion and trace element analysis [3]. Recovery rates were in the range from 90 to 110% for all measured elements.

RESULTS AND DISCUSSION

Concentrations of carcinogenic elements

According to national legislation [13], to protect human health, the allowed annual concentration for PM₁₀ is set to 40 µg/m³. The same regulation prescribes annual limits for Pb, Cd, Ni, and As contents in PM₁₀ of 500, 5, 20, and 6 ng/m³, respectively. According to data shown in Table 1, in the observed period (2017-2020), PM₁₀ levels were usually below or slightly above the prescribed annual limit at sampling points Park and Institute.

On the contrary, average annual PM₁₀ levels at sampling point Jugopetrol were constantly above the limit value. This is predominantly because the sampling locations Park and Institute are less exposed to impact to PM₁₀ emissions from the copper smelter than sampling site Jugopetrol [12]. Namely, as shown in the wind rose diagram in Figure 1, the sampling point...
Jugopetrol is at the dominant wind direction relative to the copper smelter.

According to data shown in Table 2, the Pb level in PM$_{10}$ was above the limit at the sampling point Jugopetrol in 2017, 2019, and in 2020. Exceeding Pb levels beyond the annual limit occurred due to the processing of copper concentrates with higher Pb content especially in the period 2018-2020.

Table 1. Average annual levels of PM$_{10}$ at Park (P), Institute (IN) and Jugopetrol (JP) (LV - annual limit)

| Year | PM$_{10}$ P (µg/m$^3$) | PM$_{10}$ IN (µg/m$^3$) | PM$_{10}$ JP (µg/m$^3$) |
|------|------------------------|-------------------------|-------------------------|
| 2014 | 22.6                   | 38.4                    | 31.0                    |
| 2015 | 26.5                   | 30.6                    | 27.7                    |
| 2016 | 31.7                   | 32.2                    | 31.2                    |
| 2017 | 31.7                   | 44.6                    | 51.5                    |
| 2018 | 40.2                   | 39.9                    | 44.1                    |
| 2019 | 30.3                   | 28.5                    | 50.2                    |
| 2020* | 48.8                  | 39.9                    | 46.3                    |
| LV   | 40                     | 40                      | 40                      |

* average values for 2020 represent period January - May

Table 2. Average annual levels of Pb at Park (P), Institute (IN) and Jugopetrol (JP) (LV - annual limit)

| Year | Pb P (ng/m$^3$) | Pb IN (ng/m$^3$) | Pb JP (ng/m$^3$) |
|------|----------------|-----------------|-----------------|
| 2014 | 502.0          | 289.0           | 344.0           |
| 2015 | 207.0          | 67.0            | 253.0           |
| 2016 | 129.0          | 84.0            | 541.0           |
| 2017 | 101.0          | 200.0           | 678.0           |
| 2018 | 110.0          | 199.1           | 360.0           |
| 2019 | 176.0          | 53.0            | 845.0           |
| 2020* | 162.5       | 322.5           | 1612.0          |
| LV   | 5             | 5               | 5               |

* average values for 2020 represent period January - May

Table 3. Average annual levels of Cd at Park (P), Institute (IN) and Jugopetrol (JP) (LV - annual limit)

| Year | Cd P (ng/m$^3$) | Cd IN (ng/m$^3$) | Cd JP (ng/m$^3$) |
|------|----------------|-----------------|-----------------|
| 2014 | 4.2            | 5.7             | 9.1             |
| 2015 | 4.3            | 2.0             | 10.0            |
| 2016 | 3.7            | 2.8             | 12.3            |
| 2017 | 3.1            | 4.4             | 18.0            |
| 2018 | 4.8            | 6.0             | 19.5            |
| 2019 | 10.6           | 2.7             | 44.9            |
| 2020* | 3.9           | 7.1             | 45.3            |
| LV   | 500           | 500              | 500              |

* average values for 2020 represent period January - May

According to data shown in Table 4, the content of Ni in PM$_{10}$ was below the limit value during the whole period of observation at all sampling points.

According to data shown in Table 5, the content of As in PM$_{10}$ in Bor was above the limit value during the whole period of observation at all sampling points. The citizens of Bor town urban areas are exposed to constant air pollution with As content in PM$_{10}$ particles, in concentrations even 90 times higher (at sampling point Jugopetrol in 2019) than the prescribed annual limit value.

With the building of the new copper smelter, the content of As in the PM$_{10}$ was not reduced, on the contrary, the situation deteriorated. This is due to the higher production of copper in the new copper smelter and the processing of the copper concentrate with the higher amount of As.

Such high emissions of As particles from the copper smelter pose a serious threat to human health and should be properly treated. The content of As...
determined in PM$_{10}$ in Bor were several times higher compared with those determined near the other metallurgical facilities in Serbia [13] and EU as well [14].

**Correlations between the Pb, Cd, Ni, As, and PM$_{10}$, in Bor town urban areas**

Pearson’s correlation coefficients ($r$) between average monthly values of Pb, Cd, Ni, As and PM$_{10}$ at sampling points are shown in Tables 6-8.

**Table 6. Pearson's correlation coefficients between average monthly levels of Pb, Cd, Ni, As, and PM$_{10}$ at Park (P), for the period 2017 - 2020**

|        | Pb    | Cd    | Ni    | As    | PM$_{10}$ |
|--------|-------|-------|-------|-------|-----------|
| Pb     | 1.000 |       |       |       |           |
| Cd     | .130  | 1.000 |       |       |           |
| Ni     | -.106 | .145  | 1.000 |       |           |
| As     | .533  | .710  | .085  | 1.000 |           |
| PM$_{10}$ | .043  | .234  | -.004 | .289  | 1.000     |

Values in bold: Correlation is significant at the 0.01 level (2-tailed)

A strong positive correlation ($0.8>r>0.6$, $p<0.01$) between the As and Cd is observed at sampling point Park, as well as a moderate positive correlation ($0.6>r>0.4$, $p<0.01$) between As and Pb (Table 6). These correlations are stronger than those obtained for the 2004-2015 period [1]. On the other hand, the correlations between Cd and Pb, and PM$_{10}$ and Pb are very weak ($0.2>r$) while in the previous period they were moderate [1]. Such correlation values indicate that Pb, Cd, and As at the sampling point Park originate from the same source. A very weak correlation of Ni and other elements confirms that Ni originates from a different source. Weak positive correlation ($0.4>r>0.2$, $p<0.01$) between PM$_{10}$ and Cd and PM$_{10}$ and As indicates that the PM$_{10}$ levels at this sampling point are not under the constant influence of PM$_{10}$ emissions from the copper smelter. The PM$_{10}$ level at sampling point Park depends on other sources and factors as well, for example, meteorological factors (wind speed and direction).

**Table 7. Pearson's correlation coefficients between average monthly levels of Pb, Cd, Ni, As, and PM$_{10}$ at Institute (IN) for 2017 - 2020 period**

|        | Pb    | Cd    | Ni    | As    | PM$_{10}$ |
|--------|-------|-------|-------|-------|-----------|
| Pb     | 1.000 |       |       |       |           |
| Cd     | .755  | 1.000 |       |       |           |
| Ni     | .479  | .328  | 1.000 |       |           |
| As     | .493  | .713  | .060  | 1.000 |           |
| PM$_{10}$ | .085  | .212  | -.008 | .388  | 1.000     |

Values in bold: Correlation is significant at the 0.01 level (2-tailed).

Values in underline: Correlation is significant at the 0.05 level

Sampling point Institute is characterized by the strong positive correlation between Cd and Pb and between As and Cd (Table 7). Also, a moderate positive correlation between Ni and Pb, as well as a weak positive correlation between Ni and Cd, PM$_{10}$ and Cd, and PM$_{10}$ and As was observed. These correlations are generally stronger than those obtained in [1]. Such correlation values indicate that Pb, Cd, and As at the sampling point Institute originate from the same source. Weak correlation between PM$_{10}$ and Cd, and PM$_{10}$ and As indicates that the pollution at this sampling point is not under the constant influence of PM$_{10}$ emissions from the copper smelter.

**Table 8. Pearson's correlation coefficients between average monthly levels of Pb, Cd, Ni, As, and PM$_{10}$ at Jugopetrol (JP) for the period 2017 – 2020**

|        | Pb    | Cd    | Ni    | As    | PM$_{10}$ |
|--------|-------|-------|-------|-------|-----------|
| Pb     | 1.000 |       |       |       |           |
| Cd     | .818  | 1.000 |       |       |           |
| Ni     | .377  | .233  | 1.000 |       |           |
| As     | .852  | .940  | .269  | 1.000 |           |
| PM$_{10}$ | .221  | .473  | .202  | .398  | 1.000     |

Values in bold: Correlation is significant at the 0.01 level (2-tailed).

Values in underline: Correlation is significant at the 0.05 level

Sampling point Jugopetrol is characterized by a very strong positive correlation between Cd and Pb, As and Pb, and As and Cd (Table 8). Also, a moderate positive correlation between PM$_{10}$ and Cd, and weak correlations between Ni and Pb, Ni and Cd, Ni and As, PM$_{10}$ and Pb, and PM$_{10}$ and As were observed. These correlations are stronger than those obtained in [1]. Such correlation values indicate that Pb, Cd, and As at the sampling point Jugopetrol originate from the same source. The moderate and weak, but significant, correlation between PM$_{10}$ and other elements indicates that sampling point Jugopetrol is under stronger influence of PM$_{10}$ emissions from the copper smelter compared with other sampling points. This is mostly because the Jugopetrol sampling point is at the dominant wind direction (NNW) downwind from the copper smelter complex.

Pearson’s correlation coefficients of selected elements between the measuring points Park, Institute and Jugopetrol are shown in Table 9.

The upper part of Table 9 shows the correlations of observed elements between the sampling points Park and Institute. There is a strong (As$_{P}$ and As$_{IN}$) and moderate positive correlation among the same elements at both sampling points, except Cd and Ni. Also, a strong correlation between Ni$_{IN}$ and Cd$_{P}$ and a moderate positive correlation between Cd$_{IN}$ and Pb$_{P}$, Pb$_{IN}$ and Cd$_{P}$, and As$_{IN}$ and Pb$_{P}$, was detected. Such correlations indicate that Pb, and As at the sampling points Park and Institute originate from the same source. Also, the correlation between PM$_{10}$ levels indicates that both Park and Institute are under the same magnitude of influence of the meteorological conditions relative to PM$_{10}$ pollution emissions from the copper smelter.
A middle part of Table 9 shows very weak and mostly negative correlations of observed elements between the sampling points Park and Jugopetrol. The only exception is the weak positive correlation between \( \text{PM}_{10} \) JP and \( \text{PM}_{10} \) P. Such very weak and negative correlations indicate that these sampling points are in the opposite wind directions when it comes to the winds that blowing from the copper smelter.

**Table 9. Pearson’s correlation coefficients between average monthly levels of Pb, Cd, Ni, As, and \( \text{PM}_{10} \) at Park, Institute, and Jugopetrol (JP) (2017 - 2020)**

|                | Park  | Institute | JP   |
|----------------|-------|-----------|------|
| Pb             |       |           |      |
| Cd             |       |           |      |
| Ni             |       |           |      |
| As             |       |           |      |
| \( \text{PM}_{10} \) | -0.106 | 1.147 | 0.32 |

Values in bold: Correlation is significant at the 0.01 level (2-tailed).

Values in underline: Correlation is significant at the 0.05 level

At the end of Table 9, we can see very weak correlations of observed elements between the sampling points Institute and Jugopetrol. The only exception is the moderate positive correlation between \( \text{PM}_{10} \) JP and \( \text{PM}_{10} \) IN. Such kind of correlations clearly indicate that these sampling points are in the opposite wind directions.

**CONCLUSION**

The concentrations of 4 cancerogenic elements (Pb, Cd, Ni, and As) determined in \( \text{PM}_{10} \) at 3 locations in the urban areas near the copper smelter in Bor were analyzed in the period from January 2017 to May 2020. The results presented in the paper show that the average content of As determined in \( \text{PM}_{10} \) was over the annual national limit at all sampling points in the whole period of observation, as well the contents of Cd in \( \text{PM}_{10} \) at the sampling point Jugopetrol. The content of Pb in \( \text{PM}_{10} \) was over the national annual limit only at sampling point Jugopetrol. The correlations between the As-Pb, As-Cd, and Cd-Pb, at all sampling points, mostly vary from very strong positive to moderate positive. Compared to previously obtained results, these correlations are generally stronger. Such results indicate that As, Cd, and Pb determined in \( \text{PM}_{10} \) mostly originate from the same source - the copper smelter. Opposite to that, correlations of Ni with other selected elements are mostly very weak to moderate. This indicates that Ni mostly originated from natural sources.

With the building of a new copper smelter, the content of As, Cd, and Pb in the \( \text{PM}_{10} \) was not reduced, on the contrary, the situation is worse than before. This can be explained by the higher production of copper in the new copper smelter, and the processing of the copper concentrate with a higher amount of cancerogenic elements.

The constant air pollution with the content of As, Cd and Pb particles in \( \text{PM}_{10} \) higher than the prescribed annual limits require actions in order to reduce anthropogenic emission of cancerogenic elements in suspended particles in Bor.

**REFERENCES**

[1] V. Tasić, R. Kovačević, B. Maluckov, T. Apostolovski-Trujić, M. Cocić, B. Matić, M. Stelar, “The content of As and heavy metals in TSP and \( \text{PM}_{10} \) near a copper smelter in Bor, Serbia”, *Water Air and Soil Pollution*, 228:6., 2017.

[2] S. Serbula, T. Kalinović, J. Kalinović, A. Ilic, “Exceedance of air quality standards resulting from pyrometallurgical reduction of copper: a case study, Bor (Eastern Serbia)”, *Environ. Earth Sci.*, Vol. 68 (7), 2013, pp. 1989-1998.

[3] R. Kovačević, M. Jovašević-Stojanović, V. Tasić, N. Milošević, N. Petrović, S. Stanković, S. Matić-Besarabić, “Preliminary analysis of levels of arsenic and other metallic elements in \( \text{PM}_{10} \) sampled near copper smelter Bor (Serbia)”, *Chem. Ind. Chem. Eng. Q.*, Vol.16 (3), 2010, pp. 269-279.

[4] V. Tasić, N. Milošević, R. Kovačević, M. Jovašević-Stojanović, M. Dimitrijević: “Indicative levels of PM in the ambient air in the surrounding villages of the Copper Smelter Complex Bor, Serbia”, Chemical Industry & Chemical Engineering Quarterly, 2012, Vol. 18 (4) pp. 643-652.

[5] M. Dimitrijević, A. Kostov, V. Tasić, N. Milošević, “Influence of pyrometallurgical copper production on the environment”, *J. Hazard. Mater.*, Vol. 164 (2-3), 2009, pp. 892–899.

[6] https://bor.rs/ekologija/(accessed on July 22nd 2020, in Serbian)

[7] WHO (World Health Organization) (2016). International Agency for Research on Cancer, List of Classifications, http://monographs.iarc.fr/ENG/Classification/index.php (accessed on July 22nd 2020)

[8] WHO (World Health Organization) (2000). Air Quality Guidelines for Europe, second ed., WHO Regional
ACKNOWLEDGEMENTS
This work is financially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia.

BIOGRAPHY of the first author
Aleksandar Simonovski was born in Bor, Serbia, in 1983. He has earned an M.Sc. from the University of Nis, Faculty of Occupational Safety. His main areas of research interest include air quality monitoring and environmental protection systems. He is currently working as an associate at the Mining and Metallurgy Institute in Bor, Laboratory for Chemical Testing.