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ASSESSMENT OF THE RISK TO HUMAN HEALTH FROM THE ACCUMULATION OF HEAVY METALS IN AND AROUND THE “2 JULY” NEIGHBORHOOD (MITROVICA-KOSOVO, KOSOVO)

Purpose. Determining the level of soil pollution with heavy metals in the “2 July” neighborhood, as well as researching the impact of pollution on the health of the neighborhood’s residents. The scope of the research was to know which age is most at risk from pollution based on the Theory of Risk Assessment, Non-carcinogenic risk assessment, and Carcinogenic risk assessment.

Methodology. The soil samples in the neighborhood “2 July” were taken spontaneously. After the preparation of the samples, lead, arsenic, zinc, copper, nickel, manganese, chromium, and cadmium were determined with ICP-OES. Analytical formulas were applied for the calculation of specific indicators, which include Geo-accumulation index, Enrichment factor, Chronic daily intake, Hazard index, Carcinogenic risk assessment, the total lifetime cancer risk. They show the level of soil pollution, and the risk of heavy metals affecting human health.

Findings. The results show that the content of lead, arsenic, zinc, nickel, manganese, chromium, and cadmium in the soil of the “2 July” neighborhood, in addition to copper, exceeds the values set by FAO/WHO. The value of the hazard index and total lifetime cancer risk for children for non-carcinogenic and carcinogenic risk is high, while that for adults are lower, which shows that children are more at risk.

Originality. Soil pollution in the “2 July” basin comes from three industrial dumps. This pollution affects human health through inhalation, skin, and ingestion route.

Practical value. The particular indicators of the influence of heavy metals on human health are discerned as a plausible notification for the inhabitants that they live in a highly harmful and polluted environment inducing health consequences.

Keywords: *heavy metals, hazard index, chronic daily intake, non-carcinogenic risk, carcinogenic risk*

Introduction. Pollution of soil with heavy metals has become a general peculiar concern. As long as these elements can be carried in the hydrosphere and biosphere, they present a risk to human health [1].

The economy of Mitrovica was heftily impacted by “Trepça” combine as a conglomerate enterprise that included extraction, flotation, smelting, and processing of Pb and Zn ores. The waste created by the flotation process was deposited in Zharkov Potok, whereas those from the smelter in Zvecan were on the Gornje Polje [2]. From the industrial waste created by the electrolysis of zinc, the chemical industry, and the battery industry, the industrial landfill, also known as the landfill of the Industrial Park in Mitrovica (PIM), the industrial landfills created while working in Trepça are a vast concern for the environment [3]. The utmost expand in the presence of heavy metals in soils in the world is a consequence of the development of industries, the use of chemicals, and the disposal of municipal waste. This pollution directly or indirectly affects human health through ingestion, skin contact, or inhalation [4].

Long exposure to Pb can cause developmental disorders and damage of the skeletal, circulatory, nervous, endocrine, and immune systems in humans [5]. Exposure to As can result in cardiovascular, neurological, diabetes, hearing loss, dermatological, and multiple cancers [6]. Zn has become an essential element of clinical and public health concern in the new millennium [7]. Zn is considered a multi-purpose micronutrient due to its ability to bind to more than 300 enzymes and more than 2000 transcription factors [8]; however, with the intake of extremely high doses of zinc, symptoms of toxicity (vomiting, epigastric pain, lethargy, and fatigue) appear [9]. Cu in excess amounts causes anemia, liver toxicity, skin cancer, dermal lesions, vascular diseases, and severe neurological defects [10]. The adverse consequences of exposure to Ni can cause numerous side effects on human health, such as allergies, cardiovascular, kidney, lung fibrosis, and lung and nasal cancer [11]. Exposure or excessive Mn intake leads to manganese and hepatic encephalopathy [12]. Cr affects human health depending on its oxidation state. Cr(III) plays a crucial role in human metabolism, while Cr(IV) is mutagenic and is toxic to humans, damaging the cardiovascular and liver systems [13].

Exposure to cadmium can be associated with breast, lung, prostate, nasopharynx, pancreas, and kidney cancer [14]. In order to evaluate the impact of industrial landfills on soil pollution and human health, the heavy metal index and human health risk assessment were calculated.

Materials and methods. In the region of Mitrovica, two industrial landfills contain heavy metals, that of G. Polje,

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42°54′20.62″ N, 20°51′35,17″ E and that of Z. Potok, 42°54′22.93″ N, 20°52′24,92″ E), while the third landfill of PIM is in the city, 42°52′57,59″ E, 20°52′38,95″ E. The impact of these landfills on the pollution of the city and the environment is indisputable; in this context this paper presents research on heavy metals and the impact of these metals on the health of the residents of the "2 July" neighborhood. It is characteristic that this neighborhood is subject to dust pollution from the three industrial dumps. Fig. 1 shows the dust plumes raised in the PIM.

The distance between the PIM landfill and the "2 July" neighborhood is 556.25 m. Whereas the distance between the "2 July" neighborhood and the G. Polje landfill is 2254.63 m, while from that of Z. Potok it is 1822.25 m. It is worth noting that the height above the sea level of the landfill in Z. Potok is 580.64 m, while the height above the sea level of the neighborhood is 504.89 m. The research samples were taken spontaneously at a depth of 0–0.2 m.

After the preparation of the samples using the ICP-OES (inductively coupled plasma optical emission spectrometry), the metals that are of research interest are defined.

Heavy metals indices. Geo-accumulation index, According to Miller, it is used to estimate the level of pollution with heavy metals in aquatic sediments [15]. The formula for the geo-index is as the following

$$I_{geo} = \log_2 \frac{C_n}{1.5 \cdot B_n},$$

where C_n is the measured concentration of the element; B_n is the geochemical background value of the element; 1.5 is correction factor for the variables given in the reference point caused by lithological changes.

Enrichment factor (EF). It is an indicator that is used to assess the level of anthropogenic pollutants [16], computed with the equation

$$EF = \frac{\left(C_x / C_{ref}\right)_{sample}}{\left(C_x / C_{ref}\right)_{background}},$$

where C_x is the concentration of contamination elements; C_{ref} is the concentration of reference elements. Manganese is taken as a reference element.

Human health risk assessment. This is a manner to assess human health risks, respectively, the harmful health effects in people exposed to heavy metals. Human exposure to heavy metals in soil can be categorized into three major routes: (*a*) oral ingestion, (*b*) dermal absorption, and (*c*) inhalation [17].

Chronic daily intake (CDI) from the three routes of exposure to heavy carcinogenic metals is calculated with the following equations [18]: the values used in these equations are listed in Table 1.

$$CDI_{ing} = \frac{C \cdot IR_{ing} \cdot D \cdot EF}{BW \cdot AT} CF;$$

$$CDI_{inh} = \frac{CxIR_{inh} \cdot ED \cdot EF}{PEF \cdot BW \cdot AT};$$

$$CDI_{der} = \frac{C \cdot SA \cdot SAF \cdot DAF \cdot EF \cdot ED}{BW \cdot AT} CF,$$

where CDI_{ing}, CDI_{der}, CDI_{inh}(mg/kg/d), are obtained by ingestion, skin contact, and inhalation; C is the concentration of heavy metals in the soil, manifested in Table 1.

Fig. 1. Dust plumes from the landfill in PIM

Table 1

Definition and reference value of some parameters for health risk assessment of heavy metal in urban soils

Factor Definition	Adult	Children	Ref.
Ingestion rate of soil (IR$_{ing}$), mg/day	100	200	19.23
Exposure duration (ED), years	24	6	19.23
Exposure frequency (EF), days/year	350	350	18.19
Conversion factor (CF), kg/mg	$1 \cdot 10^{-6}$	$1 \cdot 10^{-6}$	19.23
Body weight of the exposed individual (BW), kg	70	15	19
Exposed skin surface area (SA), cm^2	5700	2800	18
Skin adherence factor (SAF), mg/cm^2	0.7	0.2	23
Dermal absorption factor (DAF)	0.001	0.001	18.23
Inhalation rate of soil (IR$_{inh}$), m^3/day	20	7.63	19.23
Particle emission factor (PEF), m^3/kg	$1.36 \cdot 10^9$	$1.36 \cdot 10^9$	19.23
Average time (AT)			
For carcinogens, days	365·70	365·70	19.20
For non-carcinogens, days	365·ED	365·ED	19.20

Non-carcinogenic risk assessment. The non-carcinogenic hazard quotient (HQ_{nc}) represents the ratio between the *CDI* and the reference dose (RfD) according to equation (1).

The RfD represents the estimate of a daily dose of a substance without harmful effects from lifetime exposure [20]. The RfDs for the various metals are given in Table 2 as well as the slope factors (SF).

The hazard index (*HI*) is another coefficient used to estimate non-carcinogenic risk [21]; it represents the sum of the hazard coefficients (*HQ*). The relevant coefficients are calculated according to equations [22]

$$HQ = \frac{CDI_i}{RfD_i}; \tag{1}$$

$$HI = \sum HQ = HQ_{ing} + HQ_{inh} + HQ_{derm},$$

where $HI \leq 1$, it is estimated that there are no non-carcinogenic risks. On the other hand, when $HI > 1$, non-carcinogenic risks can be presented, so there is a possibility that with an increasing *HI* value the non-carcinogenic effect increases [22].

Carcinogenic risk assessment is seen as the probability attributed to people exposed to carcinogenic risks of developing cancer [23], and is calculated by the equation

$$CR = CDI \cdot CSF.$$

Values for SF for certain metals are given in Table 2. The total lifetime cancer risk for certain metals is calculated according to the equation. The total lifetime cancer risk (TCR) for certain metals is calculated with equation [24]

$$TCR = \sum CR = CR_{ing} + CR_{inh} + CR_{derm}.$$

Risks with values $< 1 \cdot 10^{-6}$ are considered negligible. While risks $>1 \cdot 10^{-4}$ are seen as acceptable and likely to be harmful to humans [25].

Results and Discussion. *Concentrations of Heavy Metals in Soil.* The values of the concentration of heavy metals obtained from the soil analyses in the neighborhood "2 July" are presented in Table 3, while in Fig. 2, the dependence of the concentration of metals from the analyzed samples is stated, comparing simultaneously with the allowed values.

The values of heavy metal concentrations in soil have been compared with the allowed values according to FAO/WHO [25]. In the comparison of the obtained values to the reference ones, the average values obtained are exceeded compared to the allowed values, except for Cu.

The permitted value for Pb is 100 mg/kg, while the average obtained is 1303.63 mg/kg, which is 13.06 times higher.

Table 2

Reference doses for non-carcinogenic heavy metals and slope factors for carcinogenic metals

Heavy metals (mg/kg)	RfD			SF			Reference
	Ingestion	Inhalation	Dermal	Ingestion	Inhalation	Dermal	
Pb	3.5E–03	3.52E–03	5.24E–04	8.50E–03	–	0.042	19.24
As	3.00E–04	1.23E–04	1.23E–04	1.50E+00	4.30E–03	3.66E+00	22
Zn	3.00E–01	0.30	6.00E–02	–	–	–	19.22
Cu	4.00E–02	4.00E–02	1.20E–02	–	–	–	19.23
Ni	2.00E–02	2.06E–02	5.40E–03	1.70E+00	0.84	4.25E+01	18.19
Mn	4.60–02	1.43E–05	1.84E–03	–	–	–	25
Cr	3.00E–03	2.86E–05	3.00E–03	5.01E–01	4.20E+01	2.00E01	19.23
Cd	1.00E–03	1.00E–03	1.00E–05	–	6.30E+00	–	25

Table 3

Concentration of heavy metals in soil, mg/kg

Sample	Pb	As	Zn	Cu	Ni	Mn	Cr	Cd	Average
S1	3074.37	145.88	7472.50	170.55	144.86	8814.10	238.88	44.22	2513.17
S2	1103.28	255.63	871.07	102.68	114.12	1564.40	212.89	19.13	530.40
S3	81.27	27.97	183.97	31.84	113.45	973.96	331.38	7.34	218.89
S4	385.00	138.00	779.00	48.00	106.00	1974.00	248.00	8.49	460.81
S5	159.50	17.29	223.00	44.67	122.40	1132.80	181.77	7.71	236.14
S6	6457.35	320.40	6487.38	250.30	116.07	4404.23	168.85	55.08	2282.37
S7	250.07	29.15	568.49	52.02	121.78	974.72	278.12	16.34	286.34
S8	1102.93	190.90	2431.92	110.10	110.81	3094.49	203.12	26.14	908.80
S9	199.35	11.61	255.34	36.58	78.02	823.30	168.76	8.06	197.63
S10	253.18	38.57	265.36	36.91	113.73	1205.83	306.90	8.63	278.64
Average	1306.63	117.54	1953.80	88.36	114.12	2496.18	233.87	20.11	–
FAO/WHO*	100	20	300	100	50	2000	100	3	–

Fig. 2. Concentration according to sampling sites:
Y-axys – concentration, mg · kg^{-1}; X-axys – sampling sites

The lowest concentration of Pb is in sampling site 4 (S4), 385 mg/kg, while the highest is in sampling site six (S6) 6457.35 mg/kg, so the concentration range is 385–6457.35 mg/kg. The average concentration of As is 117.54 mg/kg, which is 5.87 times higher than the allowed value of 20 mg/kg, so the range of concentrations is 11.61–320 mg/kg, sample S9 respectively S6. The average concentration of Zn is 1959.8 mg/kg, which exceeds the allowed value of 300 mg/kg – 6.513 times. The interval of zinc concentration in the researched samples is 223–7472.5 mg/kg, sample S5 respectively, and sample S1. The average concentration of Cu, 88.32 mg/kg is lower than the allowed value of 100 mg/kg. The range of Cu concentrations in the analyzed samples is 31.84–250.30 mg/kg, sample S3 and sample S6. The average concentration of Ni is 114.12 mg/kg, which is 2.28 times higher than the allowed value, 50 mg/kg. The Ni concentration interval in the analyzed samples is 78.02–144.86 mg/kg, samples S9 and S1.

The average concentration of Mn is 2496.18 mg/kg, which is 1.248 times higher than the allowed value of 2000 mg/kg.

The concentration interval of Mn is 168.76–331.38 mg/kg, samples S9, respectively S6. The average concentration of Cr is quite high, 233.86 mg/kg, 2.33 times higher than the allowed value, 100 mg/kg. According to the obtained results from analyzing the soil samples, the concentration of Cr is 168.76–331.38 mg/kg, sample S9, respectively S3. The average concentration of Cd turns out to be very high, 20.11 mg/kg or 6.7 times higher than the allowed value of 3 mg/kg. The Cd concentration interval in the analyzed samples is 7.34–55.08 mg/kg, sample S3, respectively S6.

The order of concentration of the metals in the soil is Mn > > Zn > Pb > Cr > As > Ni > Cu > Cd.

According to the sampling sites, the heavy metal pollution of the soil is in the order of S1 > S6 > S8 > S2 > S4 > S7 > S10 > > S5 > S3 > S9.

The values obtained from the calculations for geo-accumulation in the neighborhood “2 July” Table 4, while Fig. 3 shows the extent of the “2 July” neighborhood and industrial landfills. Fig. 4 gives the graphical presentation of I_{geo} depending on the samples. Table 5 gives Geo-accumulation index (I_{geo}) classification of samples according to classes expressed in percentage.

Geo-accumulation in all sampling sites was greater than one. The values were in the range 1.43(S3)–7.750(S6) with an average of 4.421 belonging to class 5. According to the classification expressed in percentage, it is 40, 30, 20 and 10 % of the samples in classes 2, 3, 4 and 6. Two values of I_{geo} for As are less than zero, the others are higher, in the range 0.52(S3)–4.04(S6), with an average of 1.793 belonging to class 2. According to the classification (Table 6), 10, 20, 20, 30 and 20 % of the samples were in classes zero, one, three, four, and five. I_{geo} for Zn in none of the soil samples is less than zero. I_{geo} values for Zn are 0.36(S3)–6.05(S1) with an average of 2.574 belonging to class three. According to the classification of samples (I_{geo}) (Table 6) 20, 10, 30 and 40 % belong to classes one, three, five, and six. In ten soil samples analyzed, I_{geo} for Cu is less than zero. The interval of values is –1.08(S3)–1.89(S6), the mean 0.025 belonging to class one. Classification of the samples (I_{geo}), 20, 20 and 60 % belong to classes zero, one, and two, respectively. I_{geo} values for Ni range from –0.38(S9) to –0.51(S1). The average value of I_{geo} is 0.1452, which belongs to category one. According to the classification of samples for I_{geo} (Table 5), the categorization according to classes is 90 % of the samples belong to class two while 10 % of the samples belong to class one. I_{geo} values for Mn are –1.70(S5) and –2.79(S1). In this range of values, five of them are less than zero. The average value is 0.3595 belongs to category one. According to Table 5, I_{geo} categorization is 10, 20, 20 and 50 % of the samples belonging to classes zero, one, two, and three, respectively.

Table 4

Results for Geo-accumulation index

Sample	Pb	As	Zn	Cu	Ni	Mn	Cr	Cd	Average
S1	6.68	2.90	6.05	1.33	0.51	2.79	0.82	6.62	3.46
S2	5.20	3.71	2.61	0.60	0.16	0.29	0.65	5.42	2.33
S3	1.43	0.52	0.36	-1.08	0.15	-0.39	1.29	4.20	0.81
S4	3.68	2.82	2.45	-0.49	0.05	0.63	0.87	4.23	1.78
S5	2.41	-0.17	0.64	-0.59	0.26	-1.70	0.43	4.09	0.67
S6	7.75	4.04	5.71	1.89	0.18	1.78	0.32	6.93	3.57
S7	3.06	0.58	2.10	-0.37	0.25	-0.38	1.04	5.18	1.43
S8	5.20	3.29	4.09	0.71	0.12	1.28	0.59	5.88	2.65
S9	2.73	-0.74	0.84	-0.88	-0.38	-0.63	0.32	4.17	0.68
S10	3.07	0.98	0.89	-0.87	0.15	-0.08	1.18	4.26	1.20
Average	4.12	1.79	2.57	0.03	0.15	0.36	0.75	5.09	–

Table 5

Geo-accumulation index (I_{geo}) classification of samples

Metals	I_{geo}, %						
	Class 0	Class 1	Class 2	Class 3	Class 4	Class 5	Class 6
	$I_{geo} < 0$	$0 < I_{geo} < 1$	$1 < I_{geo} < 2$	$2 < I_{geo} < 3$	$3 < I_{geo} < 4$	$4 < I_{geo} < 5$	$I_{geo} > 5$
Pb	–	–	10	20	30	–	40
As	20	30	–	20	20	10	–
Zn	–	40	–	30	–	10	20
Cu	60	20	20	–	–	–	–
Ni	10	90	–	–	–	–	–
Mn	50	20	20	10	–	–	–
Cr	–	70	30	–	–	–	–
Cd	–	–	–	–	–	50	50

Fig. 3. The extent of the neighborhood "2 July" and industrial landfills

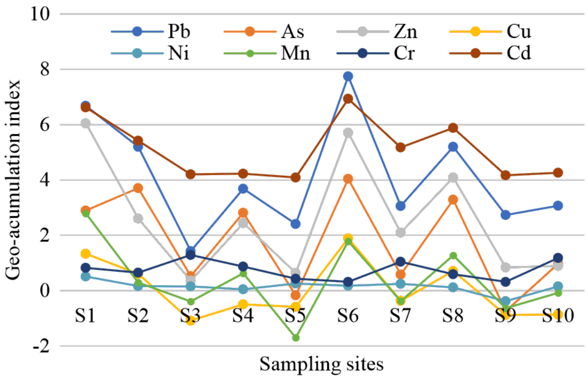

Fig. 4. Geo-accumulation Index of heavy metal in soil

The I_{geo} average for Cr is 0.7514, which belongs to toxicity class one. The interval of values is 0.32(S6, S9)–1.29(S3). According to the classification of the samples for *Igeo* values (Table 5), it turns out that 70 % belong to class one, while 30 % belong to class two.

The average value of I_{geo} for Cd is 5.098, which represents high toxicity, class 6. The interval of I_{geo} values for Cd is 4.09(S5)–6.93(S6). 50 % of the samples belong to class five, and 50 % belong to class 6. According to the sampling sites, the contamination with heavy metals in the soil is in the order of S6 > S1 > S8 > S2 > S4 > S7 > S10 > S3 > S9 > S5.

Enrichment factor (EF). The values for the enrichment factor are shown in Table 6, while the graphic presentation is in Fig. 5. The EFs for Pb are from 2.65(S6), which indicates minor enrichment to 30.01(S2), which belongs to the very severe enrichment category. In sample S3, the EF value is 3.54, which belongs to the moderate enrichment category. EF values for Pb in samples S4(8.29), and S5(5.99), belong to the moderately severe enrichment category. Samples S1(14.83), S7(10.89), S8 (15.15) and S9(10.30) belong to the severe enrichment category.

The EF for As in samples, S5(0.99) and S9(0.92) are categorized as no enrichment. EF in samples S1(1.08), S3(1.87), S7(1.95) and S10(2.09) belong to the minor enrichment category. For samples S4(4.56), S6(4.75) and S8(4.03), the EF belongs to the moderate enrichment category. While sample S2(10.72) belongs to the severe enrichment category. The EF for Zn in samples S3(1.69), S5(1.76), S9(2.77) and S10(1.96) belongs to the minor enrichment category. Samples S2(4.98) and S4(3.53) are the moderate enrichment category. In the samples S1(7.58), S7(5.21) and S8(7.03) the moderately severe enrichment category, while the sample S6(13.18) belongs to the severe enrichment category. The EF numerical values for copper are petite. The EF values in samples S1(0.36), S3(0.61), S4(0.46), S5(0.74), S8(0.67), S9(0.84) and S10(0.57) are lower than 1, belonging to no enrichment category. The EF values in samples S2(1.24), S6(1.07) and S7(1.01) are lower than value 3 belonging to the category of minor enrichment. The EF values for Ni are found to be low, indicating little influence on soil contamination.

Table 6

Results for Enrichment factor in soil

Sample	Pb	As	Zn	Cu	Ni	Cr	Cd	Average
S1	14.83	1.08	7.58	0.36	0.20	0.25	14.19	5.50
S2	30.01	10.72	4.98	1.24	0.91	1.28	34.62	11.96
S3	3.54	1.87	1.69	0.61	1.45	3.21	21.33	4.81
S4	8.29	4.56	3.53	0.46	0.67	1.18	34.44	7.59
S5	5.99	0.99	1.76	0.74	1.32	1.51	19.26	4.51
S6	2.65	4.75	13.18	1.07	0.32	0.36	35.42	8.25
S7	10.89	1.95	5.21	1.01	1.56	2.69	47.49	10.11
S8	15.15	4.03	7.03	0.67	0.44	0.61	23.93	7.41
S9	10.30	0.92	2.77	0.84	1.18	1.93	27.71	6.52
S10	8.92	2.09	1.96	0.57	1.17	2.40	20.26	5.34
Average	11.06	3.30	4.97	0.576	0.92	1.54	27.86	–

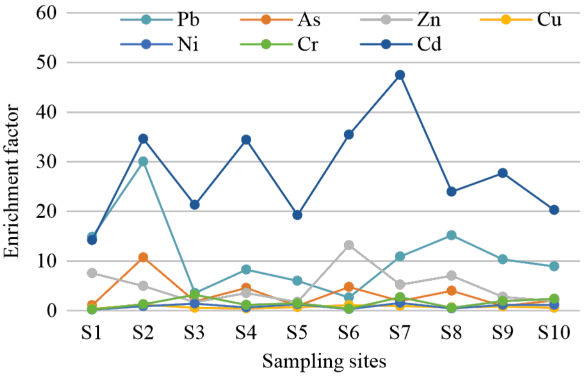

Fig. 5. Enrichment factor in soil

Samples S1(0.2), S2(0.91), S4(0.67), S6(0.32), S8(0.44) belong to the no enrichment category. The impact of Ni according to the values obtained for samples S3(1.45), S5(1.32), S7(1.56), S9(1.18) and S10(1.17) is slightly greater and belongs to the category of minor enrichment. Furthermore, the impact of Cr based on the obtained EF values is not significant. Based on the EF values for the samples S1(0.25), S6(0.36) and S8(0.61), their influence belongs to the no enrichment category. Samples S2(1.28), S4(1.18), S5(1.51), S7(2.69), S9(1.93) and S10(2.40) belong to the minor enrichment contamination category, whereas S3(3.21) belongs to the moderate category enrichment.

Based on EF values, Cd indicates a high degree of contamination. Samples S1(14.19), S3(21.33), S5(19.26) and S8(23.93) belong to the severe enrichment category, while samples S2(34.62), S4(34.44), S6(35.42), S7(47.49), S9(27.71) and S10(20.26) belong to the very severe enrichment category. If the average value of EF is taken according to the samples for metals, it is this ranking, Cd > Pb > Zn > As > Cr > Ni > Cu. If the mean value of the EF according to samples taken, the ranking is S2 > S7 > S6 > S4 > S8 > S9 > S1 > S10 > S3 > S5.

Non-carcinogenic health risk. The CDI_{ing}, CDI_{inh} values for all the investigated metals have higher values for children than for adults. The values obtained for CDI_{derm} for adults are higher than for children except for Zn, Table 7. HQ_{ing} values for Pb (4.2E+0) and As (5.0E+0) are higher than 1, suggesting harmful effects for children. For other metals, the values are lower than 1, suggesting that they do not pose a risk to children's health.

Even the values for HQ_{inh} and HQ_{derm} are less than 1. HQ_{ing}, HQ_{inh}, and HQ_{dem} for adults for non-carcinogenic health risks have values less than 1, which suggests that they do not present risk to the health of adults. However, if these values are compared with those for children in Table 7, it can be indicated that the HQ_{ing} for children is higher for all metals except Mn. Also,

Table 7

CDI, HQ and *HI* value of each metal for non-carcinogenic risk

	CDI_{ing}	CDI_{inh}	CDI_{derm}	HQ_{ing}	HQ_{inh}	HQ_{derm}	HI
Children							
Pb	1.47E–2	4.124E–7	4.677E–5	4.2E+0	1.171E–4	7.885E–2	4.2789E+00
As	1.5E–03	4.198E–8	4.207E–6	5.0E+0	1.193–4	3.420E–2	5.03E+00
Zn	2.49E–2	6.979E–7	6.994E–5	8.3E–2	2.326E–6	1.165E–3	8.42E–02
Cu	1.13E–03	3.156E–8	3.163E–6	2.825E–2	7.89E–7	2.635E–4	2.85E–02
Ni	1.46E–03	4.076E–8	4.085E–6	7.30E–2	1.978E–6	7.564E–4	7.38E–02
Mn	3.191E–2	8.917E–7	8.936E–5	6.50E–2	6.235E–2	4.856E–2	1.76E–01
Cr	2.99E–03	8.354E–8	8.372E–6	9.966E–1	2.921E–3	2.790E–3	1.00E+00
Cd	2.56E–04	7.184E–9	7.20E–7	2.56E–1	7.184E–6	7.199E–2	3.28E–01
Average	9.850E–3	2.7625E–7	2.7625E–5	1.3375E+0	8.175E–3	2.9875E–2	1.3749E+0
Adult							
Pb	1.789E–3	2.632E–7	7.141E–5	4.517E–1	6.649E–5	1.204E–1	5.720E–1
As	1.610E–4	2.367E–8	6.424E–6	5.366E–1	1.924E–4	5.222E–2	5.89E–01
Zn	2.676E–3	3.936E–7	1.067E–4	8.92E–3	1.312E–6	1.778E–3	1.07E–02
Cu	1.210E–4	1.780E–8	4.829E–6	3.025E–3	4.45E–7	4.024E–4	3.43E–03
Ni	1.563E–4	2.298E–8	6.237E–6	7.815E–3	1.115E–6	1.155E–3	8.97E–03
Mn	3.419E–3	5.028E–7	1.364E–4	7.432E–2	3.516E–2	7.413E–2	1.84E–01
Cr	3.203E–4	4.711E–8	1.278E–5	1.067E–1	1.647E–3	4.26E–3	1.13E–01
Cd	2.754E–5	4.051E–9	1.099E–6	2.754E–2	4.051E–6	1.099E–1	1.37E–01
Average	1.0575E–3	1.55E–7	4.225E–5	1.525E–1	4.6375E–3	4.55E–2	2.025e–1

the HQ_{inh} values for children are higher than those for adults for all metals except As. However, HQ_{derm} values for adults except for Cr are higher than HQ_{derm} values for children indicating that dermal contact scales for adults are more pronounced.

The values for the *HI* for non-carcinogenic health risks for children are given in Table 7, respectively Fig. 6, which reflects the change in values for Pb (4.2789E+0) and As (5.02E+0), for Cr (1.00E+0) and other metals and the allowed value. The value of Pb and As exceeds the threshold value. Thus, the HI values of these elements suggest harmful health effects on children. Cr is at the limit value. The numerical values of HI for other elements are less than 1. The values of other metals are from 3.28E–1 for Cd to 8.242E–2 for Zn.

The *HI* values for adults for non-carcinogenic health risks, which are given in Table 7, reflected in Fig. 7, are below limit value 1, and do not pose a significant health risk. However, comparing the values of the metals among themselves, we can see that As and Pb have higher values, 5.89E–01 and 5.720E–1 respectively. The smallest value is for Cu, 3.43E–3.

Carcinogenic health risk. According to the USEPA, risk values for CR and TCR, which are less than 1.0E–06, are insignificant; the values greater than 1.0E–04 can be dire for human health [22, 24]. The acquired results are demonstrated in Table 8.

From the numerical values shown in Table 8 can be seen that CR_{ing} for metals Pb (1.249E–4), As (2.25E–3), Ni (2.482E–3) and Cr (1.495E–3) for children are higher than the allowed values 10E–6 to 10E–4. If the values for CR_{ing} for children are compared with the values obtained for Pb (1.520E–5), As (2.415E–4), Ni (2.657E–4), Cr (1.604E–4) for adults, it turns out that the values CR_{ings} for children are higher, although the values for adults also exceed the limit values. Thus, the metals Pb, As, Ni, and Cr pose greater carcinogenic risks. The CR_{inh} values for As (1.805E–10), Ni (3.423E–8) and Cd (4.525E–8) for children are lower than the limit values (10E–6), except for Cr (3.508E–6), which has a higher value than the limit value. Even the CR_{inh} values for adults for As (1.017E–10), Ni (1.930E–8) and Cd (2.552E–8) are lower than the permitted values but even lower than the values obtained for children. The CR_{ing} value of Cr (1.978E–6) for adults as well as for children exceeds the limit value (10E-6-A10E-4).

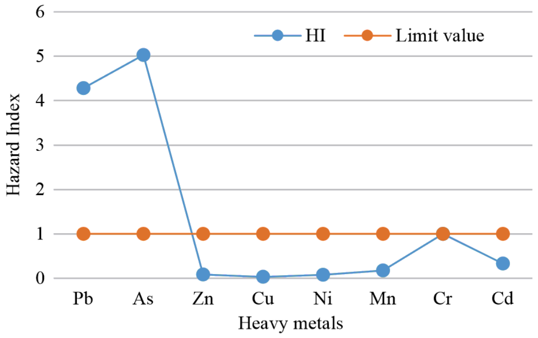

Fig. 6. Dependence of the Hazard Index of heavy metals for the non-carcinogenic risk for children

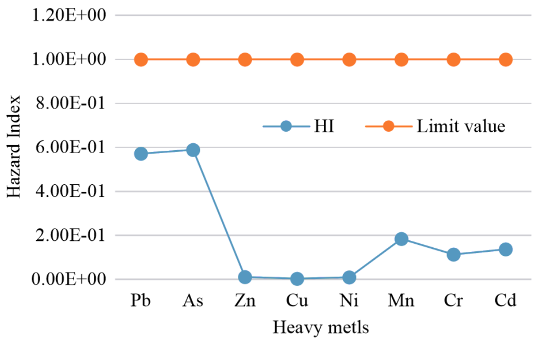

Fig. 7. Dependence of the Hazard Index of heavy metals for the non-carcinogenic risk for adults

Table 8

CR and *TCD* for Carcinogenic risk for children and adults

Carcinogenic								
	Children				Adult			
Metal	CR_{ing}	CR_{inh}	CR_{dem}	*TCR*	CR_{ing}	CR_{inh}	CR_{dem}	*TCR*
Pb	1.249E–4	–	1.964E–6	1.268E–04	1.520E–5	–	2.999E–6	1.8199E–5
As	2.25E–3	1.805E–10	1.539E–5	2.27E–03	2.415E–4	1.017E–10	2.351E–5	2.650E–4
Ni	2.482E–3	3.423E–8	1.736E–4	2.66E–03	2.657E–4	1.930E–8	2.650E–4	5.307E–4
Cr	1.495E–3	3.508E–6	1.674E–4	1.67E–03	1.604E–4	1.978E–6	2.556E–4	4.180E–4
Cd	–	4.525E–8	–	4.525E–8	–	2.552E–8	–	2.552E–8
Average	1.5875e–3	8.975e–7	8.95e–5	1.346e–3	1.7075e–4	6.375e–7	1.3675e–4	2.46e–4

For children and adults, CR_{inh} values are higher than the permissible values, 3.508E–6 for children and 1.978E–6 for adults. In contrast to CR_{ing} and CR_{inh} values that were higher for children, CR_{derm} values for adults were found to be higher. Both for children and adults, the limit values are surpassed, this indicates that exposure in contact with the skin represents a carcinogenic health risk.

The CD_{derm} value of Pb for adults is 2.999E–6, while for children it is 1.964E–6. For As, the value is 2.351E–5, 539E–5 for children. The CR_{derm} for adults for Ni is 2.650E–4, while for children 1.736E–4. The CR_{derm} value of Cr for adults is 2.556E–4 and 1.674E–4 for children. Children's TCR for metals, Table 8 in graphic form Fig. 8, show that Pb (1.268E–04), As (2.27E–03), Ni (2.66E–03) and Cr (1.604E–3) exceed the limit values except for Cd (4.525).

The limit values of TCR are exceeded even for adults, Table 8 displays in Fig. 9, Ni, 5.307E–4, Cr, 4.180E–4, As, 2.650E–4, Pb, 1.8199E–5 except for Cd, 2.552E–8, but they are lower than for children.

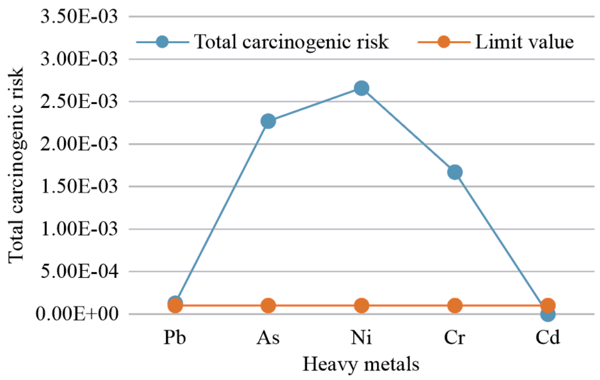

Fig. 8. Dependence of the total carcinogenic risk of heavy metals for children

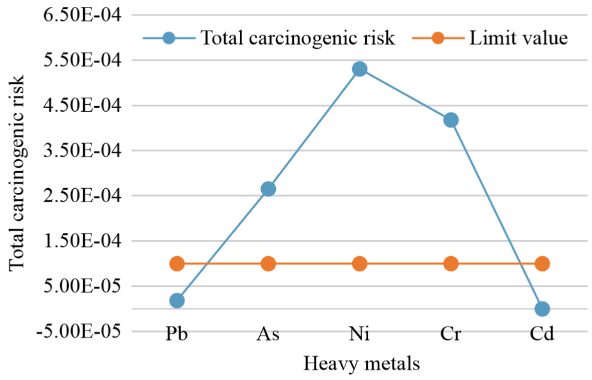

Fig. 9. Dependence of the total carcinogenic risk of metals for adults

Based on the *TCR* values for both children and adults, Pb, As, Ni, and Cr present a carcinogenic health risk. The exception was Cd, which does not present a carcinogenic health risk in both children and adults during exposure.

Conclusions. The results showed that the average concentrations of heavy metals excluding Cu are many times higher than the values allowed by FAO/WHO. The concentration of heavy metals in the soil is in the order of Mn > Zn > Pb > C > > As > Ni > Cu > Cd. Even the average results of Igeo showed that Pb belongs to the strongly to extremely contaminated pollution category, while Cd belongs to the extremely contaminated category. Zn belongs to the moderately to strongly contaminated category,

As to the moderately contaminated category, while metals, Cu, Ni, Mn, and Cr belong to the uncontaminated category. The subsequently analyzed parameter, the Enrichment factor, and from the average results of this factor for the investigated metals, it follows that Cd pollution belongs to the category of very severe enrichment pollution. Pb in the severe enrichment category, As and Zn in the moderate enrichment category, Cr in the minor enrichment category and Cu and Ni in the no enrichment category.

For children and adults, the ingestion route presents the greatest non-cancer risk followed by the dermal route. The inhalation route posed the least non-carcinogenic risk. For the carcinogenic effect, the route of ingestion for children and adults was more pronounced than the route of skin. The results indicate that the inhalation route did not pose a carcinogenic risk. Quantitative data show the need to protect the environment from heavy metals, especially for the inhabitants with special emphasis on children.

As the results show the high degree of risk for the health of the residents, the research will be expanded and based on the results obtained, the alarm will be raised that their health is subject to the risk of cancer. Then the results will be a good basis for other research such as the presence of heavy metals in the blood as well as the measures that should be taken for the rehabilitation of the area.

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Оцінка ризику через вплив важких металів на здоров’я людини в районі «Ім. 2 липня» та навколо нього (Косовська-Митровице, Косово)

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Мета. Визначення рівня забруднення ґрунту важкими металами в районі «Ім. 2 липня», а також дослідження впливу забруднення на здоров’я мешканців цього району. Мета дослідження полягала у визначенні вікової категорії, найбільш схильної до ризику впливу забруднення, на основі теорії оцінки ризику, оцінки неканцерогенного й канцерогенного ризиків.

Методика. Зразки ґрунту в районі «Ім. 2 липня» були відібрані довільно. Після підготовки зразків методом ICP-OES було визначено вміст свинцю, миш’яку, цинку, міді, нікелю, марганцю, хрому й кадмію. Для розрахунку специфічних показників були застосовані аналітичні формули, дані показники включають індекс геоакумуляції, коефіцієнт збагачення, добове споживання важких металів, індекс небезпеки, оцінку ризику розвитку онкологічних захворювань, загальний ризик розвитку онкологічних захворювань протягом життя. Вони показують рівень забруднення ґрунту й ризик наявності важких металів, небезпечних для здоров’я людини.

Результати. Результати показують, що вміст свинцю, миш’яку, цинку, нікелю, марганцю, хрому й кадмію у ґрунті в районі «Ім. 2 липня», на додаток до міді, перевищує значення, встановлені ФАО/ВООЗ. Значення індексу небезпеки й загального ризику розвитку онкологічних захворювань протягом життя у дітей відповідно до неканцерогенного й канцерогенного ризику високе, тоді як у дорослих воно нижче, що вказує на те, що діти схильні до більшого ризику.

Наукова новизна. Забруднення ґрунту на території району «Ім. 2 липня» відбувається через діяльність трьох промислових звалищ. Це забруднення впливає на здоров’я людини, потрапляючи через дихальні шляхи, шкіру та травний тракт.

Практична значимість. Розглянуті особливі показники впливу важких металів на здоров’я людини, що дозволить обґрунтовано сповістити мешканців про те, що вони живуть у високонебезпечному й забрудненому середовищі, яке викликає негативні наслідки для здоров’я.

Ключові слова: *важкі метали, індекс небезпеки, добове споживання, неканцерогенний ризик, канцерогенний ризик*

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