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Environmental and Health Risk Assessment Due to Potentially Toxic Elements in Soil near Former Antimony Mine in Western Serbia

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Abstract: Background: Anthropogenic activities have clearly affected the environment, with irreversible and destructive consequences. Mining activities have a significant negative impact, primarily on soil, and then on human health. The negative impact of the first mining activities is represented even today in the soils of those localities. Research shows that, for different types of mines, the concentrations of potentially toxic elements (PTEs) are high, especially in antimony, multi-metal and lead–zinc mines, which have adverse effects on the environment and then on human health and the economy. A large flood in 2014 in Western Serbia resulted in the breaking of the dam of the processed antimony ore dump of the former antimony mine, causing toxic tailings to spill and pollute the downstream area. Due to this accident, tailings material flooded the area downstream of the dump, and severely affected the local agriculture and population. Methods: Potentially toxic elements content, pollution indices and health indices were determined in soil samples from the flooded area, using referenced methodologies. The sources and routes of pollutants and risks were determined and quantified using statistical principal component analysis, positive matrix factorisation, and a Monte Carlo simulation. Results: The main source of As, Cd, Hg, Pb, Sb and Zn in the upper part of the study area was the tailing material. Based on the pollution indices, about 72% of the studied samples show a high risk of contamination and are mainly distributed immediately downstream of the tailings dump that was spilled due to heavy rainfall. Conclusions: Although the content of the PTEs is high, there is no non-carcinogenic risk for any PTEs except As, for which a threshold risk was determined. There is no carcinogenic risk in the study area.

Keywords: health index; non-carcinogenic risk; flooded area; pollution indices; tailing outflow; Monte Carlo simulation; positive matrix factorisation

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1. Introduction

Over the last two centuries, anthropogenic activities have transformed the environment, exerting numerous pressures with sometimes irreversible processes and destructive effects on individual components of the ecosystem. Although these processes of degradation started a long time ago, scientists and global politicians are now more aware of the importance of these problems. Numerous studies regarding soil, water and air quality have been performed worldwide, primarily with the aim of assessing the real situation as well as raising public awareness in order for them to accept the need to take concrete measures for the preservation of the environment (adopted agreements, declarations and programmes). In order to preserve the environment and perform appropriate measures, it is of particular importance to assess the risk of soil contamination [1]. Assessment of risks to environmental components, primarily to the soil, and the impact on health is a complex process that defines the sources and routes of pollution and quantifies the risks of these phenomena. The sources of contamination could be very different, from natural to anthropogenic, among which mining activities have a significantly negative impact [2,3]. The negative impact of the first mining activities is represented even today in the soils of those localities [4]. In China, it is estimated that 1.5 million ha are polluted due to mining and related industries [3]. The same authors state that the concentrations of potentially toxic elements (PTEs) in soil covered with the tailings are significantly higher than the maximum allowed, so about 50% of these soils are marked as having a potential ecological risk. Some mining areas have been assessed as a potential risk to human health. In Europe, supplies of Sb are in France, Germany, Sweden, Finland, Slovakia and Greece [5], while in Western Serbia, the Sb mine was closed in the 1980s [6]. Mine activities are accompanied by increased concentrations of PTEs, and non-ferrous metal smelting [7], as well as pyrometallurgical production [8], and thus represent a significant source of Cu, Zn, Cd, Pb, Cr, Hg, As and Sb in the environment. Based on research on different types of mines, it was determined that the concentrations of elements are the highest from antimony, multi-metal and lead–zinc mines [3]. From the processes of smelters, and accompanying mining activities, PTEs can reach different components of the ecosystem through air pollution, while smelting slags and dumped waste over time, together with the influence of erosion, can have a harmful effect on the environment [7]. The origin and sources of PTEs in the soil that arrived through wet and dry deposition are also considered in relation to the specific conditions of the locality, the distance from the pollution source and, as an example, [9] state that the Ni and Cu content in soil decreases exponentially with increasing distance from the sources of pollution. In addition, floods are generally recognised as a diffuse form of PTE pollution [10,11].

Accidental situations, caused by a variety of anthropogenic influences, from inadequate management of facilities to climate change and floods caused by storm precipitation [12,13], have a special impact on the environment. In May 2014, large floods occurred in the territory of the Republic of Serbia due to heavy rainfall, at levels unprecedented in the last 120 years in the Balkan region [13]. As a result of these floods the tailings of the former Stolica mine, more than 100,000 m^3, were spilt [14].

Environmental risk is defined as the probability of an adverse ecological effect that may occur due to exposure to one or more stressors of different origins [15] and is characterised as either a risk to human health or ecological or both [16]. Within the health risk assessment, some of the exposure parameters (e.g., body weight, intake, or dermal area) could vary, which could lead to uncertainty in the health risk assessment. There are numerous indices that can be taken into consideration, such as potential environmental risk (*RI*), pollution index (*PLI*) and others [4,9,13,17–27]. For health risk, estimates of the carcinogenic (*TCR*) and non-carcinogenic effect (*HI*) of exposure to PTEs are performed worldwide [3,16,28–35]. The calculation of various ecological risk indices and health risk indices as well as their spatial distribution, represented with modern tools and computer simulations, are used as indicators of environmental threats [23].

Floodplain soils are known for their fertility, making them ideal for agriculture. However, if these soils contain high levels of potentially toxic elements, they can pose a significant health risk [36]. PTEs can be transported over long distances in rivers with high discharge flow, frequent flooding and relatively flat surrounding terrain [37]. If there is a source of pollution near the river, such as a tailings dump, it can pose a special threat to the environment [38,39]. When a flood occurs, the tailings can be washed into nearby rivers and streams, potentially contaminating the water supply and increasing the risk of exposure to PTEs for nearby communities. In order to properly assess the human health risks, it is important to consider the potential exposure pathways for PTEs. This can include conducting environment and health risk assessments [23,31–33].

In the study area, previous research regarding the content of PTEs (Pb, Cd, Zn, Cu, Ni, Cr and Mn) accumulated in agricultural soils by deposition from the air and due to the spillage of tailings containing these harmful elements had been carried out [40]. Additionally, the PTEs availability (Pb, Cd, Zn, Cu content in 1 M ammonium acetate) for plants was analysed [41]. The research also covered the microbiological properties of the soil (number of total microflorae, fungi, actinomycetes and bacteria from the genus *Azotobacter*) [40]. In this study, the general goal is to provide information primarily about the content of Sb and As in the surface layer of the flooded soil for regional environmental management, but also to expand the understanding of the process of migration and accumulation of all PTEs in the soils of river basins in mining areas, especially when floods occur, and cause the accidents such as tailing spills.

The aim of this study is: (1) to estimate the potential environmental risk due to increased concentrations of PTEs in the soil, (2) to assess the influence of spilling tailings from the flotation of the former antimony mine on the PTEs pathways after the flood, (3) to determine the origin of PTEs in flooded soil and show their spatial distribution and, (4) to assess the carcinogenic and non-carcinogenic effect on human health, with included uncertainty analysis.

2. Materials and Methods

2.1. Study Area

The study area (Figure 1) is a flooded area from the flotation tailings of the former antimony mine located in Western Serbia, in the town of Kostajnik, along the Kostajnica river and part of the alluvial plain of the Jadar river, 44°23.830′ and 44°38.100′ N and 19°15.350′ and 19°23.750′ E. The Jadar river basin has been the potential location for the opening of a new mine for lithium extraction for the past 20 years after the discovery of "jadarite" [42]. Although the antimony mine has been closed for more than three decades, it was active since 1882 and closed in 1987 [6], its impact is visible both due to the increased content of PTEs from mining and smelting, as well as from additional problems caused by the flood and spillage of tailings material in 2014. On that occasion, the tailings slurry contaminated a 27 km length of riverbeds and 360 hectares of agricultural land [14].

In this paper, alluvial flooded soils were considered, which were covered with a sedimentary deposit of flotation tailings due to the flood wave, in a layer of 5–10 cm, with a width of between 50–75 m of the left and right riverbank, and in some sections up to 100 m [6,40]. A total of 33 samples were taken from the flooded area in June 2018. Flooded alluvial soils are characterised by a high content of sand fraction, and texturally they belong to classes from loamy sand to silty clay loam [40]. The same authors state that flooded soils are low in organic matter, while the pH value is determined by the content of calcium carbonate (7.32–8.12 pH units and belong to the classes of weakly alkaline and moderately alkaline soils).

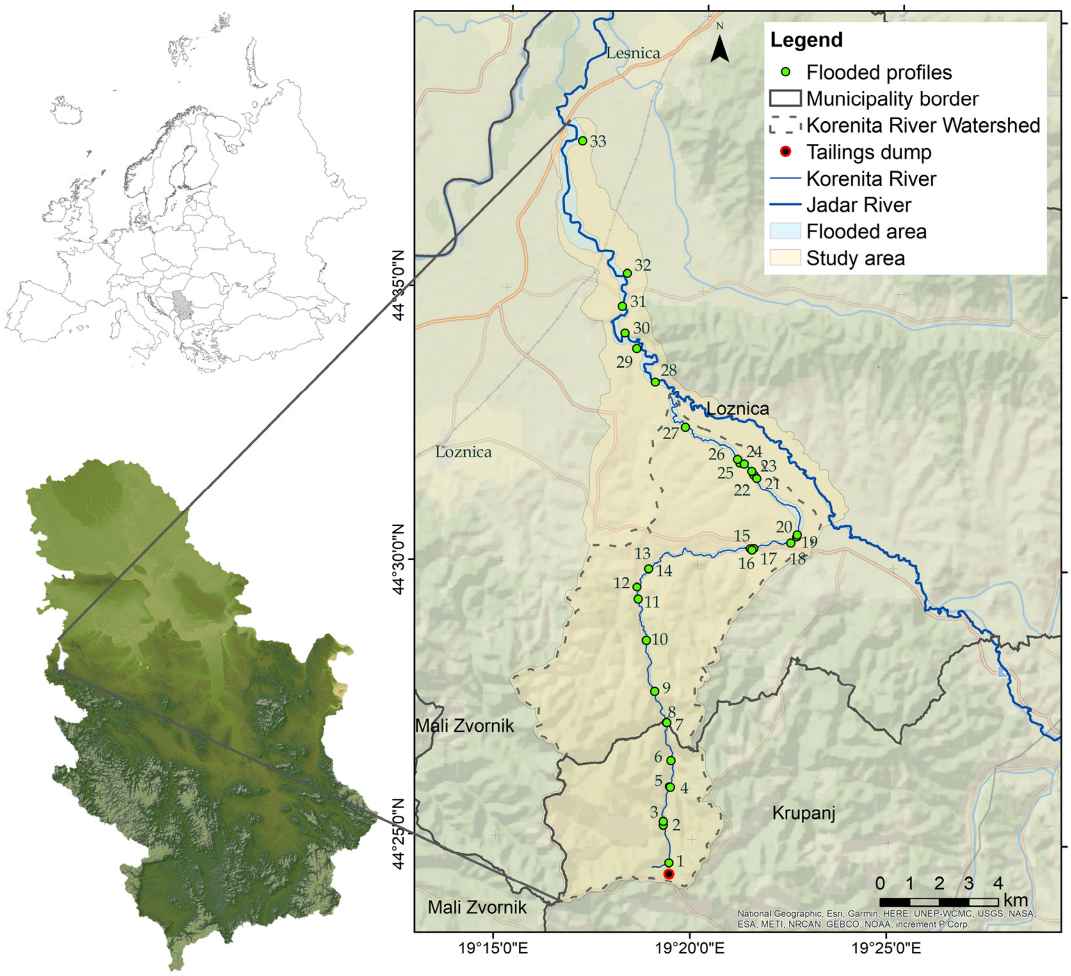

Figure 1. Study area.

2.2. Soil Analysis

Surface soil layers were sampled in a layer up to 10 cm, for analyses of physical and chemical properties, and content of PTEs (Sb, As, Hg, Pb, Zn, Cd, Cu, Ni and Cr). The granulometric composition was determined by treating the samples with sodium pyrophosphate. Soil fractionation was performed by combining the pipette method and the elutriation method using an Atterberg sieve, with a determination of the percentage content of sand (2–0.06), silt (0.06–0.002) and clay (<0.002 mm) fractions [43]. The determination of organic carbon (OC) by oxidation was carried out using a potassium dichromate/sulfuric acid mixture (SRPS ISO 14235:2005), which is used to calculate organic matter (OM = 1.72 ∗ OC).

To determine the content of PTEs, the analysis was performed according to the standard procedure (ISO 11466:1995 Soil quality, 1995). Soil samples were digested with aqua regia under reflux for 2 h with water-cooled condensers to determine the content of trace elements (ISO 11466:1995 Soil quality, 1995). Before the determination of the samples, three blank samples were prepared, which allowed for the correction of the results where necessary. The content of PTEs (Pb, Cu, Zn, Cd, Ni, Cr and Mn) was determined using the AAS method, employing the flame technique, the content of Hg was determined using the hydride technique, while As and Sb were determined with ICP spectroscopy. All analyses were performed in two repetitions, and measurements were performed for the following levels of detection by element: Zn—0.02349; Cu—0.10840; Pb—0.03244; Cr—0.13715; Cd—0.0166; Ni—0.01660; Mn—0.07508; Hg—0.002266; Sb—0.15; As—0.10 mg kg^{-1}. Quality control (QC) was performed using certified reference materials (CRM): ERM-CC-141 sample no. 0395 (loam soil) Belgium, with an exact concentration of microelements soluble in aqua regia to provide for increased accuracy of the measuring apparatus.

2.3. Pollution Indices

The content of PTEs in the soil was compared with the corrected maximum permissible and remediation values, calculated based on clay and organic matter content, according to the Decree [44].

The maximum permissible values and remediation values for PTEs are given in Table 1, according to the regulation on the limit values of pollutant, harmful and dangerous substances in the soil of the Republic of Serbia [44]. The measured PTE concentrations were compared to corrected maximum permissible and remediation values.

Table 1. Maximum permissible and remediation values for PTEs [44].

PTE	Maximum Permissible Value (SWsb) mg kg^{-1}	Remediation Value (IWsb) mg kg^{-1}
Cd	0.8	12
Cr	100	380
Cu	36	190
Ni	35	210
Pb	85	530
Zn	140	720
Hg	0.3	10
As	29	55
Sb	3	15

The maximum permissible values and remediation values for PTEs, with the exception of antimony, depend on the content of clay and organic matter in the soil. When determining the type and properties of the soil, the values from Table 1 are corrected to the values applicable to the actual soil, based on the measured content of organic matter and clay content. For PTEs, the following correction formula is used, depending on the soil type, based on which the correction is performed [44]:

$$\mathrm{SWb, IWb = SWsb,\ IWsb \times \frac{A + B \times \%\ clay + (C \times \%\ OM)}{A + B \times 25 + C \times 10}}$$

where SWb, IWb are the corrected maximum permissible and remediation values for a specific soil; SWsb, IWsb are the maximum permissible and remediation values from Table 1; % clay—the content of clay in a specific soil (<2 µm); % OM—the content of organic matter in a specific soil; A, B, C—const. depends on the element (Table S1).

Pollution load index (*PLI*) is one of the complex indices. It is a simple way to point out the deterioration of soil conditions due to the accumulation of PTEs in the soil [9,18,21,25,26,45]. It is calculated as the geometric mean of single contamination factors for each PTE, according to the following formula [18]:

$$PLI = \sqrt[n]{PI_1 \times PI_2 \times PI_3 \times \ldots \times PI_n}$$

where *PI*—single contamination factor, $_n$—total number of PTEs that is analysed.

PI is calculated according to the following formula:

$$PI = \frac{C_n}{GB}$$

where C_n is PTE concentration in soil, and *GB* is background concentration of specific PTE.

The Jadar river watershed (959 km^2), to which our study area belongs, was used for GB calculations. GB values are calculated according to the formula, based on the measured concentrations of PTEs in the soil profiles from the monitoring network 3 × 3 km [46]. Only

GB for Sb is adopted from the literature [47,48]. Background concentration is calculated according to the following formula [49]:

$$GB = MEDIAN + 2 \times MAD$$

where *MEDIAN* is the median of the PTE concentration in the soil, and *MAD* is the median absolute deviations. According to the pollution level, soils are classified into polluted soil (*PLI* > 1) or unpolluted (*PLI* < 1).

Potential ecological risk index (*RI*) is the complex index used to assess the degree of environmental risk that may be caused by high concentrations of PTEs in water, air or soil. This index was introduced by [19] and is calculated according to the following formula:

$$RI = \sum_{i=1}^{n} E_r^i$$

where *n*—total number of PTEs that are analysed, *Er*—individual environmental risk index calculated according to the formula:

$$E_r^i = T_r^i \times PI$$

where *Tr*—toxicity coefficient for specific PTE, and *PI*—calculated individual pollution factor. The values of the toxicity coefficients were taken from the literature, and for the following elements are: Zn—1, Cu—5, Pb—5, Ni—5, Cr—2, Cd—30, As—10, Sb—15, Hg—40 [19]. The potential ecological risk index (*RI*) is defined in 4 classes according to [19]: *RI* < 150 low environmental risk; 150 ≤ *RI* < 300 moderate environmental risk; 300 ≤ *RI* < 600 considerable environmental risk and *RI* ≥ 600 very high environmental risk.

2.4. Health Index/Health Risk Models

The assessment of the total non-carcinogenic risk (hazard index—*HI*) for three types of exposure (*HQing*—hazard coefficient by ingestion; *HQder*—hazard coefficient by dermal contact; *HQinh*—hazard coefficient by inhalation) is calculated according to the following formula, using the Monte Carlo simulation:

$$HI = HQing + HQder + HQinh$$
$$HQing = \frac{C \times IRSa \times RBA \times EFa \times EDa}{BWa \times ATa \times RfDo} \times 10^{-6}$$
$$HQder = \frac{C \times SAa \times AFa \times ABSd \times EFa \times EDa}{BWa * ATa * RfDo * GIABS} \times 10^{-6}$$
$$HQinh = \frac{C \times EFa \times EDa}{ATa \times RfC \times PEF}$$

where *C*—the determined concentration of a certain PTE in the soil (mg kg^{-1}), and the other parameters are given in the supplementary tables (Tables S2 and S3). Negative health effects can be expected when *HI* values are greater than 1 [28,32].

The estimate for total carcinogenic risk (*TCR*) for adults is calculated based on the formula [32], using the Monte Carlo simulation:

$$TCR = CRing + CRder + CRinh$$

where:

$$CRing = \frac{C \times IFS \times RBA \times CSFo}{ATa} \times 10^{-6}$$
$$IFS = \frac{EFa \times EDa \times IRSa}{BWa}$$
$$CRder = \frac{C \times DFS \times ABSd \times CSFo}{ATa \times GIABS} \times 10^{-6}$$
$$DFS = \frac{EFa \times EDa \times SAa \times AFa}{BWa}$$
$$CRinh = \frac{C \times EFa \times EDa \times IUR \times 1000}{ATa \times PEF}$$

where the *RBA*, relative bioavailability factor, for As—0.6, for other PTEs—1, *CRing*—represents the value of carcinogenic risk by ingestion, *CRder*—represents the value of carcinogenic risk by skin contact, and *CRinh*—represents the value of carcinogenic risk by inhalation. Other parameters are shown in the supplementary tables (Tables S2 and S3).

TCR values greater than 10^{-4} are unacceptable, while those in the range of 10^{-4} to 10^{-6} are acceptable [50,51].

2.5. Statistical Analysis, MC, PCA and PMF Analysis and Geospatial Analysis's

Descriptive statistics were obtained using SPSS 2007. For each parameter from the risk indices equations (*HI* and *TCR*), the corresponding probability distribution was determined (Table S3). Subsequently, a random value of each parameter was picked up from each distribution and, further, the risk indices (*HI* and *TCR*) were repeatedly calculated over 10,000 repetitions. The output results are represented through a probability distribution histogram and associated basic statistical indicators. Additionally, the sensitive analysis was performed to rank the assumptions of each parameter, from the most important down to the least important in the model. The sensitivity analysis is represented using a tornado diagram. The Monte Carlo simulation was performed using Oracle Crystal Ball (version 11.1.4323.0) loaded in Microsoft Excel, to obtain stable risk outputs and a sensitivity index.

A principal component analysis (PCA) with Varimax rotation (SPSS 2007) was used to determine the origin of the analysed PTEs in the soil. The Kaiser–Meyer–Olkin (KMO) measure of sampling adequacy and Bartlett's test for sphericity were used to determine the factorability.

In addition to the PCA, a positive matrix factorisation (PMF) was applied to define the source of the PTEs, using EPA PMF Version 5.0.14.21735 software [52,53]. The data were previously observed, and the outliers were removed based on interquartile ranges and histograms [54,55]. The estimation of the uncertainty of the measured concentrations (u_{ij}) is an important step in the preparation of input data and is defined thus:

$$u_{ij} = 1.05 \times \left(u_{ij,an} + \frac{2}{3} LD_{ij}\right),$$

Except in cases where $c_{ij} \leq LD_{ij}$ (c_{ij}—concentration of *j*-element in i^{th} sample; LD_{ij}—limit detection).

$$c_{ij} = \frac{1}{2} LD_{ij},\ u_{ij} \frac{5}{6} LD_{ij}$$

Details on used parameters in positive matrix factoring are given in supplementary Table (File S1).

A geospatial representation of the PTEs and pollution indices was obtained using ArcMAP (v.10.8.2). The geospatial distribution of the PLI and RI was shown on the point level for each sampling site.

3. Results

3.1. Content of PTEs and Pollution Indexes

Descriptive statistics of PTEs in the topsoil layer of the flooded area are shown in Table 2. The arithmetic mean of PTEs varies depending on the element, but a wide range with high CV values and large standard deviations is characteristic for Zn, Pb, Cd, As, Sb and Hg in the studied flooded soils.

Table 2. Summary statistics for PTEs concentration in flooded topsoil.

Elements (mg kg^{-1})	Min	Max	Median	Mean	St. Dev.	Coef. of Var. (%)
Cd	0.10	11.26	1.77	3.14	3.60	113
Cr	7.92	46.58	15.33	17.67	9.72	54
Cu	11.40	36.44	17.91	18.40	5.49	29
Ni	11.98	60.26	17.26	20.09	9.15	45
Pb	15.26	468.29	102.12	147.12	124.91	83
Zn	50.33	1999.87	289.67	516.11	585.12	111
Hg (µg kg^{-1})	10.83	7932.09	517.74	1944.86	2803.90	142
As	0.00	4936.16	622.98	1210.22	1491.45	118
Sb	0.00	1467.77	282.79	392.67	422.25	106
Mn	145.98	1265.73	949.58	920.45	145.9	16

The measured content of Zn, Pb, Cd, As and Sb is higher than the corrected remediation value in the upper part of the river course, below the tailings dump. In the middle part of the river and downstream in the river, the content of Zn, Pb and Cd is higher than the corrected maximum permissible values. The content of As is higher than the corrected remediation value in the whole study area, but the content of Sb in three cases in the lower part of the river is below the detection limit.

On the other hand, the measured values in the surface soil layers for Cu, Ni and Cr are, in most cases, lower than the maximum permissible values. In some soil samples in the upper part of the river and below the tailings dump, the content of Cu and Ni is higher than the maximum permissible values. The measured values in the surface soil layers for Cr are lower than the maximum permissible values, while the average values of Mn are slightly higher than the average content in the soils of the world (950 mg·kg^{-1}) [56].

According to the pollution level, soils are classified into polluted (*PLI* > 1) or unpolluted soils (*PLI* < 1), which is shown in Table 3. The pollution degree according to average values of PI for individual PTE is shown in Table S4. More than two-thirds of samples show that the soil is polluted. Very high pollution, as indicated by PI values, is influenced by the high content of Hg, As and Sb in the topsoil. High pollution is influenced by Cd and Zn, while Pb content causes moderate pollution. The average PI values for Cr, Cu and Ni show no degree of pollution (Table S4). Figure 2 shows the box plot and distribution of *PLI* values. Figure 3 shows the spatial distribution of the *PLI* index in the study area along the flooded zone of the Korenita and Jadar rivers, where the pollution load is present in the upper part of the river course, closer to the tailings dump.

Table 3. Pollution load index in the study area.

PLI Category	Contamination	Total Samples (%)
PLI < 1	Unpolluted soil	27.3
PLI > 1	Polluted soil	72.7

Figure 4 (boxplot) shows the distribution of the potential environmental risk index, while Table 4 shows the percentage of each category, based on the level of risk of contamination. This index is in accordance with the *PLI* index, indicating pollution risk in the upper part of the river (Figures 3 and 4) and showing that more than two-thirds of samples are in the category of very high or extremely high contamination risk. According to the average values of the individual ecological risk index (Table S5), a very high ecological risk is defined for As and Sb, a high risk for Hg and considerable ecological risk for Cd. On the other hand, the Er index shows that there is a low potential ecological risk for Cr, Cu, Ni, Pb and Zn. Figure 5 shows a similar spatial distribution of risk contamination as for the *PLI* index, i.e., great contamination risk in the upper part of the Korenita river.

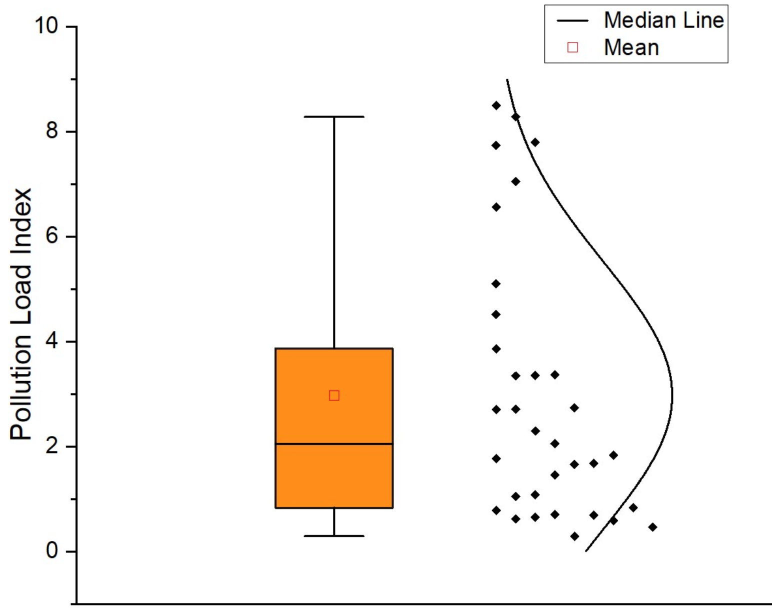

Figure 2. Boxplot of pollution load index in the study area.

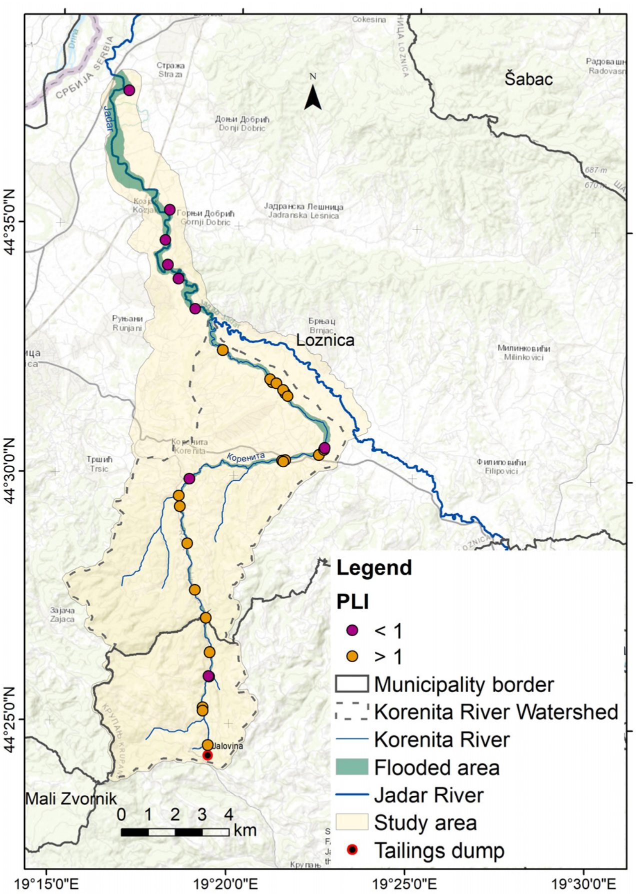

Figure 3. Pollution load index in the flooded zone of the Korenita and Jadar rivers.

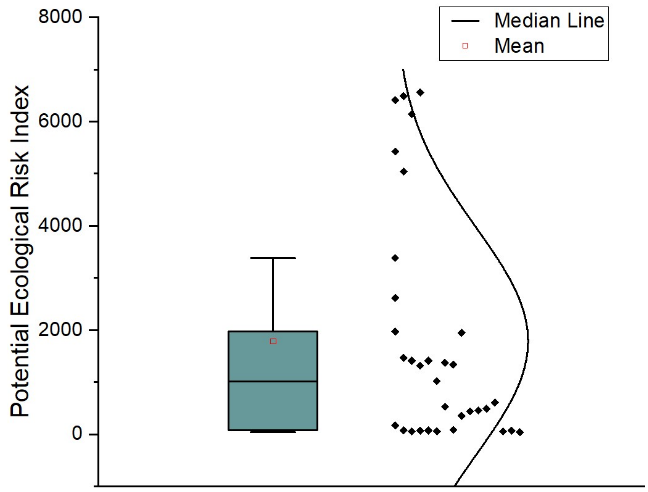

Figure 4. Boxplot of potential ecological risk index in the study area.

Table 4. Potential ecological risk index (*RI*) in the study area.

RI Category	*RI* Classes	Total Samples (%)
$RI < 150$	Low contamination risk	27.3
$150 \leq RI < 300$	Considerable contamination risk	3
$300 \leq RI < 600$	Very high Contamination Risk	15.2
$RI \geq 600$	Extremely high contamination risk	54.5

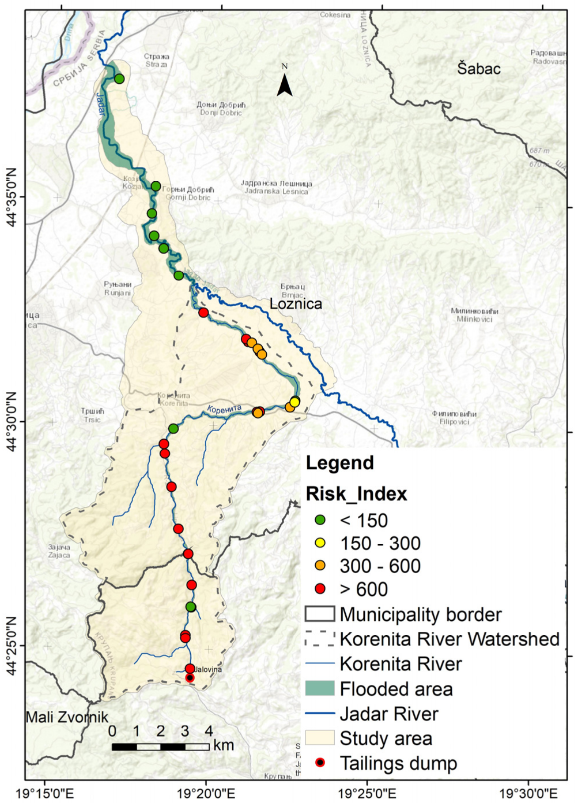

Figure 5. Risk index in the flooded zone of the Korenita and Jadar rivers.

3.2. Factors Influencing PTEs and Their Spatial Distribution

Based on the PCA analysis for the total content of PTEs, two dominant components are singled out, which explains 89.02% of the total variance. The first component, with a contribution of 65.38%, represents the influence of tailings material due to the flood wave and includes Zn, Pb, Cd, As, Sb and Hg (Table S6). The second component, with a contribution of 23.64% of the total variance, represents the geological influence and includes Cu, Ni and Mn (Table S6, Figures 6 and 7). To define the geographical position on the influence of certain factors, the studied watercourse is divided into three units: unit I—the upper part of the river course—points 1–7; unit II—points 8–21; and unit III—points 22–33 (Figure 8). The "tailings deposit" component has the greatest influence on the upper part of the studied watercourse (unit I), while the "geological substrate" component has the greatest influence on unit III of the river course, i.e., on the alluvium of the Jadar river (Figures 6 and 7; Table S6).

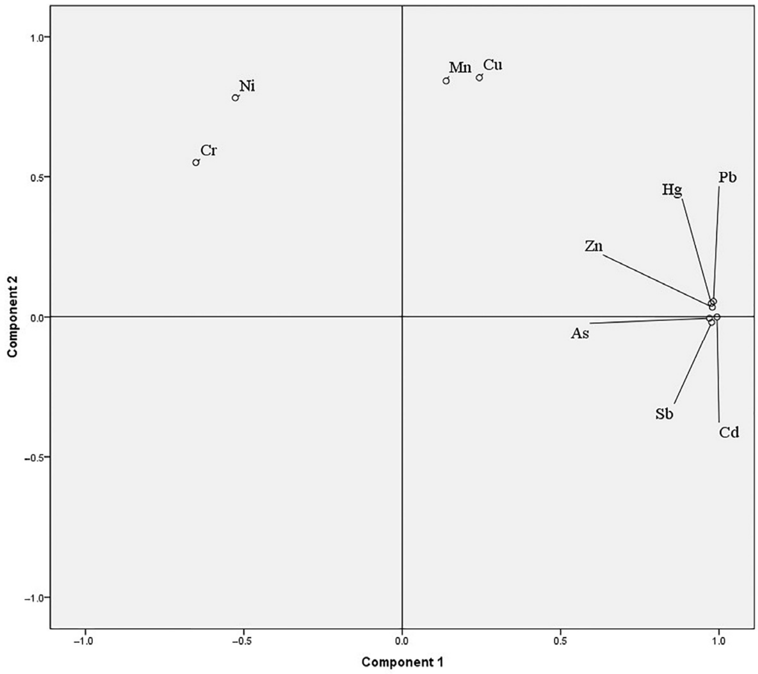

Figure 6. Loading plot for PTEs.

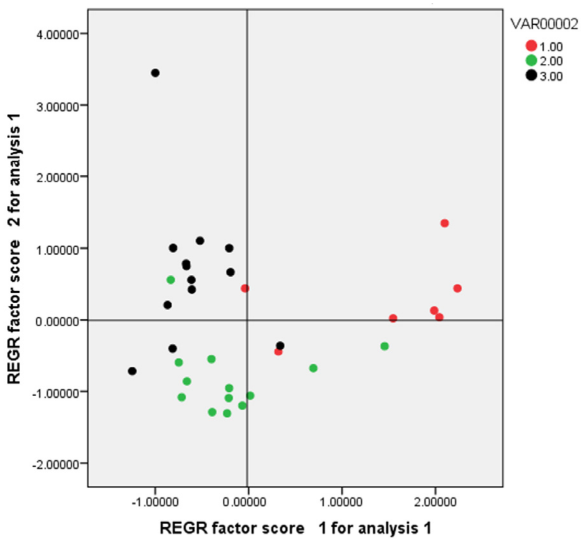

Figure 7. Score plot for PTEs.

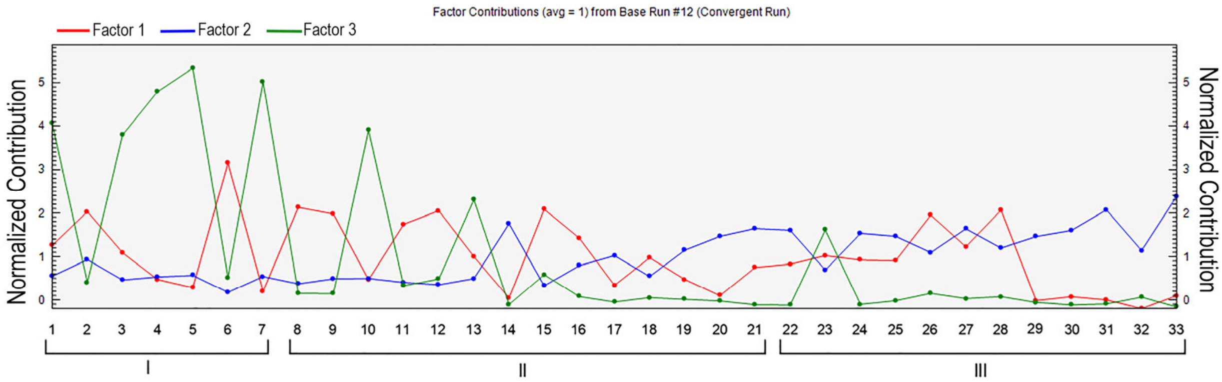

Figure 8. Graph of factor contribution (time factor series).

On the other hand, analysing the results of PTEs in the studied soils using the PMF model, with the aim of finding the best solution in terms of stability, performance and accuracy, three factors were chosen as a preliminary solution. Factor 1, with a contribution to the total variance of 28.08%, represents the influence of mining tailings and geological substrate. Pb and Sb have the greatest influence on Factor 1, with 37.8 and 35.5%, respectively, while the other studied elements show a slightly smaller influence of around 26%, but without Mn and Cu (Table 5).

Table 5. PTEs contribution in the factors, based on PMF.

Elements	Factor 1	Factor 2	Factor 3
Cd	28.8	5.8	65.3
Cr	11.8	88.2	<0.05
Cu	26.2	59.8	14.0
Ni	21.6	74.9	3.6
Pb	37.8	14.6	47.6
Zn	26.6	11.0	62.3
Hg	8.7	6.1	85.2
As	27.8	6.4	65.8
Sb	35.5	2.8	61.7
Mn	26.5	59.9	13.6
Contribution in total variance (%)	28.08	23.32	47.66

The spatial distribution of Factor 1 is generally uniform throughout the entire course, except for a sharp decrease in the part immediately connected to the mouth of the river (Figure 8). Factor 2, with a contribution of 23.32% to the total variance, represents the influence of the geological substrate. A clear geological origin is expressed by the influence of Cr, Ni, Mn and Cu, which amounts to 88.2, 74.9, 59.9 and 59.8%, respectively (Table 5). The influence of this factor increases in the middle course of the river, while it is most pronounced at the river mouth itself (Figure 8). Factor 3 has the largest contribution (47.66%) to the total variance of tailings material, where the highest percentage of influence in this factor is Hg, with 85.2%, followed by As, Cd, Zn and Sb with over 60% each. Given that this factor is characterised by tailings material, the greatest impact is in the upper course of the river, while it decreases in the middle and lower course (Figure 8).

3.3. Human Health Influence Assessment

Summary statistics of estimated non-carcinogenic (*HI*) risk from PTEs in soils are presented in Table 6.

Table 6. Summary statistics of estimated non-carcinogenic (*HI*) risk from PTEs in soils using Monte Carlo simulations.

HI	Min	Max	St. Dev.	Mean	Median	Coef. of. Var. (%)
Cd	3.62×10^{-6}	0.152	4.35×10^{-3}	9.97×10^{-4}	1.68×10^{-4}	436
Cr	6.83×10^{-5}	1.33×10^{-2}	1.80×10^{-3}	2.61×10^{-3}	2.18×10^{-3}	68.97
Cu	7.88×10^{-6}	4.11×10^{-4}	4.88×10^{-5}	9.79×10^{-5}	9.01×10^{-5}	49.86
Ni	3.48×10^{-5}	3.54×10^{-3}	2.51×10^{-4}	4.12×10^{-4}	3.51×10^{-4}	60.85
Pb	0.004	19	0.419	0.21	0.105	199
Zn	5.29×10^{-6}	0.053	1.13×10^{-3}	3.63×10^{-4}	1.18×10^{-4}	310
Hg	2.54×10^{-6}	0.521	1.07×10^{-2}	2.55×10^{-3}	3.82×10^{-4}	420
As	3.54×10^{-3}	566	8.09	0.993	0.117	815
Sb	−0.309	1.54	0.185	0.152	0.108	122

Based on the mean value of lower than 1, the non-carcinogenic hazard (*HI*) does not exist for any of the elements. However, the mean *HI* value calculated for As is the limit value (0.99), and the non-carcinogenic hazard is especially high for As, Pb and Sb when the maximum calculated values of the *HI* index are analysed (Table 6). Based on the sensitivity analysis, the effects of certain parameters on the non-carcinogenic risk for As, Pb and Sb were determined (Figure 9), where the risk is most affected by element concentration (83.7–92%), followed by exposure (*ED*) 4.8–9.9%.

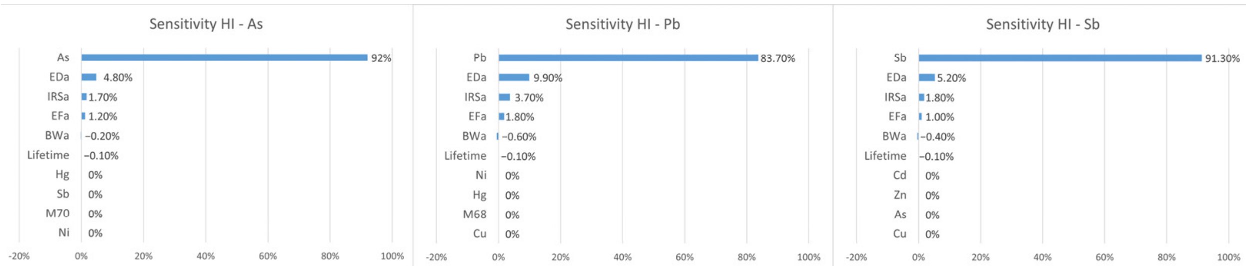

Figure 9. Sensitivity analysis for carcinogenic risk for As, Pb and Sb.

The summary statistics of the Monte Carlo simulations of carcinogenic (*TCR*) risk from PTEs in soils are shown in Table 7. The assessment was performed for PTEs for which all parameters were defined according to [28–30].

Table 7. Summary statistics of Monte Carlo simulations of carcinogenic (*TCR*) risk from PTEs in soils.

TCR	Min	Max	St. Dev.	Mean	Median	Coef. of. Var (%)
Cd	1.10×10^{-9}	5.14×10^{-5}	1.47×10^{-6}	3.37×10^{-7}	5.65×10^{-8}	438
Cr	1.27×10^{-7}	1.40×10^{-5}	1.99×10^{-6}	3.01×10^{-6}	2.55×10^{-6}	66.14
Ni	7.20×10^{-7}	7.40×10^{-5}	5.68×10^{-6}	9.17×10^{-6}	7.84×10^{-6}	61.88
Pb	4.70×10^{-9}	2.23×10^{-5}	4.91×10^{-7}	2.46×10^{-7}	1.23×10^{-7}	199
As	1.54×10^{-6}	4.07×10^{-1}	4.90×10^{-3}	4.84×10^{-4}	5.40×10^{-5}	1012

Based on the mean value, a carcinogenic hazard does not exist for the studied PTEs from the soil. The mean total carcinogenic risk (*TCR*) values for Pb, Ni, Cr, Cd and As were in the "acceptable" range, but the maximal total carcinogenic risk (*TCR*) value for As (4.07×10^{-1}) is in the unacceptable range.

4. Discussion

The total content of Sb, Hg, Pb, Cd and Zn (Table 2), as well as the values of the pollution index (Figures 3 and 5) decrease with distance from the tailings dump, which was also determined by other authors, and the maximum concentrations were measured in the samples closest to the mine area [35,40,41]. According to the PCA analysis and the values of the rotated component matrix (Table S6), it is clearly indicated that the topsoil is loaded with Zn, Pb, Cd, As, Sb and Hg content, as a result of mining activities and related industries (smelters) in the studied area, tailings spillage due to heavy rainfall and flooding of the soil along the river.

The risk of contamination is extremely pronounced in more than 69% of the flooded soil samples, as assessed by the PLI (Table 3) and the RI (Table 4). The origin of PTEs (Sb, As, Hg and partly Cd, Pb and Zn) from tailings material affected the risk of contamination below the tailings dump in the upper part of a river course. These results were expected because the analysed topsoil layers were burdened by tailings material deposition, which was also determined in earlier research in relation to the enrichment factor as well as *RI* [36].

In order to understand the process of migration and accumulation of all PTEs in the soil after flooding in the study area, PCA analysis and a PMF model were applied. The influence of mining activities is clearly visible based on the results of the PMF analysis in the central part of the river course (samples 8–21, Figure 8), and the same was confirmed by the PCA analysis (Table S6) and defined by Component 1 (which represents the tailings material in the flood wave). However, the PCA analysis did not include the central part of the river, due to the strong signal caused by the flood wave (Figure 7).

The PTEs found in the tailing material, with the highest content in the upper course of the river (As, Cd, Hg, Pb, Sb, Zn), characteristic elements in the areas of the Sb mine [57], are grouped in Component 1 (Figure 6) by the PCA analysis, which represents the tailing material in the flood wave and spatially coincides with the influence of Factor 3 in PMF (Figure 8). Hg has the greatest influence on Factor 3, which is conditioned by the connection of Hg with Sb and As [58]. However, the PMF Factor I, which is characteristic of the central part of the river (Figure 8), defines the long-term impact of the mine, considering the prevailing Pb, Cd, Sb and As, whose connection is characteristic of Sb mines [57,59].

By moving away from the spill site of tailings material, the influence of these PTEs decreases, and the influence of the geological substrate increases, which is explained by Component 2 of the PCA analysis as well as Factor 2 in the PMF model. These factors single out Cu and Mn as well as Cr and Ni, which are characteristic of the geological substrate of the Jadar river mouth [24]. The PCA analysis revealed that Cu and Mn are under the influence of Component 1, but with low loading, while Cr and Ni have a high negative factor loading regarding Component 1 (Table S6), indicating a double geological substrate of the studied middle and lower part of the basin, which was confirmed earlier [40]. Additionally, the PMF model indicates a double origin; in Factor 2 (geological substrate), primarily its influence in the lower part of the river with a high influence of Ni and Cr, compared to Cu and Mn, and in Factor 3 (tailings material in the flood wave), where Cu and Mn have a greater influence than Cr and Ni, which is conditioned by the connection of Sb and Mn [60] (Table 5 and Table S6, Figures 6–8).

The PCA analysis determined that the influence of tailings material is 65.38% (Component 1), and the influence of geological substrate is 23.64% (Component 2), while the PMF model defines the influence of mines as 28.08% (Table 5, Factor 1), and the influence of tailings material in the flood wave is reduced to 47.66% (Table 5, Factor 3). In addition, the average Cu content is lower than the average values determined for the area of Central Serbia (27 mg kg^{-1}) [61], and the *CV* (coefficient of variation) for Cu is 29%, and for Mn 16%, which is significantly lower than other PTEs and indicates their geological origin [62].

Considering the determined content of PTEs and their origin as well as the risk of pollution, the data for the estimated *HI* and TRC can also be interpreted.

Health risks due to exposure to PTEs in the vicinity of mines can occur due to the ingestion, dermal contact and inhalation of soil or indirectly through the consumption of plants and fruits. In this paper, the non-carcinogenic influence of all PTEs was considered, for which, although high concentrations were measured in the soil (Table 2), there is no non-carcinogenic risk for any PTEs except As (Table 6), where a threshold risk was determined. A sensitivity analysis (Figure 9) determined that the concentrations of As, Pb and Sb have the greatest influence on non-carcinogenic risks. The carcinogenic influence of Pb, Ni, Cr, Cd and As were considered (Table 7) and there is no carcinogenic risk in the studied area, except for the maximum value of As. The authors [3] determined, depending on the type of mine, that exposure to As concentrations is the highest in the case of multi-metal and antimony mining areas, and with it, the possible carcinogenic risk. It should be emphasised that different locations of mining areas in the world have different characteristics, which also affect the condition of the soil in the immediate vicinity [38,39,63].

5. Conclusions

The flooded soils are loaded with Zn, Pb, Cd, As, Sb and Hg content in the surface layers, in addition to the load with tailings material and due to the influence of mining activities and related industries (smelters) in the studied area. The total content of Sb, Hg, Pb, Cd and Zn, as well as the pollution index values decreases with distance from the tailings dump. Risk of contamination is determined in more than 54% of the flooded soil samples, as assessed by the *PLI*, and extremely pronounced in over 72%, assessed by the *RI*. PTEs found in the tailing material As, Cd, Hg, Pb, Sb and Zn, by content, are the highest in the upper course of the river, which is defined by the PMF model and PCA analysis. Hg has the greatest influence on the overburdened material, based on the PMF model, which is conditioned by the connection of Hg with Sb and As. The influence of mining activities is clearly visible, based on the results of the PMF analysis in the central part of the river course. In all studied samples of flooded soil, increased As content was found, which is expected considering that As is a companion of the ore deposits of the study area.

The non-carcinogenic impact of all PTEs was considered, for which, although high concentrations were measured in the soil, there is no non-carcinogenic risk for any, except As, for which a borderline risk was determined. A sensitivity analysis determined that the concentrations of PTEs have the greatest impact on non-carcinogenic risks. Based on the analysis, there is no carcinogenic risk in the studied area.

The study area is sensitive to threats from the accessibility of PTEs in the environment. Therefore, in the future, it will be necessary to establish continuous monitoring of the content of PTEs as well as analysis of available forms of PTEs.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/land12020421/s1, Table S1: Metal-dependent constants; Table S2: Toxicological parameters values for heavy metals; Table S3: Toxicological parameters for *HI* and *TCR* calculation; Table S4: The average values of PI for individual PTE; Table S5: The average values of Er for individual PTE; Table S6: rotated component matrix and total variance explained; File S1: Details of the parameters used in positive matrix factoring.

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References

1. Adriano, D.C. *Trace Elements in Terrestrial Environments: Biogeochemistry, Bioavailability and Risks of Metals*, 2nd ed.; Springer: New York, NY, USA, 2001; p. 867. [CrossRef]
2. Wu, Y.; Xu, Y.; Zhang, J.; Hu, S.; Liu, K. Heavy metals pollution and the identification of their sources in soil over Xiaoqinling gold-mining region, Shaanxi, China. *Environ. Earth Sci.* **2011**, *64*, 1585–1592. [CrossRef]
3. Tong, R.; Qingli, J.; Xiaofei, M.; Yingqian, F.; Wang, W. Comprehensive comparison of probabilistic health risks of soil heavy metals in China's mining areas, Human and Ecological Risk Assessment. *Int. J.* **2020**, *26*, 2059–2077. [CrossRef]
4. Wang, X.; He, M.; Xie, J.; Xi, J.; Lu, X. Heavy metal pollution of the world largest antimony mine-affected agricultural soils in Hunan province (China). *J. Soils Sediments* **2010**, *10*, 827–837. [CrossRef]
5. European Commission, Directorate-General for Internal Market, Industry, Entrepreneurship and SMEs; Blengini, G.; El Latunussa, C.; Eynard, U.; de Matoss, C.M.; Wittmer, D.; Georgitzikis, K.; Pavel, C.; Carrara, S.; Mancini, L.; et al. Study on the EU's List of Critical Raw Materials (2020): Final Report, Publications Office. 2020. Available online: https://data.europa.eu/doi/10.2873/11619 (accessed on 30 December 2022).
6. Vidojević, D.; Jovičić, M.; Dimi, B.; Baćanović, N. Environmental Degradation due to Damage to the Mine Tailings "Stolice" Kostajnik in 2014 (Degradacija Životne Sredine Usled Oštećenja Jalovišta Rudnika "Stololice" u Kostajniku 2014. Godine). Agency for Environmental Protection, Belgrade, Serbia. 2015. Available online: http://www.sepa.gov.rs/download/DegradacijaRudnikStolice.pdf (accessed on 21 December 2022). (In Serbian)
7. Nematollahi, M.J.; Keshavarzi, B.; Zaremoaiedi, F.; Ali Rajabzadeh, M.; Moore, F. Ecological-health risk assessment and bioavailabilityof potentially toxic elements (PTEs) in soil and plantaround a copper smelter. *Environ. Monit. Assess.* **2020**, *192*, 639. [CrossRef]
8. Kalinović, J.V. Possibilities of Using Wild Rose, Hawthorn and Blackthorn for Biomonitoring and Phytoremediation. Ph.D. Thesis, University of Belgrade, Technical faculty in Bor, Belgrade, Serbia, 2019.
9. Weissmannová, H.D.; Pavlovský, J. Indices of soil contamination by heavy metals—Methodology of calculation for pollution assessment (minireview). *Environ. Monit. Assess.* **2017**, *189*, 616. [CrossRef]
10. Martínez-Santos, M.; Probst, A.; García-García, J.; Ruiz-Romera, E. Influence of anthropogenic inputs and a high-magnitude flood event on metal contamination pattern in surface bottom sediments from the Deba River urban catchment. *Sci. Total Environ.* **2015**, *514*, 10–25. [CrossRef]
11. Shaheen, S.M.; Kwon, E.E.; Biswas, J.K.; Tack, F.M.G.; Ok, Y.S.; Rinklebe, J. Arsenic, chromium, molybdenum, and selenium: Geochemical fractions and potential mobilization in riverine soil profiles originating from Germany and Egypt. *Chemosphere* **2017**, *180*, 553–563. [CrossRef] [PubMed]
12. Guo, X.; Wang, K.; He, M.; Liu, Z.; Yang, H.; Li, S. Antimony smelting process generating solid wastes and dust: Characterization and leaching behaviors. *J. Environ. Sci.* **2014**, *26*, 1549–1556. [CrossRef] [PubMed]
13. Antić-Mladenović, S.; Kresović, M.; Čakmak, D.; Perović, V.; Saljnikov, E.; Ličina, V.; Rinklebe, J. Impact of a severe flood on large-scale contamination of arable soils by potentially toxic elements (Serbia). *Environ. Geochem. Health* **2018**, *41*, 249–266. [CrossRef] [PubMed]
14. WISE Uranium Project. 2022. Available online: https://www.wise-uranium.org/ (accessed on 15 April 2022).
15. EPA. Environmental Protection Agency, Guidelines for Ecological Risk Assessment (Published on May 14, 1998, Federal Register **1998**, *63*, 26846–26924). Available online: https://www.epa.gov/sites/default/files/2014-11/documents/eco_risk_assessment1998.pdf (accessed on 15 April 2022).
16. Goldblum, D.K.; Rak, A.; Ponnapalli, M.D.; Clayton, C.J. The Fort Totten mercury pollution risk assessment: A case history. *J. Hazard. Mater.* **2006**, *136*, 406–417. [CrossRef] [PubMed]
17. Guan, Y.; Shao, C.; Ju, M. Heavy metal contamination assessment and partition for industrial and mining gathering areas. *Int. J. Environ. Res. Public Health* **2014**, *11*, 7286–7303. [CrossRef] [PubMed]
18. Jeffrey, D.W.; Wilson, J.G.; Harris, C.R.; Tomlinson, D.L. The Application of Two Simple Indices to Irish Estuary Pollution Status. In *Estuarine Management and Quality Assessment*; Wilson, G., Halcrow, W., Eds.; Springer: Boston, MA, USA, 1985; pp. 147–161. [CrossRef]
19. Håkanson, L. An ecological risk index for aquatic pollution control. A sedimentological approach. *Water Res.* **1980**, *14*, 975–1001. [CrossRef]
20. Luo, W.; Lu, Y.L.; Gisey, J.P.; Wang, T.Y.; Shi, Y.J.; Wang, G.; Xing, Y. Effects of land use on concentrations of metals in surface soils and ecological risk around Guanting Reservoir, China. *Environ. Geochem. Health* **2007**, *29*, 459–471. [CrossRef]
21. Pejman, A.; Bidhendi, G.N.; Ardestani, M.; Saeedi, M.; Baghvand, A. A new index for assessing heavy metals contamination in sediments: A case study. *Ecol. Indic.* **2015**, *58*, 365–373. [CrossRef]
22. Belanović Simić, S.; Knežević, M.; Košanin, O.; Kadović, R.; Miljković, P.; Vićentijević, M.; Beloica, J. Potencijalni ekološki rizik od sadržaja štetnih mikroelemenata u zemljištima opštine Pančevo (Srbija), (eng. Potential ecological risk from the content of harmful microelements in the soils of the municipality of Pančevo (Serbia). In Proceedings of the Integrated Meeting "Soil 2015"), Zbornik Radova—Integrisani Skup "Zemljište 2015", Sremski Karlovci, Serbia, 12 May 2015; pp. 37–45.
23. Kowalska, J.B.; Mazurek, R.; Gąsiorek, M.; Zaleski, T. Pollution indices as useful tools for the comprehensive evaluation of the degree of soil contamination–A review. *Environ. Geochem. Health* **2018**, *40*, 2395–2420. [CrossRef]

24. Čakmak, D.; Perović, V.; Antić-Mladenović, S.; Kresović, M.; Saljnikov, E.; Mitrović, M.; Pavlović, P. Contamination, risk, and source apportionment of potentially toxic microelements in river sediments and soil after extreme flooding in the Kolubara River catchment in Western Serbia. *J. Soils Sediments* **2018**, *18*, 1981–1993. [CrossRef]
25. Miljković, P. Утицај начина коришћења земљишта на квлитет суспендованог наноса у сливу реке Расине (eng. The Influence of Land cover on the Quality of Suspended Sediment in the Rasina River Watershed). Ph.D. Thesis, Faculty of Forestry, University of Belgrade, Belgrade, Serbia, 2020.
26. Jiang, H.H.; Cai, L.M.; Wen, H.H.; Hu, G.C.; Chen, L.G.; Luo, J. An integrated approach to quantifying ecological and human health risks from different sources of soil heavy metals. *Sci. Total Environ.* **2020**, *701*, 134466. [CrossRef]
27. Kang, M.; Tian, Y.; Zhang, H.; Lan, Q. Distribution, ecological risk assessment, and source identification of heavy metals in river sediments from Hai River and its tributaries, Tianjin, China. *Water Air Soil Pollut.* **2020**, *231*, 38. [CrossRef]
28. USEPA (1989): Risk assessment guidance for superfund, Volume I: Human health evaluation manual (Part A), Interim Final, Office of Emergency and Remedial Response, EPA/540/1-89/0 02. Available online: https://www.epa.gov/sites/default/files/2015-09/documents/rags_a.pdf (accessed on 30 December 2022).
29. USEPA: Regional Screening Levels (RSLs)-User's Guide. 2020. Available online: https://www.epa.gov/risk/regional-screening-levels-rsls-users-guide (accessed on 2 July 2020).
30. USEPA: Regional Screening Levels (RSLs)—Equations. 2020. Available online: https://www.epa.gov/risk/regional-screening-levels-rsls-equations (accessed on 2 July 2020).
31. Čakmak, D.; Perović, V.; Kresović, M.; Pavlović, D.; Pavlović, M.; Mitrović, M.; Pavlović, P. Sources and a Health Risk Assessment of Potentially Toxic Elements in Dust at Children's Playgrounds with Artificial Surfaces: A Case Study in Belgrade. *Arch. Environ. Contam. Toxicol.* **2020**, *78*, 190–205. [CrossRef]
32. Čakmak, D.; Pavlović, D.; Matić, M. Procena štetnog uticaja potencijalno toksičnih elemenata (PTE) iz zemljišta na zdravlje ljudi (eng. Assessment of harmful effects of potentially toxic elements (PTE) from soil on human health). In *Procena Degradacije Zemljišta—Metode i Modeli (eng. Soil Degradation Assessment—Methods and Models)*; Simić, S.B., Ed.; University of Belgrade, Faculty of Forestry: Belgrade, Serbia, 2022; pp. 420–438.
33. Jadoon, S.; Muhammad, S.; Hilal, Z.; Ali, M.; Khan, S.; Khattak, N.U. Spatial distribution of potentially toxic elements in urban soils of Abbottabad city, (N Pakistan): Evaluation for potential risk. *Microchem. J.* **2020**, *153*, 104489. [CrossRef]
34. Varol, M.; Sünbül, M.R.; Aytop, H.; Yılmaz, C.H. Environmental, ecological and health risks of trace elements, and their sources in soils of Harran Plain, Turkey. *Chemosphere* **2020**, *245*, 125592. [CrossRef]
35. Wang, G.; Liu, H.Q.; Gong, Y.; Wei, Y.; Miao, A.J.; Yang, L.Y.; Zhong, H. Risk Assessment of Metals in Urban Soils from a Typical Industrial City, Suzhou, Eastern China. *Int. J. Environ. Res. Public Health* **2017**, *14*, 1025. [CrossRef] [PubMed]
36. Rinklebe, J.; Antoniadis, V.; Shaheen, S.M.; Rosche, O.; Altermann, M. Health risk assessment of potentially toxic elements in soils along the Central Elbe River, Germany. *Environ. Int.* **2019**, *126*, 76–88. [CrossRef] [PubMed]
37. Du Laing, G.; Rinklebe, J.; Vandecasteele, B.; Meers, E.; Tack, F.M.G. Trace metal behaviour in estuarine and riverine floodplain soils and sediments: A review. *Sci. Total Environ.* **2009**, *407*, 3972–3985. [CrossRef] [PubMed]
38. Lumbroso, D.; McElroy, C.; Goff, C.; Collel, M.R.; Petkovsek, G.; Wetton, M. The potential to reduce the risks posed by tailings dams using satellite-based information. *Int. J. Disaster Risk Reduct.* **2019**, *38*, 101209. [CrossRef]
39. Kossoff, D.; Dubbin, W.E.; Alfredsson, M.; Edwards, S.J.; Macklin, M.G.; Hudson-Edwards, K.A. Mine tailings dams: Characteristics, failure, environmental impacts, and remediation. *Appl. Geochem.* **2014**, *51*, 229–245. [CrossRef]
40. Belanović Simić, S.; Delić, D.; Miljković, P.; Beloica, J.; Lukić, S.; Stajković-Srbljinović, O.; Knežević, M.; Kadović, R. Impact of Tailing Outflow on Soil Quality Around the Former Stolice Mine (Serbia). In *Advances in Understanding Soil Degradation*; Saljnikov, E., Mueller, L., Lavrishchev, A., Eulenstein, F., Eds.; Springer: Cham, Switzerland, 2022; pp. 553–570. [CrossRef]
41. Belanović Simić, S.; Miljković, P.; Beloica, J.; Lukić, S.; Baumgertel, A.; Ilić, V.; Đukić, T.; Kadović, R. The impact of tailing outflow on the availability of potentially toxic elements (Zn, Cu, Pb, Cd) in soils near to former mine Stolice (Serbia). In Proceedings of the Abstracts of the Soils for the Future under Global Challenges, Sokobanja, Serbia, 21–24 September 2021; Available online: https://congress.sdpz.rs/wp-content/uploads/2021/09/Book-of-Abstracts_draft-2.pdf (accessed on 30 December 2022).
42. Stanley, C.J.; Jones, G.C.; Rumsey, M.S.; Blake, C.; Roberts, A.C.; Stirling, J.A.R.; Carpenter, G.J.C.; Whitfield, P.S.; Grice, J.D.; Lepage, Y. Jadarite, LiNaSiB3O7(OH), a new mineral species from the Jadar Basin, Serbia. *Eur. J. Mineral.* **2007**, *19*, 575–580. [CrossRef]
43. Yugoslav Society for Soil Science. *Chemical Methods of Soil Surveying, Book 1*; Yugoslav Society for Soil Research: Belgrade, Serbia, 1966. (In Serbian)
44. Official Gazette of RS, no. 30/2018 and 64/2019. Regulation on the Limit Values of Pollutant, Harmful and Dangerous Substances in the Soil (in Serbian: Uredba o Graničnim Vrednostima Zagađujućih, Štetnih i Opasnih Materija u Zemljištu). Available online: https://www.ekologija.gov.rs/sites/default/files/old-documents/Zemljiste/Uredbe/Uredba-o-granicnim-vrednostima.pdf (accessed on 13 January 2023).
45. Varol, M. Assessment of heavy metal contamination in sediments of the Tigris River (Turkey) using pollution indices and multivariate statistical techniques. *J. Hazard. Mater.* **2011**, *195*, 355–364. [CrossRef]
46. Mrvić, V.; Antonović, G.; Martinović, L.J. *Fertility and Content of Toxic and Dangerous Materials in Soil of Central Serbia*; Institute of Soil Science: Belgrade, Serbia, 2009. (In Serbian)

47. USEPA. *Hazardous Waste Land Treatment*; Report SW-874; Office of Soild Waste and Emergency Response: Washington, DC, USA, 1983.
48. Bowen, H.J.M. *Trace Elements in Biochemistry*; Academic Press: New York, NY, USA, 1966; p. 202.
49. Reimann, C.; Filzmoser, P.; Garrett, R.G. Background and threshold: Critical comparison of methods of determination. *Sci. Total Environ.* **2005**, *346*, 1–16. [CrossRef]
50. Hu, B.; Shao, S.; Fu, T.; Fu, Z.; Zhou, Y.; Li, Y.; Lin, Q.; Chen, S.; Shi, Z. Composite assessment of human health risk from potentially toxic elements through multiple exposure routes: A case study in farmland in an important industrial city in East China. *J. Geochem. Explor.* **2020**, *210*, 106443. [CrossRef]
51. USEPA. Risk Assessment Guidance for Superfund: Volume III-Part A, Process for Conducting Probabilistic Risk Assessment, 20460; Environmental Protection Agency, Office of Emergency and Remedial Response: Washington, DC, USA. EPA 540-R-02-002. 2001. Available online: https://www.epa.gov/sites/default/files/2015-09/documents/rags3adt_complete.pdf (accessed on 2 July 2022).
52. EPA PMF—The United States Environmental Protection Agency through its Office of Research and Development funded and collaborated in the research described here under Contract Number EP-D-09-097 to Sonoma Technology, Inc. Portions of the code are Copyright©2005-2013 ExoAnalytics Inc. and Copyright©2007-2013 Bytescout. Available online: https://www.epa.gov/air-research/positive-matrix-factorization-model-environmental-data-analyses (accessed on 15 September 2022).
53. Zhi, Y.; Li, P.; Shi, J.; Zeng, L.; Wu, L. Source identification and apportionment of soil cadmium in cropland of Eastern China: A combined approach of models and geographic information system. *J. Soils Sediments* **2015**, *16*, 467–475. [CrossRef]
54. Guan, Q.; Wang, F.; Xu, C.; Pan, N.; Lin, J.; Zhao, R.; Yang, Y.; Luo, H. Source apportionment of heavy metals in agricultural soil based on PMF: A case study in Hexi Corridor, northwest China. *Chemosphere* **2017**, *193*, 189–197. [CrossRef] [PubMed]
55. Yang, S.; He, M.; Zhi, Y.; Chang, S.X.; Gu, B.; Liu, X.; Xu, J. An integrated analysis on source-exposure risk of heavy metals in agricultural soils near intense electronic waste recycling activities. *Environ. Int.* **2019**, *133*, 105239. [CrossRef] [PubMed]
56. Ride, D.R. Section 14, Geophysics, Astronomy and Acoustics, Abundance of Elements in the Earth's Crust and in the Sea. In *CRC Handbook of Chemistry and Physics*, 85th ed.; Carmichae, R.S., Ed.; CRC Press: Boca Raton, FL, USA, 2005.
57. Zhou, S.; Hursthouse, A.; Chen, T. Pollution Characteristics of Sb, As, Hg, Pb, Cd, and Zn in Soils from Different Zones of Xikuangshan Antimony Mine. *J. Anal. Methods Chem.* **2019**, *2019*, 2754385. [CrossRef]
58. Hazen, R.; Golden, J.; Downs, R.T.; Hystad, G.; Grew, E.S.; Azzolini, D.; Sverjensky, D.A. Mercury (Hg) mineral evolution: A mineralogical record of supercontinent assembly, changing ocean geochemistry, and the emerging terrestrial biosphere. *Am. Mineral.* **2012**, *97*, 1013–1042. [CrossRef]
59. Čakmak, D.; Perović, V.; Saljnikov, E.; Jaramaz, D.; Sikirić, B. Spatial modeling of ecological areas by fitting the limiting factors for As in the vicinity of mine, Serbia. *Environ. Sci. Pollut. Res.* **2014**, *21*, 3764–3773. [CrossRef]
60. ATSDR: Agency for Toxic Substances and Disease Registry; Atlanta, G. Toxicological Profile for Antimony. 2019. Available online: https://www.atsdr.cdc.gov/ToxProfiles/tp.asp? (accessed on 13 December 2022).
61. Mrvić, V.; Sikirić, B.; Jaramaz, D.; Koković, N.; Nikoloski, M. Background and threshold values of potentially toxic elements in soil at Central part of Republic of Serbia. *Ratar. Povrt.* **2019**, *56*, 1–6. Available online: https://scindeks-clanci.ceon.rs/data/pdf/1821-3944/2019/1821-39441901001M.pdf (accessed on 30 December 2022). [CrossRef]
62. Karim, Z.; Qureshi, B.A.; Mumtaz, M.; Qureshi, S. Heavy metal content in urban soils as an 436 indicator of anthropogenic and natural influences on landscape of Karachi—A multivariate spatio–437 temporal analysis. *Ecol. Indic.* **2014**, *42*, 20–31. [CrossRef]
63. Ordónez, A.; Alvarez, R.; Charlesworth, S.; De Miguel, E.; Loredo, J. Risk assessment of soils contaminated by mercury mining, Northern Spain. *J. Environ. Monit.* **2011**, *13*, 128–136. [CrossRef] [PubMed]