

HEALTH RISK ASSESSMENT OF THE POPULATION OF THE CITY OF BOR (SERBIA) DUE TO THE INCREASE IN COPPER SMELTER CAPACITY

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Abstract: This study presents the results of research on the increased risk of non-carcinogenic health threats to children and adults, as well as the carcinogenic risk to the citizens of the city of Bor (Serbia), due to the 2.5-fold increase in the capacity of the copper smelter in Bor in mid-2023 and the exploitation of the "Čukaru Peki" mine with an increased arsenic (As) content multiple times above the limited values. After the stabilization of conditions in the new smelter, an analysis of the ambient air quality in the urban part of the city of Bor for the year 2024 was performed, as well as its impact on the risk of non-carcinogenic and carcinogenic effects on human health. The obtained results for the Hazard Quotient (HQ) < 1 indicate that the non-carcinogenic risk is acceptable. The results for carcinogenic risk (CR) = $5.58 \text{ E-}4$ for the measured maximum values of pollutant content in ambient air for 2024 indicate a highly unacceptable carcinogenic risk. For the average air quality values for 2024, CR = $1.24 \text{ E-}4$, which gives an assessment of a slightly unacceptable risk. The obtained results indicate that As and cadmium (Cd) have a predominant influence on CR values, while nickel (Ni) has a negligible influence. The influence of lead (Pb) requires a separate analysis using the Integrated Exposure Uptake Biokinetic Model (IEUBK) methodology.

Keywords: air pollution, PM₁₀, Pb, Cd, Ni, As, risk assessment,

Introduction

Ambient air pollution in industrially developed regions worldwide poses serious risks to human health [1], which is also the case in Serbia, especially in mining regions [2]. Many studies indicate that the concentration of particulate matter (PM) plays a major role in air pollution, primarily due to their chemical composition, which under aerodynamic conditions varies within diameters of 2.5 and 10 μm . PM particles have been identified as having an impact on human health during long-term exposure to high concentrations, which the World Health Organization (WHO) limited to 20 $\mu\text{g}/\text{m}^3$ in 2019 [3]. The air quality standard in the European Union (EU), defined by the European Environment Agency (EEA), sets annual limit values for PM₁₀ at 40 $\mu\text{g}/\text{m}^3$ as well as the content of heavy metals in them: Pb (0.5 $\mu\text{g}/\text{m}^3$), As (6 ng/m^3), Cd (5 ng/m^3), and Ni (20 ng/m^3) [4]. The legal regulations in Serbia are the same as in the EU [5]. It is necessary to point out the fact that the European Environment Agency (EEA) in 2024 adopted new limit values until 2030 as well as target values until 2050, where the value for PM₁₀ is reduced by 50%, while the values for Pb, Cd, Ni, and As remain at the same limit values [6,7].

According to the report of the International Agency for Research on Cancer (IARC), Cd seriously affects the health of children and adults, belonging to Group 1 of carcinogenic metals. Cd causes lung and kidney cancer since it enters the bloodstream. In children, it increases respiratory infections, reduces cognitive abilities, while in adults it causes hypertension, chronic kidney failure, and lung cancer [8]. Lead (Pb), which is also found in PM₁₀ particles, accumulates cumulatively in the bloodstream and is difficult to excrete from the body. In children, it causes learning and memory disorders, causes permanent brain damage, and reduces intelligence quotient (IQ). In adults, it causes cardiovascular problems, kidney failure, and osteoporosis [9]. Nickel (Ni) accumulates in the lungs and bloodstream. IARC classifies Ni and its compounds into Group 1 of carcinogenic elements. Ni is associated with cancer of the lungs, larynx, and nasal cavity, as well as DNA damage [10]. Arsenic (As) is also classified by IARC into Group 1 of carcinogenic substances, and WHO emphasizes that there is no safe level of As in ambient air [39]. In children, it causes bronchitis and respiratory tract infections, and in combination with Ni, it negatively affects the development of the nervous system and cognitive abilities, as well as cancer in

adulthood. In adults, it negatively affects the cardiovascular system, most often causing lung, bladder, and liver cancer [11,12].

SIGNIFICANCE AND AIM OF THE STUDY

The study is conducted to provide an answer about the level of risk from inhaling polluted air, after the 2.5-fold increase in the capacity of the copper smelter in Bor (Serbia) in mid-2023 [5], from the standpoint of exposure to PM10 particles containing heavy metals (Pb, Cd, Ni, and As).

Information from the Institute for Mining and Metallurgy in Bor (Serbia), available on the website of the City of Bor administration, was used [13].

In this study, PM10 particles were chosen instead of PM2.5 for the following reasons [12]:

- a) PM10 particles are a verified pollutant harmful to human health. The new WHO air quality guidelines from 2021 provide recommendations for six pollutants, one of which is PM10, which significantly affects human health independently of PM2.5 [39],
- b) Although PM2.5 penetrates the lungs more easily than PM10, the impact of particle exposure on human health depends on their chemical composition, not just their size.
- c) It should also be noted that PM10 particles correspond to particles with a smaller aerodynamic diameter than 10 μm , which also includes PM2.5 [14, 15].

The main aim of this study is the analysis of spatial and temporal variation of heavy metals (As, Cd, Pb, and Ni) and the assessment of the Hazard Quotient (HQ) and Cancer Risk (CR) in children and adults using different routes of pollutant intake into the body: inhalation, ingestion, and dermal absorption [1].

For the analysis of the set goals, available data from measuring stations that were operational in the territory of the urban part of the city of Bor (Serbia) in the period after the 2.5-fold increase in the capacity of the copper smelter in Bor were used [5]. Annual results for 2024, when production in the copper smelter stabilized, were analyzed, indicating that the same ambient air quality can be expected in the coming period. The exceedances of heavy metal concentrations in the considered year 2024 in PM10 particles indicate an increased risk of cancer in both children and adults [1,16,17],

which indicates the justification of the research whose results are presented in this paper.

The problems of ambient air pollution in Bor, especially after the 2.5-fold increase in smelter capacity, do not pose a risk to human health only in the area of this agglomeration, but can have potential cross-border consequences, considering that the air distance to the border with Bulgaria is about 20 km, and to Romania, an EU member state, about 80 km. These circumstances indicate the need for enhanced monitoring of ambient air quality and consistent tracking of compliance with European Union standards in this area, which further confirms the relevance of the conducted study.

MATERIAL AND METHODS OF RESEARCH

The ambient air quality in the Bor agglomeration was problematic primarily due to the copper smelter that began operation at the beginning of the 20th century. Episodes of extremely high concentrations of sulfur dioxide SO₂ were problematic [18] until the construction of the new smelter in 2015, when the SO₂ concentration was reduced to acceptable limits [5]. In addition to the SO₂ content in ambient air, the concentration of PM10 particles with increased heavy metal content, primarily Pb, Cd, Ni, and As [19], in the air but also in the soil in the wider surroundings of the smelter [20], has always been problematic. Air contamination with heavy metals contained in PM10: As, Cd, Pb, Ni, which is continuously measured, still represents a problem for the citizens of Bor [16], especially after 2023 [5]. In mid-2023, the foreign owner of the copper smelter in Bor reconstructed it and increased the smelter's capacity by 2.5 times compared to the previous state, which represents a great challenge for the ambient air quality in Bor. The reconstructed smelter uses Flash Smelting and Converting Furnaces technology [21], achieving temperatures up to 1300 °C. Undesirable heavy metals under such conditions—Pb, Cd, Ni, and As—melt at 327 °C, 321 °C, 1455 °C, and 614 °C, respectively, with As sublimating at that temperature. Cd, Pb, and Ni boil at the following temperatures: 767 °C, 1749 °C, and 2913 °C, respectively, indicating that As and Cd are converted to a gaseous state during the process, and during cooling, they transform into fine particles that are found in ambient air in the form of oxides [21], while the content of Pb and

Ni partly comes from dust from copper concentrate and mining production.

The problem of ambient air quality and negative impacts on human health is increased by the opening of the new copper mine "Čukaru Peki" with a copper content in the ore of 2.71% Cu and 1.75 g/t Au, with full ownership by a foreign company and a mining royalty of only 3%, which is extremely attractive for accelerated exploitation. In the obtained copper concentrate from processing this ore, the Cu content ranges from 20–30% Cu (which is optimal for the technological smelting process) and copper utilization ranges from 88–95%. A major problem arises from the fact that As concentrations in the copper concentrate range from 0.52–2.5% [22]. Copper concentrate with such a high As content, according to the laws of the EU and Serbia, should not be smelted in copper smelters [5, 23]. According to the law of the Republic of Serbia, the upper limit of As content in copper concentrate that can be treated in a copper smelter is 0.2% As, which in real conditions in the Bor copper smelter is more than ten times higher. However, the copper smelter and the mine are owned by a foreign company that does not respect the laws of Serbia. In addition to copper concentrate produced in Serbia, this company imports concentrates from abroad, and their chemical composition is not available to the public. Also, copper concentrate from Bor is exported through the port of Bar (Montenegro), where the concentrate is transshipped from trucks to ships. Recently, an increased Pb content in the blood of these workers was determined. The allowed limit of Pb in human blood is 2.8 µg/dL. Much higher values were found in 58 out of 63 tested workers who experienced visible health problems. The Pb content in the blood ranged from 8.0–15.9 µg/dL, and in one worker, a content of 25.1 µg/dL was determined. At the same time, an increase in Pb content in the blood was registered in workers at the copper smelter in Bor who sought medical help [24]. EU directives have lowered the limit values for Pb content in the blood of workers in plants with increased Pb concentration from 40–70 µg/dL to 15 µg/dL, which indicates that after the increase in the capacity of the copper smelter in Bor, monitoring of air quality in the smelter as well as in the ambient air in the city of Bor must be increased.

The problem of PM10 concentration in the ambient air in Bor, as well as in the working environment of the copper smelter, greatly increases concern. By measuring the concentration of these particles in a closed classroom at the Technical Faculty in Bor in the period March 5–19, 2018 (winter period when the windows and doors of the classroom were closed), a concentration of PM10 particles inside the classroom of 28.2 µg/m³ was determined, while the concentration of these particles outside was 46.1 µg/m³. The concentration of carcinogenic metals in them was: As 17 ng/m³, Cd 1.4 ng/m³, and Pb 456.7 ng/m³. About 20 students stay in this classroom for 4–6 hours daily [25]. Also, in the period March 1 – April 1, 2025, measurements of PM10 and PM2.5 concentrations were carried out in 15 selected apartments where people live. The measurements determined the mean concentration in the apartment ambient of PM10 and PM2.5 at 31.3 µg/m³ and 17.6 µg/m³, respectively. The content of heavy metals was not determined, but the obtained results deserve special attention and justified concern [26].

In addition to the ambient air quality in the city of Bor, during more than a century-long tradition of copper production in the copper smelter, continuous contamination of the soil in the vicinity of this smelter is present. Research at 12 locations in the wider area around the copper smelter at about 20 km showed the following mean results of heavy metal content in the soil at a depth of about 30 cm: 913.33 µg/kg Cu, 86.67 µg/kg Pb, 2.92 µg/kg Cd, 36.83 µg/kg Ni, 1070 µg/kg Mn, and 59.08 µg/kg Hg, 0.133 µg/kg [20]. These results indicate the distribution of deposited heavy metals in the soil that can be further distributed through groundwater and surface water, and plants used by the population for food, which increases the risk to human health. These facts require a separate study, especially on the impact of Pb on human health using the Integrated Exposure Uptake Biokinetic Model (IEUBK), a methodology prescribed by the United States Environmental Protection Agency (US EPA) as early as 2007 [27].

In the vicinity of the copper smelter in Bor, continuous measurement of the concentration of SO₂, PM10, and the content of As, Pb, Cd, and Ni in PM10 particles in ambient air is carried out, which is the predominant impact on human health. Measurements have

been carried out at eight measuring points since 2024, and monthly and annual reports of the Institute for Mining and Metallurgy in Bor are published on the website of the city of Bor [13].

RESULTS AND DISCUSSION

Health status of people in the city of Bor (Serbia)

The State Institute for Public Health of Serbia "Dr. Milan Jovanović Batut" in Belgrade publishes annual results on cancer incidence and mortality by region in Serbia. Table 1 shows the results for the period 2016-2022 for the Bor region, compared with the results in the region of Central Serbia and Serbia as a whole, from the aspect of new cases and the number of deaths from cancer [28].

Table 1. Number of newly diagnosed cases and number of deaths from cancer in the period 2016-2022 [28]

Year	Whole Serbia A		Whole Serbia B		Central Serbia A	
	A	B	A	B	A	B
2016	570	305	553	295	621	321
2017	587	306	570	300	657	324
2018	597	309	578	303	710	309
2019	609	307	585	300	739	295
2020	600	301	576	230	714	277
2021	611	292	595	285	730	264
2022	625	291	604	285	793	313

A: Number of new cancer cases per 100,000 inhabitants B: Number of deaths from cancer per 100,000 inhabitant

The results presented in Table 1 indicate a visibly higher rate of new cases and deaths from cancer per 100,000 inhabitants in the observed period in the Bor region compared to the region of Central Serbia as well as Serbia as a whole. With the 2.5-fold increase in the capacity of the copper smelter in Bor in mid-2023, as well as the increased content of carcinogenic metals in PM10, an increase in the number of new cases and deaths from cancer should be expected in the coming period.

Considering that the data given in Table 1 refer to the Bor District, which besides Bor

also includes the cities of Negotin, Kladovo, and Majdanpek, where exposure to polluted air is much lower, and that the city of Bor has about 35,000 inhabitants, a realistic estimate is that the number of new cases and deaths from cancer in the city of Bor is much higher than the figures stated in Table 1.

Due to increased mortality and migration trends, the population in Serbia is generally decreasing, but this decrease in Bor is about three times greater due to increased mortality in this city compared to the rest of Serbia, Table 2.

Table 2. Population decrease in Serbia in the period 2016 – 2022 [28]

Period	Whole Serbia		Whole Serbia		Central Serbia	
	Number	%	Number	%	Number	%
2016-2022	411319	5,83	270192	5,22	15502	13,30

A: Number of inhabitants that decreased B: Percentage (%) of decreased number of inhabitants

Health risk assessment from direct inhalation of heavy metals in PM10 has been applied in many studies [29, 12, 30, 31, 17].

For the assessment of health risk to human health in the city of Bor from direct inhalation of heavy metals in PM10 particles in ambient air from the aspect of non-carcinogenic and carcinogenic effects, the US EPA methodology [27] was used.

Non-carcinogenic effects

The Estimated Daily Intake (EDI) was performed according to the methodology [29]:

$$EDI = (C \times IR \times AF \times F \times ED) / (BW \times AT) \quad (1)$$

$$AT = ED \times 365$$

Meaning of individual symbols

Table 3. Symbols, names, and units of measure used in equations (1)-(5)

Symbol	English term	SERBIAN TERM	Translation
EDI	Estimated Daily Intake	procenjeni dnevni unos	estimated daily intake
C	Contaminant Concentration	koncentracija kontaminanta	contaminant concentration
IR	Intake Rate	stopa unosa/udisanja	intake/inhalation rate
AF	Bioavailability Factor	faktor bioraspoloživosti	bioavailability factor

F	Frequency of Exposure	učestalost izloženosti	frequency of exposure
ED	Exposure Duration	trajanje izloženosti	exposure duration
BW	Body Weight	telesna masa	body weight
AT	Averaging Time	vreme usrednjavanja	averaging time

The parameter for non-carcinogenic risk (HQ) represents the sum of all hazards for different substances [27], i.e., the HQ hazard quotient represents the ratio between the estimated exposure dose and the reference dose RfD.

That is:

$$HQ = EDI / RfD \dots\dots\dots (2)$$

where RfD represents the reference dose ($\mu\text{g}/\text{kg}$ body weight/day).

Values for reference doses RfD for different substances for non-carcinogenic risk assessment were used from reference databases [32,33]. If:

$HQ < 1$ risk acceptable.

$HQ > 1$ possible health problems.

The total non-carcinogenic risk HQ is determined by equation (3) ACCORDING to inhalation of a larger number of substances at the same time:

$$\Sigma HQ = HQ1 + HQ2 + \dots\dots + HQn \dots\dots\dots (3)$$

where 1–n represents the number of analyzed pollutants in the air..

Carcinogenic effects

Carcinogenic risk (CR) represents the lifetime risk of cancer. It is estimated that a person will develop cancer during their lifetime due to exposure to carcinogenic components [27, 32,33, 34]:

$$CR = EDI \times SF \dots\dots\dots (4)$$

where CR, EDI, and SF represent, respectively, carcinogenic risk (dimensionless quantity), estimated daily intake ($\mu\text{g}/\text{kg}$ body weight/day), and inhalation slope factor (SF) [$(\mu\text{g}/\text{kg}$ body weight/day) $^{-1}$].

Values of slope factors (SF) used for carcinogenic risk assessment for different substances were taken from relevant reference databases [35, 32, 33]. Total CR is used as a summary indicator for all carcinogenic substances, as the probability of cancer occurrence due to exposure:

$$\Sigma CR = CR1 + CR2 + \dots\dots + CRn \dots\dots\dots (5)$$

Acceptable risk limits are: CR: less than 10^{-6} - negligible risk; 10^{-6} - 10^{-4} - acceptable risk; $>10^{-4}$ - high risk.

For the impact of Pb from ambient air on general health and carcinogenic impact, a special procedure prescribed by IEUBK developed by US EPA 2021 is used [36]. This model includes the total intake of Pb into the body: from soil, water, house dust, food, and inhalation (which makes up about 10% of the total amount of Pb ingested), based on which the blood lead level (BLL) is calculated, which is not the subject of this study, considering the availability of only data on Pb content in ambient air [36,37].

The level of ambient air pollution in the urban part of Bor, measured at eight measuring stations by the concentration of PM10 particles, as well as the content of heavy metals in them, according to the US EPA standard [27]: Pb, Cd, Ni, and As. Table 4 shows the results of mean annual contents of the mentioned pollutants, maximum daily content, as well as the number of days during the calendar year when the upper limit values were exceeded, which served as starting values for health risk assessment in the Bor city agglomeration..

Table 4. Measured values of PM10, Pb, Cd, Ni, and As in ambient air in 2024 measured in the territory of the city of Bor

Measuring site		PM10 ($\mu\text{g}/\text{m}^3$)	Pb ($\mu\text{g}/\text{m}^3$)	Cd (ng/m^3)	Ni (ng/m^3)	As (ng/m^3)
Jugopetrol	X1	169,8	2,898	286	17,4	471
	X2	37	0,243	19,8	2,4	42
	X3	77	14	46	0	66
Oštrelj	X1	107,5	0,113	16,7	17,9	28,5
	X2	36,7	0,015	13,6	2	3,3
	X3	75	0	3	0	44
Brezonik	X1	139,5	0,390	28,3	12,6	88
	X2	30,6	0,029	2,65	2	5,6
	X3	86	0	53	0	75

Gradski park	X1	57,1	0,063	4,94	15,6	13,4
	X2	22,6	0,008	0,72	2	2,30
	X3	3	0	0	0	6
Ind. zona	X1	139,5	3,293	116,9	10,1	221,9
	X2	32,8	0,11	8,01	2	15,1
	X3	34	0	54	0	92
Krivelj	X1	85,3	0,121	26,8	17	35,8
	X2	26,8	0,070	0,68	2	14
	X3	16	0	5	0	9
Institut	X1	71,30	0,43	33,6	5,2	47,7
	X2	30,7	0,073	3,91	2	6,7
	X3	4	0	14	0	21
Metovnica	X1	57,1	0,063	4,94	15,6	13,4
	X2	22,6	0,08	0,72	2	2,3
	X3	3	0	0	0	8

X1 – Maximum measured mean daily value at the measuring site

X2 – Annual mean value at the measuring site

X3 – Number of days in which the allowed limit value was exceeded at the measuring site

Considering the fact that all eight measuring sites in the Bor city agglomeration are distributed at different locations in accordance with the existing wind rose, as well as the fact

that people move throughout the entire city area and are exposed to the effects of polluted air in the entire area where air monitoring was carried out. Therefore, the mean value of maximum concentrations measured at individual measuring sites (X1), the mean value of average values at all measuring sites (X2), and the mean value of the number of days when limit values were exceeded (X3) were calculated, and the obtained results are shown in Table 5.

Table 5. Annual mean values of pollutant concentrations at all measuring sites in the territory of the city of Bor in 2024.

Scenario	PM10 ($\mu\text{g}/\text{m}^3$)	Pb ($\mu\text{g}/\text{m}^3$)	Cd (ng/m^3)	Ni (ng/m^3)	As (ng/m^3)
X1	103,38	0,921	64,77	15,15	114,96
X2	29,97	0,0748	4,56	2,05	11,41
X3	37,25	1,78	21,87	0	40,19

X1- Arithmetic mean of measured maximum values in the territory of the city of Bor

X2- Arithmetic mean of mean annual values at all measuring sites in the territory of the city of Bor

X3- Arithmetic mean of the number of days when limit values of pollutants were exceeded in the territory of the city of Bor

Table 6 shows a comparative analysis of data by scenarios: X-1, X-2, and X-3 for mean values for all measuring sites in the Bor agglomeration for 2024 and 2025. In 2025, according to Scenario X-1, a decrease of $4.13 \mu\text{g}/\text{m}^3$ for PM10, a decrease of $0.431 \mu\text{g}/\text{m}^3$ for Pb, a decrease of $30.71 \text{ ng}/\text{m}^3$ for Cd, a decrease of $4.2 \text{ ng}/\text{m}^3$ for Ni, and an increase of $17.89 \text{ ng}/\text{m}^3$ for As were determined. According to Scenario X-2, an increase of $5.53 \mu\text{g}/\text{m}^3$ for PM10, an increase of $0.011 \mu\text{g}/\text{m}^3$ for Pb, a decrease of $2.4 \text{ ng}/\text{m}^3$ for Cd, a decrease of $0.04 \text{ ng}/\text{m}^3$ for Ni, and a decrease of $2.01 \text{ ng}/\text{m}^3$ for As were determined. According to Scenario X-3, the variation in the number of days of exceeding limit values for each pollutant individually is within the range of

(+/-) three days. The values for the first five months in 2026 are within the range of (+/-) 5% for all three scenarios. These facts indicate that the operation of the reconstructed copper smelter has stabilized, and that variations in the content of pollutants in the ambient air in the urban part of the city of Bor can affect the level of risk HQ and CR to human health, compared to the results obtained for 2024, with variations within limits below 5% in the coming period. The greatest danger arises from constant exposure of people to the stated concentrations of pollutants in ambient air over a longer period of time due to the cumulative effect that leads to a growing level of CR.

Table 6. Dependence of pollutant concentrations in ambient air of the city of Bor 2024/2025 according to scenario X-1 and X-2

Scenario	PM10 ($\mu\text{g}/\text{m}^3$) 2024/2025	Pb ($\mu\text{g}/\text{m}^3$) in PM10 2024/2025	Cd (ng/m^3) in PM10 2024/2025	Ni (ng/m^3) in PM10 2024/2025	As (ng/m^3) in PM10 2024/2025
X-1	103.38/99.25	0.921/0.496	64.77/34.06	15.15/10.95	114.96/132.85
X-2	29.97/35.5	0.078/0.089	4.56/2.15	2.05/2.01	11.41/9.40

For scenario X3, values vary within the range of (+/-) 3 days, indicating that the values from 2024 have not changed.

The results presented in Table 5 were used for health risk assessment for non-carcinogenic risks: Estimated Daily Intake (EDI) and HQ for children and adults, as well as for CR assessment for children and adults using equations (1) - (5). For calculating these values, the following parameters were used for children (7 years of age, 20 kg body weight, and inhalation rate of $10 \text{ m}^3/\text{day}$) and for adults (30 years of age, 70 kg body weight, and $20 \text{ m}^3/\text{day}$). For health risk assessment for metals in PM10 (Pb, Cd, Ni, and As), available data from the California Environmental Protection Agency (CalEPA 2016) and US EPA 2016 databases for RfD and slope factor (SF) were used, which enable the calculation of EDI, HQ, and CR for children and adults.

Health Risk Assessment

Assessment of non-carcinogenic risks

Assessment of non-carcinogenic risk by calculating the Estimated Daily Dose (EDD) was performed according to equation (1), and HQ assessment was performed using equation (2) with recommended values in databases [35,32] for children and adults.

a) Non-carcinogenic risk assessment for children
The calculated HQ1 values for children for individual toxic elements in PM10 for maximum pollutant content values in 2024 (Scenario X-1) are as follows: HQ1 - As = 0.18; HQ1 - Cd = 0.062; HQ1 - Ni = 0.00036. Total HQ1 = $0.24236 < 1$. The obtained results indicate that the non-carcinogenic risk for children is negligible based on maximum pollutant values in ambient air (Scenario X-1).

The values for mean annual concentrations of pollutants in ambient air of the city of Bor for 2024 (Scenario X-2) are as follows: HQ2-As = 0.018; HQ2-Cd = 0.0044; HQ2-Ni = 0.00005.

Total: HQ2 = $0.02245 < 1$.

The obtained results indicate that the non-carcinogenic risk for children is negligible based

on mean annual values of pollutants in ambient air in the city of Bor (Scenario X-2).

The values for HQ1 and HQ2 for children are < 1 , indicating that there is currently no acute non-carcinogenic risk. As shows the highest potential danger, which in long-term exposure to these concentrations of As and Cd pollutants can cumulatively be very dangerous for the health of the young population in this agglomeration.

b) Non-carcinogenic risk assessment for adults

For adults, HQ1 values based on maximum values for individual pollutants in ambient air in the city of Bor during 2024 (Scenario X-1) are:

HQ1-As = 0.11; HQ1-Cd = 0.036; HQ1-Ni = 0.00021. Total value: HQ1 = $0.14621 < 1$.

Non-carcinogenic risk assessment for adults based on mean annual values of pollutant content in ambient air of the city of Bor (Scenario X-2) was performed in the same way by assessing HQ2 values for each pollutant in ambient air:

HQ2-As = 0.010; HQ2-Cd = 0.0026; HQ2-Ni = 0.00003.

Total value: HQ2 = $0.01263 < 1$.

The obtained results indicate that the total non-carcinogenic risk HQ1 < 1 for adults based on maximum recorded values of pollutant concentrations in ambient air during 2024 (Scenario X-1) is negligible. Also, the total non-carcinogenic risk HQ2 < 1 for adults based on mean values of pollutant concentrations in ambient air during 2024 (Scenario X-2) is negligible.

In all cases, the non-carcinogenic risk for children and adults according to Scenario X-1 and Scenario X-2 has a decreasing trend in the series: HQAs $>$ HQcd $>$ HQNi. For Pb, the impact was not calculated because its impact requires a special IEUBK procedure, but considering its low content in ambient air, its impact could increase total HQ values by at most 10%, which would not affect the total HQ values.

Carcinogenic risk assessment

A) Carcinogenic risk assessment for the child population

CR calculation was performed using equation (4) and for the total annual risk equation (5). The obtained CR values for individual pollutants for

maximum values in 2024 for the child population are as follows (Scenario X-1):

CR1-As = $8.2\text{E-}5$; CR1-Cd = $4.7\text{E-}4$; CR1-Ni = $6.0\text{E-}6$. Total CR1 = $5.58\text{E-}4$.

For mean annual values for 2024, the following values were obtained (Scenario 2):

CR2-As = $8.1\text{E-}5$; CR2-Cd = $3.3\text{E-}5$; CR2-Ni = $5.0\text{E-}6$. Total CR2 = $1.24\text{E-}4$.

According to Scenario X-1, total CR = $5.58\text{E-}4$ is 5.6 times higher than the EPA value and represents an unacceptable risk in which Cd contributes 84.2%, As 14.7%, and Ni 1.1%. According to Scenario X-2, total CR = $1.24\text{E-}4$, which is about 24% above the EPA value and represents a slightly unacceptable risk in which As = 66.9%, Cd = 26.9%, and Ni = 6.5% participate.

B) Carcinogenic risk assessment for adults

Carcinogenic risk (CR) assessment for adults based on maximum pollutant values in PM10 during 2024 (Scenario X-1) shows the following values: CR1-As = $4.8\text{E-}4$; CR1-Cd = $2.7\text{E-}5$; CR1-Ni = $3.0\text{E-}6$. Total CR1 = $5.07\text{E-}4$.

The share of individual pollutants in total CR according to Scenario X-1 is as follows: As $\approx 94.7\%$, Cd $\approx 5.3\%$, and Ni $\approx 0.6\%$.

Carcinogenic risk assessment for mean annual values of pollutant concentrations in ambient air in the urban part of the city of Bor (Scenario X-2) shows the following values: CR2-As = $4.7\text{E-}5$; CR2-Cd = $2.0\text{E-}5$; CR2-Ni = $2.1\text{E-}6$. Total CR2 = $6.91\text{E-}5$.

The share of individual pollutants in total CR2 according to Scenario X-2 is as follows: As $\approx 68\%$, Cd $\approx 28.9\%$, and Ni $\approx 3\%$.

The value of total CR1 = $5.07\text{E-}4$ is multiple times higher than the limit value defined by the EEA of $1.0\text{E-}4$ and represents an unacceptable risk to the health of adults. For Scenario 2, CR2 = $6.91\text{E-}5$, which is within the limits between $1.0\text{E-}4$ and $1.0\text{E-}6$, so the risk is considered to be within acceptable limits. However, considering the fact that As has a predominant influence on CR and that its concentration during 2024 was above the allowed limit for a total of 40.19 days (Table 5), this indicates that the CR for ambient air in the studied region can be considered unacceptable..

Multivariate analysis

Based on bivariate analysis of annual concentrations of pollutants in ambient air in the urban zone in Bor, Pearson correlation coefficients were calculated in Table 7. Statistical analysis of data was performed using the SPSS statistical software package, with assessment of statistical significance of relationships between observed variables [38]. A positive correlation of 0.99 represents a high level of agreement ($p < 0.01$) between As concentration and Cd concentration. Also, a good positive correlation exists between As concentration and Ni of 0.93, as well as between Cd and Ni of 0.94. There is also a negative correlation between Pb concentrations and Cd: -0.96; Ni: -0.83; and As: -0.95, respectively. The obtained high positive correlation coefficients between As, Cd, and Ni indicate their relationship in the concentrates treated during 2024 in good correlation, while the negative correlation of Pb with As, Cd, and Ni indicates that the Pb content in the concentrate was variable..

Table 7. Pearson correlation coefficients between pollutants in PM10 particles

	Pb	Cd	Ni	As
Pb	1			
Cd	-0,96	1		
Ni	-0,83	0,94	1	
As	-0,95	0,99	0,93	1

Table 8 shows Pearson correlation coefficients between HQ and CR values for children and adults for both scenarios of pollutant concentrations in ambient air (Scenario X-1 and Scenario X-2). The obtained results show a high degree of positive correlation between values for child and adult populations for HQ within the range of 0.93 – 0.98, indicating a high correlation between non-carcinogenic health risk for child and adult populations according to

both scenarios X-1 and X-2, i.e., $(\text{HQ}_{1,2})\text{A} / (\text{HQ}_{1,2})\text{B} = 0.93\text{--}0.98$.

Positive correlation within the range of 0.96–0.99 between CR risk in child and adult populations according to Scenario X-1 and X-2, i.e., $(\text{CR}_{1,2})\text{A} / (\text{CR}_{1,2})\text{B} = 0.96\text{--}0.99$ indicates equal cancer risk for both populations. The lowest degree of positive correlation was found for the ratio of HQ and CR for Scenario X-1 and X-2, within the range of 0.78 – 0.83 for the adult population, and for the child population within

the range of 0.83-0.88. Taking into account that the HQ/CR correlation is positive for the child population relative to the same ratios for the adult population $(HQ_{1,2}/CR_{1,2})_A > (HQ_{1,2}/CR_{1,2})_B$, the probability that children

will be exposed to CR over time is higher. The correlation between $(CR_{1,2})_A / (CR_{1,2})_B = 0.96-0.99$ indicates that the probability of CR for both populations is in a high positive correlation..

Table 8. Pearson correlation coefficients between HQ and CR for children and adults according to scenario X-1 and X-2

	HQ ₁ -A	HQ ₂ -A	HQ ₁ -B	HQ ₂ -B	CR ₁ -A	CR ₂ -A	CR ₁ -B	CR ₂ -B
HQ ₁ -A	1							
HQ ₂ -A	0.98	1						
HQ ₁ -B	0.97	0.96	1					
HQ ₂ -B	0.95	0.94	0.93	1				
CR ₁ -A	0.88	0.85	0.84	0.82	1			
CR ₂ -A	0.86	0.83	0.82	0.80	0.99	1		
CR ₁ -B	0.87	0.84	0.83	0.81	0.98	0.98	1	
CR ₂ -B	0.84	0.81	0.80	0.78	0.97	0.96	0.98	1

(1) – Scenario X-1; (2) Scenario X-2; A- Child population; B- Adult population

CONCLUSION

The increase in the capacity of the copper smelter in Bor (Serbia) in the second half of 2023 by 2.5 times and the exploitation of the Čukaru Peki mine with increased As content in the ore, which in the copper concentrate has a content more than ten times above the allowed limit of 0.2% As, as well as the increase in Cd content in many ways, reduces the quality of ambient air in the urban area of the city of Bor. Also, the increased content of As and Cd in PM₁₀ particles in ambient air for years has led to increased illness and mortality from cancer in Bor, which is much higher than in the rest of Serbia. These facts justifiably lead to an increased risk to the health of people in the city of Bor after the increase in the capacity of the copper smelter, which is located in the immediate vicinity of the urban area of the city of Bor.

The results of the non-carcinogenic risk assessment for children and adults $(HQ_{1,2})_A < 1$ $(HQ_{1,2})_B < 1$ indicate that the non-carcinogenic risks according to both scenarios (1 and 2) for children (A) and adults (B) are currently at an acceptable level. However, long-term continuous increased content of As and Cd in PM₁₀ particles in ambient air in the urban environment of the city of Bor, due to their accumulation in the

human body, will over time increase the carcinogenic risk.

The carcinogenic risk assessment in the city of Bor according to the scenario of maximum values recorded during 2024 (Scenario X-1) is $CR_1 = 5.58E-4$ for children (A) and $CR_1 = 5.07E-4$ for adults (B), which are multiple times above the limit values (1.0 - 4) defined by EU standards, representing an unacceptable risk. According to the scenario of mean annual values (Scenario X-2), $CR_2 = 1.24E-4$ for children (A) and $CR_2 = 6.9E-5$ for adults (B), indicate a slightly unacceptable risk for the child population (A) and an acceptable risk for the adult population (B), which are within the limits (10^{-4} - 10^{-6}). The predominant influence on CR values is exerted by the concentrations of As and Cd in PM₁₀, whose concentrations in ambient air are in high mutual positive correlation of 0.99. Since these heavy metals accumulate in the human body, with long-term exposure to their contents in ambient air, the probability of increased CR increases. In conditions of increased capacity of the copper smelter, the risk to human health in the city of Bor increases, and due to the proximity of the border with Bulgaria and Romania, an EU member state..

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