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Potentially toxic elements from different environmental compartments of the River Watershed in Eastern Serbia – assessment of the human health risk

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Abstract: This study assessed human health risks due to exposure to potentially toxic elements (PTE$_S$) in soil and river water in eastern Serbia. Concentrations of As, Cu, Cd, Zn, Pb, Ni, and Cr were measured in soil and river water from the Vlasina watershed area. The concentrations of Cl^-, SO_4^{2-} and NO_3^- were also measured in the river water. According to the Regulation of the Republic of Serbia, the water quality of the investigated rivers corresponds to the surface water quality Class I and II. The content of PTEs in soil was below soil guideline values. Children were more sensitive than adults when exposed to PTE in water and soil. Arsenic was the dominant contributor to the total non-carcinogenic and carcinogenic risks for exposure to PTE in water. For PTE in soil, As had the dominant contribution to non-carcinogenic risks, and Ni to carcinogenic risks. All hazard index (HI) values for adults and children are less than 1, which indicates that the impact of PTEs in the examined river water and soil on human health is insignificant. Ingestion route is a major contributor to both total non-carcinogenic and carcinogenic risks.

Keywords: health risk; toxic elements; river water; soil; resident; recreator.

INTRODUCTION

Potentially toxic elements (PTEs) are considered to be among the most hazardous contaminants in aquatic ecosystems and soil because of their toxicity, non-biodegradability, and due to the fact that they can be bioaccumulated.[1] PTEs can occur in soil and surface water as a result of natural processes, but their presence in soil and surface water, often in high concentrations, can be a

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consequence of human activities. Rock weathering is the major natural source of PTEs in soil, while for surface water, additionally, erosion of soil is the important natural source of PTEs. Regarding anthropogenic sources of PTEs, mining, industrial and agricultural activities are their main sources. Once in these environmental compartments, PTEs can enter the food chain and, as a result of chronic exposure, they can pose a health risk to humans, even in low concentrations.[2] PTE pollution of soil and surface water has become a significant worldwide problem.[3,4] For that reason, methods for the estimation of threats that PTEs pose to human health have been developed. Health risk assessment indices have been introduced to assess the threatening effects of PTEs on human health.[5] For the assessment of both carcinogenic and non-carcinogenic risks that PTEs in soil and surface water pose to human health, the methodology developed by USEPA is widely used.[6]

In the present study river water and soil samples were taken in the Vlasina River Watershed area and analyzed for PTEs. Additionally, anion concentrations were determined in water samples. The objectives of this research are: (1) to investigate distribution characteristics of PTE in river water and soil, (2) to estimate contamination levels of PTEs by comparison with surface water and soil quality standards, and (3) to assess the impacts of PTEs on human health through ingestion and dermal contact pathways for exposure to water, and, ingestion, dermal contact and inhalation pathways for exposure to soil. Non-carcinogenic and carcinogenic risks associated with human exposure to As, Cu, Cr, Ni and Zn in the river water, and As, Cu, Cr, Ni, Pb, Zn and Cd in soil were estimated in this research. The results obtained in this study could provide valuable information for drinking water source management and the protection of human health.

EXPERIMENTAL

Collection of river water and soil samples

Water samples (17) of the river Vlasina, important components in its watershed (Gradska River, Tegošnička River, Ljuberađa, Pusta River, Bistrička River, Rastavnica) and Zelenička River were collected in August 2018. Soil samples (15) were taken near the river water sampling locations. Details regarding the study area and sampling can be found in the Supplementary material.

Chemical analysis

For soil samples, the optimized BCR (Community Bureau of Reference) three-step sequential extraction procedure[7-9] was applied and subsequently, the residue was digested with aqua-regia. In this manuscript, the total extractable element content of the applied four-step sequential extraction procedure was taken into account.[10,11] Analytical techniques of Inductively Coupled Plasma-Optical Emission spectrometry (Thermo Scientific ICP-OES iCap 6500 Duo) and Inductively Coupled Plasma-Mass spectrometry (Thermo Scientific ICP-MS iCap Q) were used for the measurement of the element concentrations in water samples and the obtained soil extracts, while ion chromatography technique (Metrohm 761 Compact IC) was applied for the

determination of anions in river water. Further information on analytical measurements can be found in the Supplementary material.

Human health risk assessment

Humans can be exposed to pollutants in soil through ingestion, dermal contact and inhalation, while the main exposure pathways for humans to pollutants in water are ingestion and dermal contact. In this paper, potential health risks for humans due to exposure to PTE in soil and river water were assessed according to US Environmental Protection Agency (USEPA) guideline documents.[6,12-14] Human exposure to PTEs was estimated through the calculation of average daily dose (ADD, followed by the calculation of hazard quotients (HQs) and hazard indices (HIs), as a sum of HQs, for the assessment of non-carcinogenic health risks, while the carcinogenic health risks are assessed by calculating cancer risks (CRs) and their sum - total cancer risks (TCR).

Details regarding the health risk assessment procedure applied in this study are given in the Supplementary material.

RESULTS AND DISCUSSION

Concentrations of the investigated elements and indicators of nutrient content and salinity in river water and comparison with surface water quality standard

The concentrations of investigated elements (Zn, As, Cr, Ni Cu) and anions, representatives of salinity (Cl^-, SO_4^{2-}) and nutrients (NO_3^-), in the investigated rivers locarted in the Vlasina River catchment area, are presented in Fig. 1. The concentration values ranged from: <DL to 6.40 μgL^{-1} for Zn, 0.236 μgL^{-1} to 3.05 μgL^{-1} for As, 0.039 μgL^{-1} to 0.194 μgL^{-1} for Cr, 0.128 μgL^{-1} to 0.486 μgL^{-1} for Ni, <DL to 1.05 μgL^{-1} for Cu, 10.34 mgL^{-1} to 39.92 mgL^{-1} for Cl^-, <DL to 9.66 mgL^{-1} for NO_3^-, and 10.03 mgL^{-1} to 21.00 mgL^{-1} for SO_4^{2-}. The concentrations of Pb, Cd and PO_4^{3-} were below the detection limit in all investigated samples. The values of detection limits are given in the Supplementary material. Higher concentrations of Zn, compared to other water samples of the Vlasina watershed investigated rivers, were found in sample 5 - Tegošnica River (near the village Doroviš, downriver from the stone pit) and sample 15 - Vlasina River (upstream of the intake for water supply). The highest concentrations of As (Fig. 1) were found in Ljuberađa River (samples 7-9), whose upper course is mostly made from karst springs' waters, and in the lower course Ljuberađa River formed a gorge through lower cretaceous carbonate rocks.[15] Our previous paper[16] revealed that As in the rivers of the Vlasina watershed was strongly correlated with Ca and Sr. Higher concentrations of As (up to 17 μgL^{-1}) have already been found in karst springs in Greece where carbonate formations are in contact with metamorphic and metavolcanic formations.[17] For Cr, the highest concentrations were detected in Rastavnica River (sample 14) and Vlasina River, downriver from Vlasotince (sample 16). Among investigated rivers, the highest concentrations of Cu were found in Gradska River (sample 2), also higher concentrations of Cu than in other investigated river water samples, were found in sample 1 -Vlasina River (before receiving Gradska River), sample 2 - Gradska River, sample 5 - Tegošnička River (near the village Doroviš), sample 10

(Vlasina, after receiving Ljuberađa) and sample 16 (Vlasina River, downriver from Vlasotince).

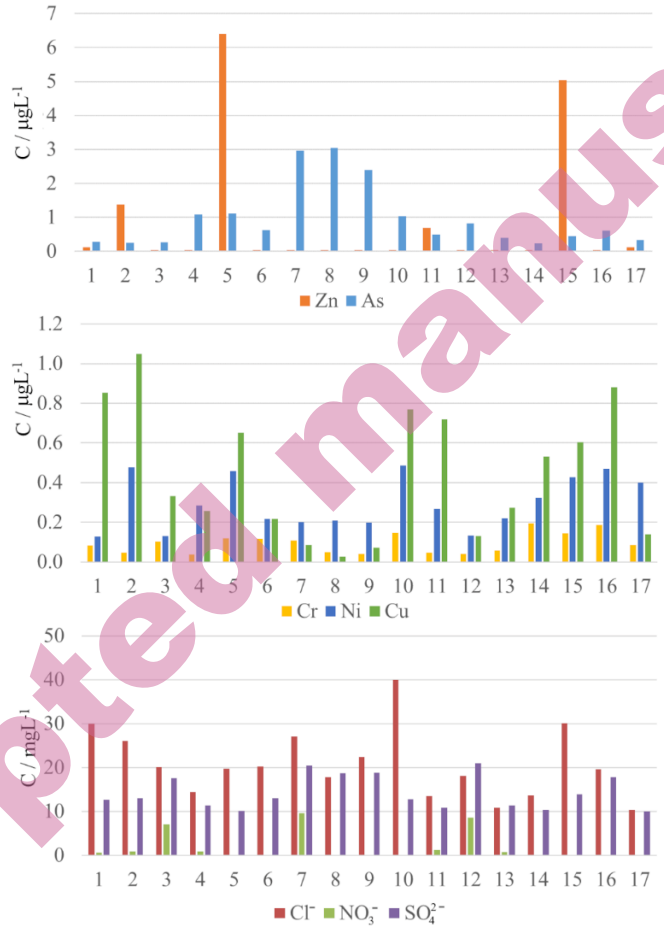

Fig. 1. Concentration of Zn, Cr, Ni, Cu, As, chloride, nitrate and sulphate in river water.

The concentrations of elements, and anions (nutrient content and salinity indicators) in the investigated river water samples (Fig. 1) were compared with the limit values for pollutants in surface waters (TABLE S-V) prescribed by the Regulation on limit values for pollutants in surface and ground waters and sediment and deadlines for their achievement.[18] Excluding the values of nitrate content in river water samples of Ljuberađa - middle course, sample 7 (2.181 mgNL^{-1}), Vlasina - downstream of the confluence with Pusta River, sample 12 (1.953 mgNL^{-1}), Vlasina - upstream of the confluence with Tegošnička River, sample 3 (1.586 mgNL^{-1}), which correspond to the Class II surface water quality, the values of the measured parameters in the rest of the examined river water

samples are in the ranges that are characteristic for surface water quality Class I. Surface waters of Class I and II quality can be used for drinking water supply with prior filtration and disinfection treatment, bathing and recreation, irrigation, industrial use (process and cooling water).

Content of the investigated elements in soil and comparison with soil quality standards

The content of Zn, Ni, Cu, Cr, Pb, Cd, and As in studied soils are shown in Fig. 2 and TABLE I.

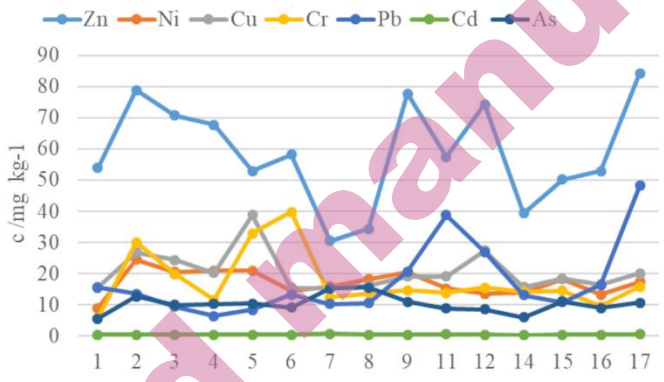

Fig. 2. Content of elements in studied soil.

Based on the results of the comparison of the Cd, Ni, Pb, Cu, and Zn total content with the limits for the element content prescribed by the European Union directive 86/278/EEC[19] and ecological investigation levels (EIL), defined by the Assessment Level for Soil, Sediment, and Water (Government of Western Australia)[20], it can be concluded that the mean values (Mean V, TABLE I), as well as the maximum contents of all studied toxic elements (Max V, TABLE I) are lower than the values which are defined by this legislation.

When comparing the mean content of elements in the soil from Vlasina region with the element content in Šabac[21] and Belgrade soil[22] it is possible to see that all values of the mean content of the studied elements in Vlasina region soils are lower than the average value of element content in other localities. In relation to results for European agricultural soils (EAS)[23], similar values were observed for Ni, Cu, Cr, and Pb, and slightly higher values were observed for Zn, Cd and As.

As a result of comparing our results with the soil content from the Srem locality[24], it is possible to conclude that similar contents were observed for Zn, Pb, Cd, and Zn, lower for Ni and Cr, and slightly higher for As.

TABLE I. Contents of PTEs in the soils in this study, other worldwide soils and quality standards

	Zn	Ni	Cu	Cr	Pb	Cd	As
Mean V[a]	58.9	17.1	20.6	17.6	17.5	0.44	10.2
Max V	84.29	24.50	38.79	39.76	48.17	0.66	15.49
Srem[24]	65.9	51.6	28	49.3	21.6	0.36	6.55
ŠS[21]	n.d.	47.6	37.6	59.8	82.0	1.6	n.a.
EAS[23]	45	15.0	15	20.0	16	0.18	5.5
Belgrade[22]	268	124	122	70.2	350	8.90	n.a.
EU[19]	150-300	30-75	50-140	n.a.	50-300	1-3	n.a.
EIL[20]	200	60.0	100	400	600	3.00	20.0

[a] Vlasina soil (mean and maximum values)

Health risk assessment

Non-carcinogenic risk for exposure to PTE in river water

Hazard index (HI) values for As, Cr, Zn, Ni and Cu from human exposure to river water, and their sum, representing non-carcinogenic health hazards of all PTEs combined from all exposure pathways, for different receptors are shown in Fig 3. The values of HIs for all receptors were in the following descending order: As > Cr > Ni > Cu > Zn. The highest values of hazard indices were calculated for As in Ljuberađa River (samples 7-9) for both residential receptors (0.33-0.42 for children and 0.22 – 0.28 for adults) and recreational receptors (0.0076 -0.0098 for children and 0.0019 – 0.0025 for adults) (Fig. 3).

Average values of hazard quotients (HQs), hazard indices of individual PTE, representing non-carcinogenic health risks of PTE from combined exposure through ingestion of water and dermal contact with water, hazard indices of all PTE combined for each exposure pathway, and total hazard indices (THI) as hazard indices of all PTEs combined from all exposure pathways are presented in TABLES S-VI and S-VII, for residential receptors and recreational receptors, respectively.

Total non-carcinogenic health hazards (THI) for resident receptors (Fig. 3 a and b) were from 0.039 to 0.42 (mean value 0.14, TABLE S-VI) for children, and from 0.025 to 0.28 (mean value 0.091, TABLE S-VI) for adults. The corresponding values of THI for recreational adults and children (Fig. 3 c and d) were from 0.00097 to 0.0098 (mean value 0.033, TABLE S-VII), and from 0.00031 to 0.0025 (mean value 0.0009, TABLE S-VII), respectively. The obtained results indicate that the potential for non-carcinogenic health effects is higher for residential receptors than recreational receptors and that children, compared to adults, are more sensitive to developing non-carcinogenic health effects as a result of exposure to PTE in water, and this is in accordance with findings of other studies.[1,3,25]

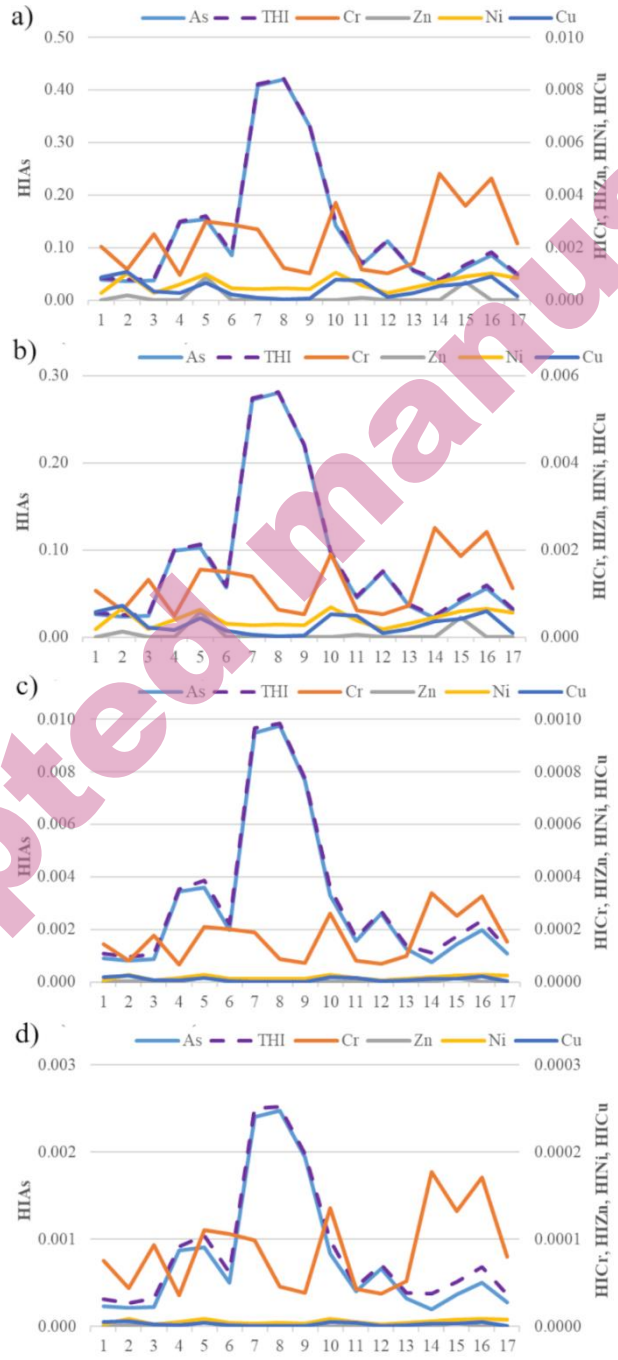

Fig. 3. Non-carcinogenic risks (HI) from exposure to PTE in river water: a – residential children, b – residential adults, c – recreational children, d – recreational adults.

Among investigated rivers, the highest values THI were calculated for Ljuberađa River (samples 7-9), for both residential receptors (0.33-0.42 for children and 0.22 – 0.28 for adults) and recreational receptors (0.0077 -0.0098 for children and 0.0020 – 0.0025 for adults) (Fig.3). Given that hazard index values for both residential and recreational receptors were < 1 (TABLES S-VI and S-VII, Fig.3), detrimental non-carcinogenic effects on human health from PTE in the investigated rivers of the Vlasina watershed, through water ingestion and dermal contact with water, are not expected.

The contributions (%) of individual PTE to the total non-carcinogenic health risk (risks of all potentially toxic elements combined from all exposure pathways, THI) are presented in Fig. 4 (a and b) for residential children and adults, and in Fig. 4 (c and d) for recreational children and adults. Arsenic was the dominant contributor to THI for both residential children (97%) and adults (98%) (TABLE S-VI and Fig. 4 a and b), and recreational children (94%) and adults (87%) (TABLE S-VII and Fig. 4 c and d). A high contribution of As to THI was also observed for exposure to PTE in surface waters in Turkey.[1]

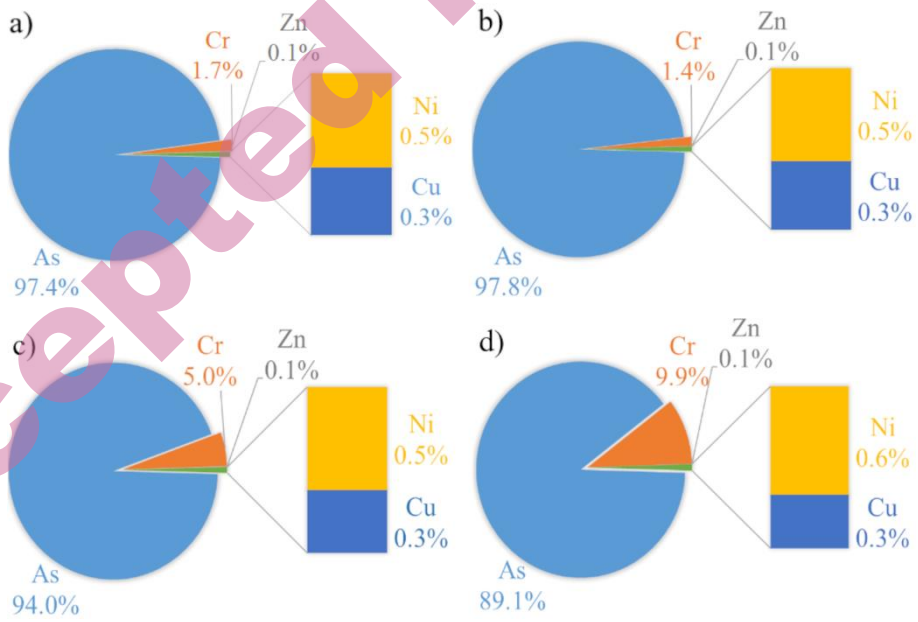

Fig. 4. Contributions of non-carcinogenic risks (HI) of individual PTEs to the total non-carcinogenic risk: a – residential children, b – residential adults, c – recreational children, d – recreational adults.

Average HI values as a result of exposure to all PTE via water ingestion for residential children and adults were 0.13 and 0.090, respectively, and from dermal absorption of PTE in water were 0.0025 and 0.00084 for children and adults,

respectively (TABLE S-VI). For recreational receptors, average non-carcinogenic risks of all PTE combined, through ingestion of river water and dermal contact with river water were 0.0030 and 0.00070 (children and adults), and 0.00032 and 0.00018 (children and adults) (TABLE S-VII). For all receptors, and both exposure pathways, the values of HQs calculated for investigated PTE decreased in the following order: As > Cr > Ni > Cu > Zn.

Obtained results of the assessment of non-carcinogenic risk of all PTE combined from each exposure pathway (TABLES S-VI and S-VII) show that the water ingestion pathway has a dominant contribution to the potential occurrence of non-carcinogenic health effects for all receptors - 98% for residential children, 99% for and residential adults and 79% and 90% for recreational children and adults, respectively. Also, for both exposure pathways, non-carcinogenic risk of all PTE is higher for children than adults, which is in agreement with the results of previous studies.[1,3-5,25] Regarding water ingestion pathway for both residential and recreational receptors, the highest HQ values of all PTE, by far, were for As, which contributed 98% to non-carcinogenic health risks via water ingestion. The largest contribution to non-carcinogenic health risks through dermal contact with water for both residential and recreational receptors was from As (55%) and Cr (43%). For Cr, the dermal contact pathway contributes much more to HI than for other PTE, 45% for residential children, 29% for residential adults, and 83% and 92% for recreational children and adults, respectively. Similar was observed in other studies.[1,3,25]

Carcinogenic risk for exposure to PTE in river water

Potentially toxic elements that have cancer slope factors were used to assess carcinogenic risks, As and Cr. Average values of carcinogenic risks for exposure to PTE in river water through ingestion ($CR_{ingestion}$) and dermal contact (CR_{dermal}) and the total carcinogenic risks (TCR) for residential and recreational receptors are presented in TABLES II and III.

As can be noticed in TABLES II and III, values of TCR of both elements were lower than the target risk (1×10^{-4}) for both residential receptors (6.00E-05 and 4.00E-05 for As, for children and adults, respectively, and 3.54E-06 and 1.84E-06 for Cr, for children and adults, respectively) and recreational receptors (1.39E-06 and 3.53E-07 for As, for children and adults, respectively, and 1.64E-06 and 1.30E-07 for Cr, for children and adults, respectively).

TABLE II. Average values of carcinogenic risks for exposure to PTE in river water through ingestion ($CR_{ingestion}$) and dermal contact (CR_{dermal}) pathways, and total carcinogenic risks (TCR) (residential receptors)

	Child			Adult		
	$CR_{ingestion}$	CR_{dermal}	TCR	$CR_{ingestion}$	CR_{dermal}	TCR
As	5.94E-05	6.12E-07	6.00E-05	3.98E-05	2.07E-07	4.00E-05
Cr	1.94E-06	1.60E-06	3.54E-06	1.30E-06	5.42E-07	1.84E-06
All elements	6.13E-05	2.21E-06	6.35E-05	4.10E-05	7.50E-07	4.18E-05

TABLE III. Average values of carcinogenic risks for exposure to PTE in river water through ingestion ($CR_{ingestion}$) and dermal contact (CR_{dermal}) pathways, and total carcinogenic risks (TCR) (recreational receptors)

	Child			Adult		
	$CR_{ingestion}$	CR_{dermal}	TCR	$CR_{ingestion}$	CR_{dermal}	TCR
As	1.31E-06	7.87E-08	1.39E-06	3.07E-07	4.60E-08	3.53E-07
Cr	4.28E-08	2.06E-07	2.48E-07	1.00E-08	1.20E-07	1.30E-07
All elements	1.35E-06	2.84E-07	1.64E-06	3.17E-07	1.66E-07	4.83E-07

Results of the carcinogenic risk assessment presented in TABLES II and III indicate that, for residential and recreational receptors, As was the predominant contributor to the total carcinogenic risk of Cr and As combined. The contribution is higher for residential children and adults (94% and 96%) than for recreational children and adults (85% and 73%). Results of the assessment of carcinogenic risks of Cr and As for different exposure pathways show that the water ingestion pathway contributes more than the dermal pathway to TCR for all receptors (TABLES II and III). For both As and Cr values of CR via water ingestion and dermal contact with water were higher for residents than recreators. For both exposure pathways carcinogenic risk of As and Cr are higher for children than adults (TABLES II and III). Arsenic was the predominant contributor to the CR through water ingestion pathway for residential and recreational receptors (97%). Conversely, Cr contributed 72 % to the CR via dermal contact with water for residents and recreators.

Non-carcinogenic risk for exposure to PTE in soil

HQ trend (TABLE S-VIII) in both, adults and children was found in order: HQing > HQderm > HQinh, except for Cd in children where the following trend was observed: HQder > HQing > HQinh. It should be noted that the differences between the values of HQder and HQing for Cd were not large. HI values for adults were from: 0.0255 to 0.0714 for As; 0.0031 to 0.0221 for Cr; 0.0026 to 0.0194 for Pb; 0.0006 to 0.0017 for Ni; 0.0007 to 0.0013 for Cd; 0.0005 to 0.0013 for Cu and 0.0001 to 0.0004 for Zn (Fig. 5). HI values for children were from: 0.2370 to 0.6782 for As; 0.0276 to 0.2649 for Cr; 0.0251 to 0.1891 for Pb; 0.0066 to 0.00180

for Cd; 0.0058 to 0.0163 for Ni; 0.0051 to 0.0128 for Cu and 0.0004 to 0.0010 for Zn Fig. 6).

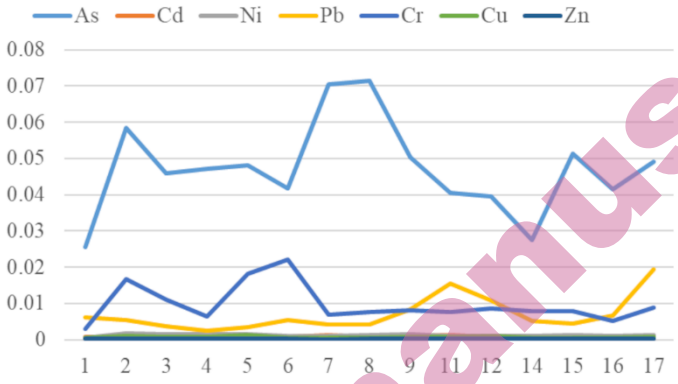

Fig. 5. Hazard index (HI) for non-carcinogenic risk in adults.

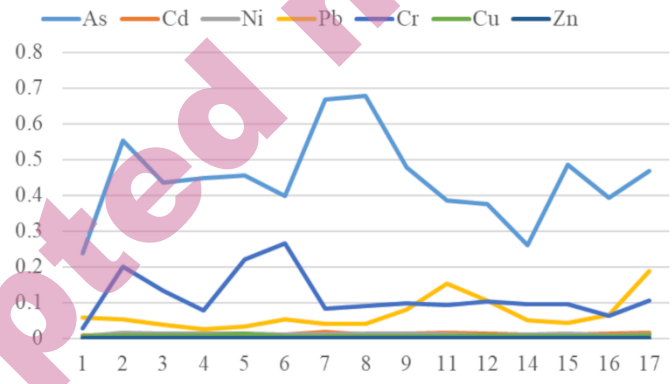

Fig. 6. Hazard index (HI) for non-carcinogenic risk in children.

All HI values for adults and children are less than 1, which indicates that the impact of PTEs is insignificant in the examined soils. For children, the highest HI values were observed for As, Cr, Pb, Cd, Ni, Cu and the lowest for Zn. For adults, the highest HI values are for As, Cr, Pb, Ni, Cd = Cu, and the lowest for Zn. Many HI values are 10 times higher for children than for adults. This trend was also observed in Alarifi[26] and the mentioned scientists explained that noncarcinogenic risks of heavy metal exposure for children are higher than for adults due to their physiological characteristics. The highest values of HI for children and adults were observed in the soil at the sampling sites 8 and 7 for As, and for Pb at sites 17 and 11.

Carcinogenic risk for exposure to PTE in soil

Carcinogenic human health risk values (CR and TCR) are shown in TABLES S-IX and S-X, and Figs. 7 and 8. TCR values for adults were from: 3.22E-05 to 1.15E-04 for As; 2.85E-06 to 5.56E-06 for Cd; 2.30E-05 to 6.28E-05 for Ni; 7.49E-08 to 5.64E-07 for Pb; and 4.55E-06 to 3.19E-05 for Cr. CR values for children were from: 1.07E-04 to 3.05E-04 for As; 2.68E-05 to 5.23E-05 for Cd; 2.09E-04 to 6.82E-04 for Ni; 7.04E-07 to 5.29E-06 for Pb; and 4.04E-05 to 3.69E-04 for Cr. The TCR values, for adults and children, were in the following descending order: Ni, Cr, As, Cd, Pb, and Ni, As, Cr, Cd, Pb, respectively. The highest CR values were observed at sites 7 and 8 (for As), site 2 (for Ni), and site 6 (for Cr). For adults, all TCR values belong to the acceptable and no-risk category. Regarding children, the TCR values for As, Cr, and Ni are greater than 10^{-4}, excluding values for Cr at two localities (1 and 16). As can be seen in Table S-X, the ingestion route is a major contributor to TCR followed by dermal and inhalation pathways. Also, TCR values for children were higher than for adults, and therefore, children are more at risk than adults in this study area.

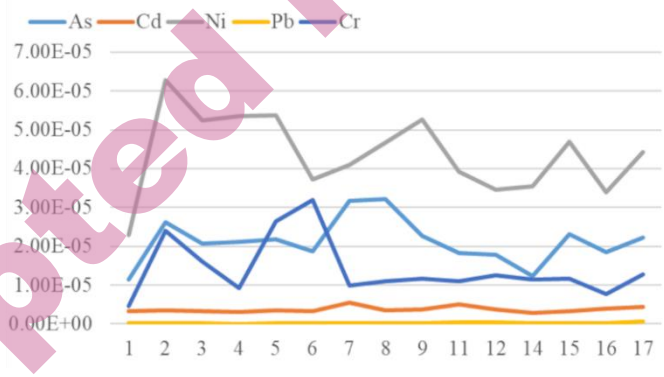

Fig. 7. Carcinogenic risk value for adults.

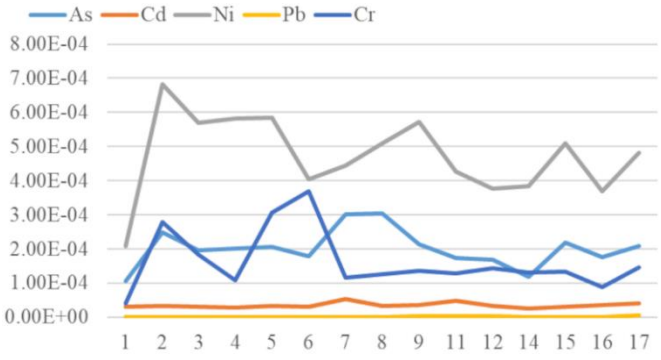

Fig. 8. Carcinogenic risk value for children.

CONCLUSION

PTEs in river water and soil in the Vlasina River drainage basin were studied in relation to contamination and human health risk assessment. Regarding studied elements, nutrient content and salinity indicators, the water quality of the investigated rivers corresponds to surface water quality Class I and Class II. Results of the comparison with limit values for PTE in soil indicate that the studied region is not under significant anthropogenic influence. According to the results of non-carcinogenic risk assessment, adverse non-carcinogenic effects of PTE in river water (As, Cu, Cr, Ni and Zn) and soil (As, Cu, Cr, Ni, Pb, Zn and Cd) on human health are not expected. The TCR values of all considered PTE (As and Cr) for exposure to river water were below the target risk. Regarding exposure to PTE in soil, all TCR values for adult receptors belong to the acceptable and no-risk category. For children, the TCR values of As, Cr, and Ni were slightly higher than the acceptable limit of 1×10^{-4}. The results of the health risk assessment indicate that children are more susceptible to the detrimental effects of PTE on health. Arsenic was a predominant contributor to non-carcinogenic risk for exposure to PTE in water and soil. Dominant contribution to carcinogenic risks was from As for exposure to water, and from Ni for exposure to soil. These are the first results of the assessment of human health risks posed by PTEs in river water and soil in the Vlasina River basin. We believe that the results of this study could be beneficial for the protection of human health and drinking water source management.

SUPPLEMENTARY MATERIAL

Additional data are available electronically at the pages of journal website: https://www.shd-pub.org.rs/index.php/JSCS/article/view/13105, or from the corresponding author on request.

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И З В О Д

ПОТЕНЦИЈАЛНО ТОКСИЧНИ ЕЛЕМЕНТИ У ВОДАМА РЕЧНОГ СЛИВА И ОКОЛНОМ ЗЕМЉИШТУ У ИСТОЧНОЈ СРБИЈИ – ПРОЦЕНА РИЗИКА ПО ЉУДСКО ЗДРАВЉЕ

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У овој студији су процењени ризици по здравље људи услед изложености потенцијално токсичним елементима (ПТЕ) у земљишту и речним водама у источној Србији. Садржај As, Cu, Cd, Zn, Pb, Ni, и Cr мерен је у водама река из слива Власине и околном земљишту.

Концентрације Cl^-, SO_4^{2-} и NO_3^- су такође мерене у речној води. Према Уредби Републике Србије, квалитет воде истраживаних река одговара квалитету површинских вода класе I и II. Садржаји ПТЕ у земљишту су нижи од граничних вредности прописаних међународним правилницима. Резултати процене ризика по здравље показују да су деца осетљивија од одраслих када су изложена ПТЕ у води и земљишту. За изложеност људи ПТЕ у води, доминантан допринос укупним неканцерогеним и канцерогеним ризицима потиче од As. За ПТЕ у земљишту, As је имао доминантан допринос не-канцерогеним ризицима, а Ni канцерогеним ризицима. Све вредности HI за одрасле и децу су мањи од 1, што указује да је утицај ПТЕ-а у испитиваној речној води и земљишту на људско здравље занемарљив.

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