CONCENTRATIONS AND CHEMICAL COMPOSITION OF PM\textsubscript{10} AND PM\textsubscript{2.5} IN THE TOWN LIBRARY IN BOR, SERBIA

**Abstract:** This paper presents the PM\textsubscript{10} and PM\textsubscript{2.5} concentrations and results of chemical analyses of PM samples collected at the public library in Bor town, Serbia. Two sampling campaigns were carried out during six consecutive working days in June 2015 and in March 2016. The results show that PM\textsubscript{10} and PM\textsubscript{2.5} concentrations in the library were strongly connected with the respective PM concentrations in ambient air. So, most PM particles in the library originate from the outdoor air. High PM\textsubscript{2.5}/PM\textsubscript{10} ratios in both indoor and outdoor environments indicate the considerable influence of anthropogenic air pollution sources, in this case, metallurgical processes in copper smelting plants. Because the new copper smelting plant started operating in 2016, it is necessary to conduct a new measurement campaign to determine whether there are changes in the concentration levels and chemical composition of PM in the indoor air of public and residential buildings in Bor.

**Key words:** particulate matter, monitoring, air pollution, chemical analyses, arsenic.

INTRODUCTION

Exposure to particulate matter (PM) air pollution has been associated with respiratory and cardiovascular diseases [1-4]. Considering that people spend most of their lives indoors [5], it is very important to determine the impact of indoor PM pollution on human health.

In the Republic of Serbia, there is an insufficient number of studies about the PM levels and chemical composition of PM inside the buildings where people work and live. As a result, relations between PM inside and outside the buildings have not been sufficiently known and explored. The research of indoor air quality in public and educational buildings has been carried out periodically within the framework of scientific projects supported by EU funds or by the Ministry of Education, Science and Technological Development of the Republic of Serbia. This work is a part of the research on the characterization of suspended particles inside the educational and public institutions in Serbia. The town of Bor is assumed as a representative urban-industrial environment in Serbia because of the emissions of sulfur oxides and particulate matter from the copper smelter facilities situated close to the town urban areas.

In the past years (2011-2019), the measurements of indoor PM levels in Bor were carried out in the kindergartens, primary and secondary schools, hospitals, and residential apartments [6, 7]. This paper presents the results of measurements of PM in the town library in Bor aiming to determine the impact of outdoor PM pollution, as well as visitor and staff activities, on PM levels inside the library. The second aim is to assess the chemical composition of PM\textsubscript{10} and PM\textsubscript{2.5} particle fractions in the library.

METHODOLOGY

**Library characteristics**

The town library in Bor is located in the so-called House of Culture, at a distance less than 500 m from the town centre on one side and the main entrance to the copper smelting plant on the other side, as shown in Figure 1. It is situated between the two main streets (less than 100 m far from the library) and Town Park, as shown in Figure 2. The library has a collection of around 80000 books in a purpose-built area of 1113 m$^2$. The library has several departments: the children's literature department, the informative department, the exhibition hall and a hall for public events, the adult literature department, and the special collection departments.

![Figure 1. Location of town library relative to the copper smelting plant in Bor](image-url)
Sampling location and equipment used during measurement campaigns

The measurements of PM concentrations in the library were carried out in two sampling campaigns during June 2015 and March 2016. The first campaign was carried out in the no-heating period, from June 12th to June 19th of 2015. The second campaign was carried out in the heating period from March 14th to March 22nd of 2016. The samples were collected during working hours (WH) from 8 AM to 8 PM, and also during non-working hours (NWH) from 8 PM to 8 AM the next day.

The referent low-volume samplers, Sven/Leckel LVS3 [8], were used to simultaneously collect PM inside the library and in the ambient air, at the balcony. Two samplers were placed in the middle of the department for adults, on the library third floor, as shown in Figure 3. The department for adults has a volume of approximately 275 m³. The area was carpeted, without an air conditioning system and with the surface of a window of 15 m². During the measurement campaign in the no-heating period, one window remained half-opened. The other two samplers were placed on the balcony at a height of 10 m above ground.

The direct reading aerosol monitoring device, Turnkey OSIRIS Particle Monitor (Model 2315) [9], was placed near the LVS3 devices to access real-time changes in PM levels in the library. The data from the OSIRIS monitor were originally available as 15-min averages. For the calculation of daily averages, a minimum capture of 90% of 15-min averages was required. The results obtained by OSIRIS were corrected as it was suggested by Ramachandran et al. [10] by using the average daily indoor PM concentrations obtained by the gravimetric method.

Samples preparation and analyses

The flow rate of the LVS3 samplers (38.3 l/min) was calibrated at the beginning of measurements using a certified flow meter. PM mass concentrations were obtained from the gravimetric analysis of filters. Quartz fiber filters (Whatman QMA 47 mm diameter filters) were used to collect the PM samples. Pre-conditioning and post-conditioning of filters were undertaken in accordance with the general requirements of SRPS EN 12341:2015 standard.

After measuring the mass of the exposed filters, they were further prepared for chemical analysis in accordance with the procedure of SRPS EN14902:2008 [11]. Major elements (Fe, Al, Na, Mg, Ca, and K) and trace elements (As, Cd, Pb, and Ni among others) were analyzed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP OES) and Inductively Coupled Plasma Mass Spectrometry (ICP MS), respectively. In this way, the mass concentrations of 15 chemical elements from the PM samples were determined. For the purpose of quality control and verification of the dissolution and analysis process, standard reference material (NIST 1648a [12]) was analyzed in the same way. Recovery rates were in the range from 90 to 110% for most of the chemical elements.

RESULTS AND DISCUSSION

Daily averages of meteorological parameters during the measurement campaigns are shown in Table 1. The meteorological data were taken from the automatic monitoring station (AMS Bor Park) situated in Town Park about 200 m from the library. During the first measurement campaign, the weather was mostly calm and stable. During the second measurement campaign, the weather was cold, with snow and icy rain.

| Measurement period | T (°C) | RH (%) | WS (m/s) | P (mbar) |
|--------------------|-------|--------|----------|----------|
| 12.06. - 19.06.2015 | 21.5  | 67.5   | 2.2      | 967.8    |
| 14.03. - 21.03.2016 | 5.3   | 68.7   | 1.7      | 978.4    |

Table 1. Meteorological conditions during the PM measurement campaigns (daily averages)
The indoor environment in the library is influenced by environmental conditions such as humidity and temperature as well as gaseous and PM pollution. The chemical composition of particles is an important factor that affects the preservation of objects inside libraries due to soiling and chemical reactions from harmful compounds inside the particles or on the surface between the particle and the deposited surface.

### Table 2. Average daily PM concentrations (µg/m³), and I/O ratios

| Measurement period | PM₁₀ in | PM₁₀ out | PM₁₀ I/O ratio |
|--------------------|---------|----------|----------------|
| 12.06. - 19.06.2015 | 33.2    | 31.2     | 1.06           |
| 14.03. - 21.03.2016 | 28.8    | 39.4     | 0.73           |

### Table 3. Chemical composition of PM₁₀ (working hours -WH, non-working hours - NWH)

|     | PM₁₀ in | PM₁₀ out |
|-----|---------|----------|
|     | WH      | NWH      | WH      | NWH      |
| µg/m³ | ng/m³ | µg/m³ | ng/m³ |
| PM₁₀ | 38.5    | 27.9    | 34.0    | 28.5     |
| As   | 31.5    | 45.6    | 8.3     | 73.7     |
| Cd   | 1.8     | 4.9     | 1.4     | 7.5      |
| Pb   | 112.5   | 63.2    | 24.8    | 95.5     |
| Cu   | 452.5   | 140.5   | 173.1   | 61.5     |
| Zn   | 116.9   | 125.0   | 170.8   | 129.1    |
| Ni   | 2.0     | 3.1     | 9.9     | 18.0     |
| Se   | 4.5     | 1.7     | 2.5     | 3.5      |
| Ag   | 4.4     | 1.3     | 5.0     | 2.4      |
| Mn   | 13.1    | 10.9    | 20.7    | 9.7      |
| Fe   | 1745.4  | 886.8   | 1664.4  | 1193.5   |
| Ca   | 2624.1  | 1925.2  | 3308.8  | 1626.0   |
| Al   | 634.7   | 518.7   | 1140.4  | 508.8    |
| Mg   | 520.0   | 409.1   | 674.6   | 328.8    |
| Na   | 130.9   | 122.3   | 200.3   | 97.9     |
| K    | 759.6   | 392.3   | 793.5   | 465.5    |

Chemical compositions of PM₁₀ and PM₂.₅ samples during the first measurement campaign are presented in Table 3 and Table 4. I/O and WH/NWH ratios for
chemical elements determined in PM samples are presented in Table 5 and Table 6. According to national legislation [15], the allowed annual limits for Pb, Cd, Ni, and As contents in PM$_{10}$ are 500, 5, 20, and 6 ng/m$^3$, respectively.

From Tables 3 and 4 it can be noticed that the average daily concentration of As detected in the library as well as in the ambient air in both PM$_{10}$ and PM$_{2.5}$ fractions was above the annual limit value.

Arsenic is a human carcinogen. People living near emission sources of inorganic arsenic, such as smelting plants, have a moderately elevated risk of lung cancer because there is no recommended safe level for inhalation exposure for As.

**Table 4. Chemical composition of PM$_{2.5}$ (working hours - WH, non-working hours - NWH)**

| Element | WH | NWH | WH | NWH |
|---------|----|-----|----|-----|
| As      | 18.6 | 43.2 | 7.9 | 64.0 |
| Cd      | 1.6  | 4.9  | 0.5 | 6.2 |
| Pb      | 57.7 | 59.2 | 19.2 | 89.1 |
| Cu      | 219.3 | 124.0 | 131.2 | 40.1 |
| Zn      | 103.9 | 107.4 | 132.2 | 95.5 |
| Ni      | 1.0  | 1.0  | 3.2 | 8.8 |
| Se      | 3.3  | 1.4  | 2.3 | 2.3 |
| Ag      | 2.8  | 1.2  | 4.0 | 2.3 |
| Mn      | 12.5 | 7.4  | 13.1 | 5.4 |
| Fe      | 1688.8 | 555.6 | 1236.5 | 768.0 |
| Ca      | 2017.2 | 1609.7 | 2832.0 | 1382.2 |
| Al      | 372.4 | 190.1 | 596.0 | 173.5 |
| Mg      | 426.1 | 287.1 | 633.8 | 218.1 |
| Na      | 123.0 | 67.5 | 189.7 | 67.5 |
| K       | 447.2 | 145.9 | 771.4 | 233.4 |

**Table 5. I/O and WH/NWH ratios for chemical elements determined in PM$_{10}$ samples**

| Element | PM$_{10}$ in/out | WH/NWH | IN | OUT |
|---------|------------------|--------|----|-----|
| As      | 3.8              | 0.6    | 0.7 | 0.1 |
| Cd      | 1.3              | 0.6    | 0.4 | 0.2 |
| Pb      | 4.5              | 0.7    | 1.8 | 0.3 |
| Cu      | 2.6              | 2.3    | 3.2 | 2.8 |
| Zn      | 0.7              | 1.0    | 0.9 | 1.3 |
| Ni      | 0.2              | 0.2    | 0.6 | 0.6 |
| Se      | 1.8              | 0.5    | 2.7 | 0.7 |
| Ag      | 0.9              | 0.5    | 3.4 | 2.1 |
| Mn      | 0.6              | 1.1    | 1.2 | 2.1 |
| Fe      | 1.0              | 0.7    | 2.0 | 1.4 |
| Ca      | 0.8              | 1.2    | 1.4 | 2.0 |
| Al      | 0.6              | 1.0    | 1.2 | 2.2 |
| Mg      | 0.8              | 1.2    | 1.3 | 2.1 |
| Na      | 0.7              | 1.2    | 1.1 | 2.0 |
| K       | 1.0              | 0.8    | 1.9 | 1.7 |

The content of As in PM samples in both measurement campaigns was above the annual limit value. This requires concrete actions in order to reduce the anthropogenic emission of suspended particles enriched with arsenic in Bor.

The elements Ca, Fe, Mg, Na, Cu, and Zn were most present in all PM samples. The dust raised from the ground contains crustal elements Ca, Fe, Mg, Na, Al, K. Also, it is known that the major sources of Fe, As, Cd, Cu, Zn, and Pb particles are emissions of waste gasses from the metallurgical facilities such as the copper smelting plant in Bor. For most of the major elements (Ca, Fe, Mg, Na, Al, and K) detected in PM$_{10}$ and PM$_{2.5}$ in the library, as well in the outdoor air, WH/NWH ratios were higher than 1.

This points to the fact that in addition to the activities in the library that cause the resuspension of particles from both PM fractions, another phenomenon arises in the outside air. Namely, under the influence of meteorological conditions, primarily changes in the direction and wind speed, there is a regular occurrence of increased PM pollution in the outdoor air during the day compared to the PM pollution during the night. This can be also attributed to lowering the production activities in the copper smelter during the night.

The average wind speed is lower over the night than over the day. Wind direction and temperature are also changed during the night, which changes particle resuspension dynamics in ambient air [14].

**Table 6. I/O and WH/NWH ratios for chemical elements determined in PM$_{2.5}$ samples**

| Element | PM$_{2.5}$ in/out | WH/NWH | IN | OUT |
|---------|------------------|--------|----|-----|
| As      | 2.4              | 0.7    | 0.4 | 0.1 |
| Cd      | 3.4              | 0.8    | 0.3 | 0.1 |
| Pb      | 3.0              | 0.7    | 1.0 | 0.2 |
| Cu      | 1.7              | 3.1    | 1.8 | 3.3 |
| Zn      | 0.8              | 1.1    | 1.0 | 1.4 |
| Ni      | 0.3              | 0.1    | 1.0 | 0.4 |
| Se      | 1.4              | 0.6    | 2.3 | 1.0 |
| Ag      | 0.7              | 0.5    | 2.3 | 1.7 |
| Mn      | 0.9              | 1.4    | 1.7 | 2.4 |
| Fe      | 1.4              | 0.7    | 3.0 | 1.6 |
| Ca      | 0.7              | 1.2    | 1.3 | 2.0 |
| Al      | 0.6              | 1.1    | 2.0 | 3.4 |
| Mg      | 0.7              | 1.3    | 1.5 | 2.9 |
| Na      | 0.6              | 1.0    | 1.8 | 2.8 |
| K       | 0.6              | 0.6    | 3.1 | 3.3 |

Figures 4 and 5 show PM concentrations in the library measured by the real-time PM monitor OSIRIS [9]. Both figures clearly show that variations of PM concentrations in the library follow almost similar measurement patterns. PM concentrations in the library rise at the start of the workday, at 8 AM, and fall at the closing time, after 8 PM. Significant fluctuations of PM$_{10}$ concentrations in relation to PM$_{2.5}$ concentrations
are also observed, which indicates the occurrence of resuspension of larger particles due to activity in the library during working hours.

In the literature, copper smelting is associated with significant concentrations of Cu, as well as with elevated levels of As, Zn, and Cd [16]. All mentioned chemical elements were determined in both PM$_{10}$ and PM$_{2.5}$ fractions in the library. Under the influence of changes in meteorological conditions, and lower production activities in the copper smelting plant over the night, the regular decrease in concentrations of the majority of chemical elements in PM samples has been identified. The exceptions are the elements As, Cd, Pb, and Ni, whose concentrations in PM samples from both fractions in outdoor air are higher during non-working hours. This can be attributed to the increased impact of fugitive PM emissions from metallurgical plants during the night due to changes in meteorological conditions.

**CONCLUSION**

In this paper, the mass concentrations and chemical composition of PM$_{10}$ and PM$_{2.5}$ particles in the library and the ambient air in Bor are presented. The results show that PM concentrations in the library were strongly connected with the respective PM concentrations in ambient air. Thus, most of the PM pollution in the library originates from the outdoor air. High PM$_{2.5}$/PM$_{10}$ ratios in both the indoor and outdoor environments point out the considerable influence of pollution sources of anthropogenic origin, in this case, air pollution from the copper smelter. Due to the fact that the new copper smelting plant started operating in 2016, it is necessary to conduct a new measurement campaign to determine whether there has been a change in the chemical composition of PM in the indoor air of public and residential buildings in Bor town.

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KONCENTRACIJE I HEMIJSKI SASTAV SUSPENDOVANIH ĆESTICA PM<sub>10</sub> I PM<sub>2.5</sub> U BIBLIOTECI U BORU, SRBIJA

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Rezime: U radu su prikazane koncentracije suspendovanih čestica PM<sub>10</sub> i PM<sub>2.5</sub> i rezultati hemijskih analiza PM uzoraka sakupljenih u gradskoj biblioteci u Boru, Srbija. Sprovedene su dve kampanje uzorkovanja u trajanju od po šest uzastopnih radnih dana u junu 2015. godine, i tokom marta 2016. Rezultati merenja ukazuju na to da su koncentracije PM<sub>10</sub> i PM<sub>2.5</sub> u unutar biblioteke bile jako korelisanе sa odgovarajućim koncentracijama PM u atmosferskom vazduhu. Dakle, može se zaključiti da najveći dio PM čestica u biblioteci počine iz spoljašnje sredine. Visoki odnos PM<sub>2.5</sub>/PM<sub>10</sub> u biblioteci kao i u spoljašnjem ambijentalnom vazduhu ukazuju na znatan uticaj izvoza zagađenja antropogenog porekla, u ovom slučaju metalurških procesa u topionici bakra. Zbog činjenice da je nova topionica bakra počela sa radom tokom 2016. godine, potrebno je sprovesti novu kampanju merenja kako bi se utvrdilo da li postoje promene u koncentracijama i hemijskom sastavu suspendovanih čestica u unutrašnjem vazduhu javnih objekata i u objektima za stanovanje u Boru.

Ključne reči: suspendovane čestice, monitoring, zagađenje vazduha, hemijske analize, arsen.