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# Probabilistic Assessment of the Heavy Metal Pollution in Debrecen's Topsoil

Zsolt Zoltán Fehér<sup>1</sup>, Péter Tamás Nagy<sup>2</sup>

<sup>1</sup> Debrecen University of Agricultural Sciences

<sup>2</sup> University of Debrecen

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## Abstract

Understanding better the spatial and subsurface infiltration patterns of heavy metal distribution in urban soils can help in environmental and health risk assessment and the development of effective environmental policy. The present paper investigates the overall environmental quality of the Debrecen area in terms of heavy metal pollution and describes a simulation procedure for the spatial and statistical patterns of heavy metals in atmospheric deposited dust samples and the spatial diversity of health vulnerability. The research is based on the evaluation of 300 soil samples from Debrecen and its surroundings. Maps of topsoil major heavy metal distributions, including As, Cd, Cr, Co, Cu, Mo, Ni, Pb, and Zn, were obtained using sequential Gaussian simulation. Then, the pollution levels were determined from the stochastic maps, thus obtaining a comprehensive quantitative pollution characterization of the nine elements in the city. According to the results, the potential risk of pollutants to the environment is in the order of  $Cd > Mo > As > Cu > Ni > Cr > Pb > Co > Zn$ , with a pollution load of 0.66. Cd, Mo, and Cu are the main toxic pollutants in Debrecen topsoils, with mean concentrations of 1.9 mg/kg, 77.3 mg/kg, and 1.4 mg/kg, exceeding the threshold values by 0.9 mg/kg, 2.3 mg/kg, and 0.4 mg/kg, respectively. The stochastic models assessed the uncertainties and risks related to the spatial distribution of heavy metals in soil within the contaminated areas, and a positive correlation can be found between the increase in pollution values above the predetermined threshold limits and the corresponding increase in threshold levels. Additionally, there is a consistent decrease in the relative area of excess contamination, although the ecological pollution index (96.9) revealed the Debrecen region as a hotspot area for considerable risk of contamination that needs continuous monitoring and remediation.

**Zsolt Zoltán Fehér<sup>\*</sup>**, and **Péter Tamás Nagy**

*University of Debrecen, Institute of Water and Environmental Management,  
Böszörményi u. 146b, Debrecen, Hungary*

<sup>\*</sup>Email: [feher.zsolt@agr.unideb.hu](mailto:feher.zsolt@agr.unideb.hu)

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## 1. Introduction

Soil continues to play a very vital role in providing ecosystem services to man and his surroundings. The exploitation of soil resources for economic benefit, such as urbanization, industrialization, and intensive agricultural production practices, has become a major concern for the environment due to the degradation effects caused by pollutant substances released from these activities, and among these substances, heavy metal elements could be contained (Wang et al., 2023). The rapid growth of economic activities in Hungary is on the rise and started about 5 decades ago, with prior developments giving inadequate consideration to environmental management. The region continues to face high industrialization, urbanization, energy production, transportation, and mechanized agricultural growth with a lot of environmental threats, especially heavy metal pollutants. Sources of these heavy metal pollutants in the environment could be of natural forms or human induced (Lu et al., 2012). The natural forms of these elements are usually from soil formation processes such as the breakdown of rock particles that cause lower harm to the ecological systems (Javed et al., 2020). The human-induced forms of heavy metal pollutants are of multiple sources and can cause serious environmental threats, damage, and thus need to be given adequate attention (Zhou et al., 2020).

For effective remediation and mitigation, the concentrations and sources of these pollutants need to be investigated (Huang et al., 2015). However, the differences in elevation, edaphic, and other natural factors cause a lot of variabilities in these elements across the entire region (Liu et al., 2016). These heterogeneities can effectively be captured spatially by employing geostatistical analyses and multivariate statistical analyses for their sources and relationships (Hou et al., 2017). However, most of these methods don't clearly capture the minor and major heterogeneities of these pollutants, with only emphasis given to their spatial distribution (Shi et al., 2018). Further, earlier research studies in determining health risks associated with these pollutants have used deterministic approaches that focus on the use of single point values to assess environmental risks associated with these elements, which result in uncertainties in the obtained results (Brtnický et al., 2019; yang et al., 2019). These uncertainties could be attributed to various factors such as pollutant concentration, source, and interactive behavior within the environments (yang et al., 2019).

To overcome these limitations, this study uses deterministic approaches and probabilistic methods such as Gaussian simulation to provide concrete results for the risk assessments associated with heavy metal pollution. The study was conducted in Debrecen urban and surrounding areas with the overall objective of investigating the environmental quality of the region with regard to heavy metal pollution and specially determining (i) concentration of the heavy metal pollutants, (ii) possible sources and interactions of these elements, (iii) spatial distribution, and (iv) assess the ecological risks associated with elements.

## 2. Materials and methods

## 2.1. Area of study

Debrecen is the second largest city in Hungary by population and third by land area, with about 200,000 people and 461.25 km<sup>2</sup> respectively. It is situated in Hajdú-Bihar County, bordered by Hajdúság and Nyírség landscapes in the eastern region of the country. Due to soil sealing and natural deposition, the soil surface depth ranges between 2 to 3 meters (Csorba, 2008), with previous research studies indicating the distribution of heavy metal contamination originating from transportation, urban settlements, and activities. The 2009 environmental protection program of Debrecen identified the pharmaceutical company (TEVA), fuel stations, airport, food companies, plastic industries, train service station (MÁV), and communal waste dumping sites to be among the other polluting agents within the area.



**Fig. 1.** Location and sampling procedures of the study area

## 2.2. Soil Sampling

A total of 300 soil samples at uniformly designated areas with the help of the geographic coordinate system were excavated using soil augers and shovels from the top surface of 0 to 20 cm depth across the entire Debrecen urban and non-urban areas. Materials such as stones, roots, and plant debris were separated in situ from the soil particles and carefully packed in polythene bags and labelled for laboratory analysis.

## 2.3. Analytical Procedures

The collected samples were taken to the laboratory and air dried for 48 hours. The dried samples were sieved to obtain fine soil particles, which were then subjected to crushing in a mortar to obtain fine soil particles and homogenize the soil fractions. The homogenized soil samples were placed into sample bags and introduced to a portable handheld Niton XL5 Plus X-ray fluorescence (XRF) analyzer. After a few seconds to several minutes, the device detected element pollutant and trace element concentration, whose values were then noted down. The elements analyzed included arsenic (As), calcium (Ca), cadmium (Cd), total chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), potassium (K), manganese (Mn), molybdenum (Mo), nickel (Ni), lead (Pb), titanium (Ti), vanadium (V), and zinc (Zn).

## 2.4. Assessment of Heavy Metal Pollution in the Soil

Various indices were applied to assess the contamination of heavy metals and trace elements in the top soil – water system, and among them, pollutant accumulation index (PGI), heavy metal enrichment index (HMEI), ecological risk index (ERI), and heavy metal pollution load index (HMPLI) were used.

### 2.4.1. Pollutant Accumulation Index (PGI)

In assessing the risk of contamination to the soil and other environmental parameters, the human activity impact on the extent of each heavy metal element in the soil segments was assessed using the pollutant accumulation index (Muller, 1969), as follows;

$$PGI = \log_2 \frac{\text{conc}(n)}{xB(n)}$$

where Conc(n) = measured concentration of the individual heavy metal / pollutant

x = correction index (1.5) to cater for the lithogenic effects, and B(n)= maximum permissible concentration of the element in Debrecen. In Debrecen, the maximum permissible concentration values of As, Cd, Co, Cr, Cu, Ni, Pb, and Zn are; 15, 1, 30, 75, 75, 40, 100, and 200 mg/kg, respectively (Hungarian legislation 6/2009. (IV. 14.) KvVM-EüM-FVM, Appendix 1). The extent of pollution can be categorized as:  $PGI < 0$ , no pollution; 1-2, low pollution; 2 - 3, moderate pollution; 3 - 4, high pollution; and  $PGI \geq 4$ , very high pollution (Muller 1981).

#### 2.4.2. Heavy Metal Enrichment Index (HMEI)

The enrichment factor index was used to determine the increment of the pollutant in the soil medium relative to the amount of the element naturally occurring in the environment as a result of human activity;

$$HMEI = \frac{[\text{Conc}(n)/\text{Conc}(X)]}{[B(n)/\text{Conc}(X)]} = \frac{\text{conc}(n)}{B(n)}$$

Where Conc (n) = measured concentration of the individual heavy metal in polluted soil, Conc(x) = total concentration of a reference / baseline element for normalization. In this case, the total iron concentration (mg/kg) is used as a reference element, and B(n)= maximum permissible concentration of the element in unpolluted soil (Abraham and Parker 2008; Wang and Lu, 2011). The degree of enrichment can be categorized as follows: HMEI value  $< 1$  = deficiency or no enrichment, 1 to 3 = moderate enrichment, 3 to 6 = considerable enrichment,  $> 6$  = very high enrichment (Gyamfi et al., 2022).

#### 2.4.3. Risks of the Pollutants to the Ecosystem

The degree of heavy metal pollution and potential ecological risk to the environment in Debrecen was assessed using the ecological risk index (Hakanson, 1980).

$$Y_r^n = W_r^n \times \frac{\text{conc}(n)}{B(n)}$$

$$ERI = \sum^n W_r^n \times \frac{\text{conc}(n)}{B(n)}$$

Where  $Y_r^n$  = Potential risk index of individual heavy metals;  $W_r^n$  = Toxicity response parameter / coefficient values of each heavy metal; and ERI= sum of all ecological risk indices of the heavy metals.

The toxicity coefficients for heavy metals are as follows: As = 10, Cd = 30, Co = 5, Cr = 2, Cu = 5, Ni=5, Mo=15, Pb = 5, and Zn=1. The levels of ecological risk can be grouped as follows:  $ERI < 40$  [low risk], 40 - 80 [moderate risk], 80 - 160 [considerable risk], 160 -320 [high risk], and  $ERI \geq 320$  [very high risk] (Darko et al., 2019).

#### 2.4.4. Heavy Metal Pollution Load Index (HMPLI)

The total extent of contamination in the soil was calculated as follows:

$$HMPLI = \left( HMEI_{As} \times HMEI_{Cd} \times HMEI_{Co} \dots \times HMEI_{Zn} \right)^{1/t}$$

where t is the total number of heavy metals assessed in the study, and HMEI is the Heavy Metal Enrichment Index of each heavy metal (Tomlinson et al., 1980). The categorization of HMPLI is as follows:  $HMPLI \leq 0$  = control, 0-1 = baseline level of pollutants,  $>1$  = continuous degradation of the environment due to increased heavy metal contamination (Gupta et al., 2013).

#### 2.5. Statistical Analysis

ArcGIS Pro was used to analyze the spatial distribution of the heavy metals by applying kriging interpolation and stochastic simulation (Gaussian simulation). Multivariate methods in *Statgraphics Centurion 18* software were used to determine the relationships among the heavy metals, such as (1) multiple variable analysis to calculate the summary statistics for each metal and their correlations; (2) principal component analysis (PCA) to show large variations existing among the heavy metals and their linear combinations; (3) cluster analysis (CA) to group the heavy elements in accordance with their similarities.

### 3. Results and Discussion

#### 3.1. Statistical Description for the Pollutants and Trace Elements in the Topsoil of Debrecen

The chemical characteristics of the topsoil across Debrecen's urban and non-urban areas are summarized (Table 1) and compared to the city environmental standards.

**Table 1.** Statistical summary for the eight pollutant elements and seven trace element concentration of Debrecen top soil

Element	No. of samples	Median (mg/kg)	Mean (mg/kg)	Standard deviation (mg/kg)	Coefficient of variation (%)	Lower limit (95% CI)	Upper limit (95% CI)	Pollution limit value (Soil) of Debrecen (mg/kg organic dry matter compounds)	Pollution limit value (Water) of Debrecen (µg/L inorganic compounds)
<b>Cu</b>	295	28.4	<b>77.3</b>	136.9	176.9	61.7	93.0	75	200
<b>Cd</b>	276	1.7	<b>1.9</b>	1.0	52.3	1.8	2.0	1	5
<b>Mo</b>	285	1.4	<b>1.4</b>	0.6	43.4	1.3	1.5	1	20
<b>As</b>	295	9.2	9.9	5.0	50.6	9.3	10.4	15	10
<b>Cr</b>	285	68.4	65.3	35.6	54.5	61.1	69.4	75	50
<b>Co</b>	289	8.1	7.7	3.0	38.3	7.4	8.1	30	20
<b>Ni</b>	253	16.9	17.5	11.3	64.4	16.1	18.9	40	20
<b>Pb</b>	169	15.9	29.7	35.9	120.8	24.3	35.2	100	10
<b>Zn</b>	296	65.7	89.1	90.1	101.1	78.8	99.4	200	200
<b>Ca</b>	295	24378.2	18360.9	12276.6	66.9	16954.2	19767.7		
<b>Fe</b>	288	8164.5	6563.4	5131.8	78.2	5968.3	7158.6		
<b>K</b>	293	8452.8	7233.6	5246.7	72.5	6630.4	7836.9		
<b>Mn</b>	295	412.5	375	220.0	58.7	349.8	400.3		
<b>Ti</b>	289	2272.5	1899	1125.8	59.3	1768.7	2029.3		
<b>V</b>	286	74.7	69.3	35.7	51.5	65.1	73.4		

*CI signifies cumulative interval.*

The mean value concentration of Cu, Cd, Mo exceeded the permissible limits of the Debrecen region by 2.3, 0.9, and 0.4 mg/kg, respectively. However, the total element concentration in the region is in the order of Ca > K > Fe > Ti > Mn > Zn > Cu > V > Cr > Pb > Ni > As > Co > Cd > Mo (Table 1). The coefficients of variation for Cu, Pb, and Zn, respectively, were very high (> 100 %), portraying an indication of human interference in their concentrations in the environment (Chen et al., 2019). Moderate to low variability was exhibited by Ti, Mn, Cr, Cd, V, As, Mo, Co, with variation coefficient values of 59.3%, 58.7%, 54.5%, 52.3%, 51.5%, 50.6%, 43.4%, and 38.3%, respectively (Table 1), indicating minimal to no interference on their concentrations by human-induced activities and that their sources of origin could have been similar.

### 3.2. Spatial pattern (Vertical and horizontal distribution of pollutants and trace elements) in Debrecen urban and non-urban top soils

The spatial distribution and continuity of the pollutants are presented in Fig. 2 and 3, respectively. The horizontal and vertical distribution of Mn, Zn, Cr, Pb, Ni, As, Co is quite similar to each other, with the exception of Cu and Cd (Fig. 2), with the highest concentrations situated in the western central region of Debrecen for the seven pollutants and the eastern central region for the two pollutants (Cu and Cd). The overall heavy metal concentration in the area is in the order of Mn >



Zn > Cu > Cr > Pb > Ni > As > Co > Cd (Table 1). Mn is the most abundant pollutant in the topsoil of Debrecen due to mining and the abundance of oxides, carbonates, and sulphates in the soil. It is considered an essential micronutrient for plants and animals, but, however, higher intake can cause serious health problems (Dey et al., 2023).

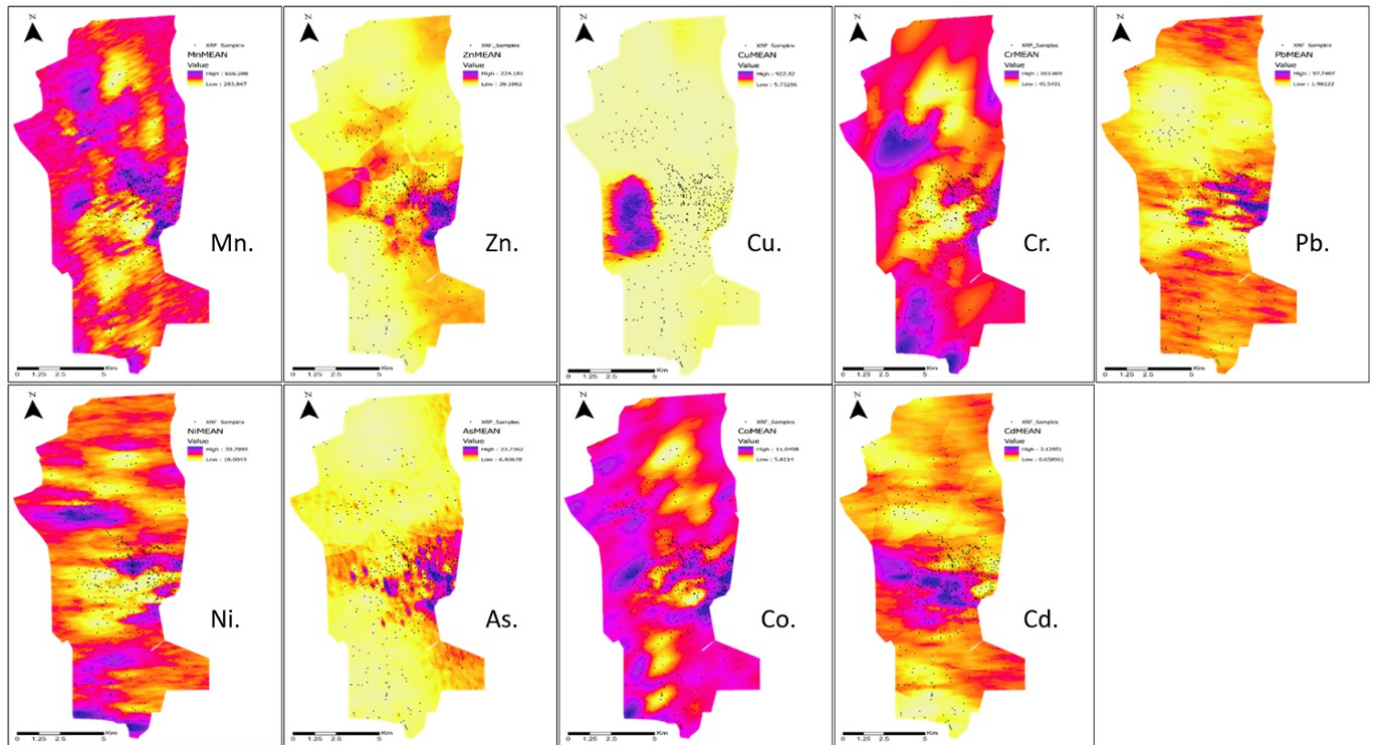


Fig. 2. Spatial distribution maps for the heavy metal concentration: expected type estimation

Fig. 3 shows how the heavy metals stretch across the entire study area. Cr and Co major and minor ellipsoids are very similar and stretch towards the northwestern direction. Mn, Zn, Cu, Pb, and As all stretch towards the northern direction. Ni and Cd stretch differently from the rest of the elements, where Ni is greatly found in the central region stretching from the East to the western region and Cd from the southwestern to northeastern direction (Fig. 3).

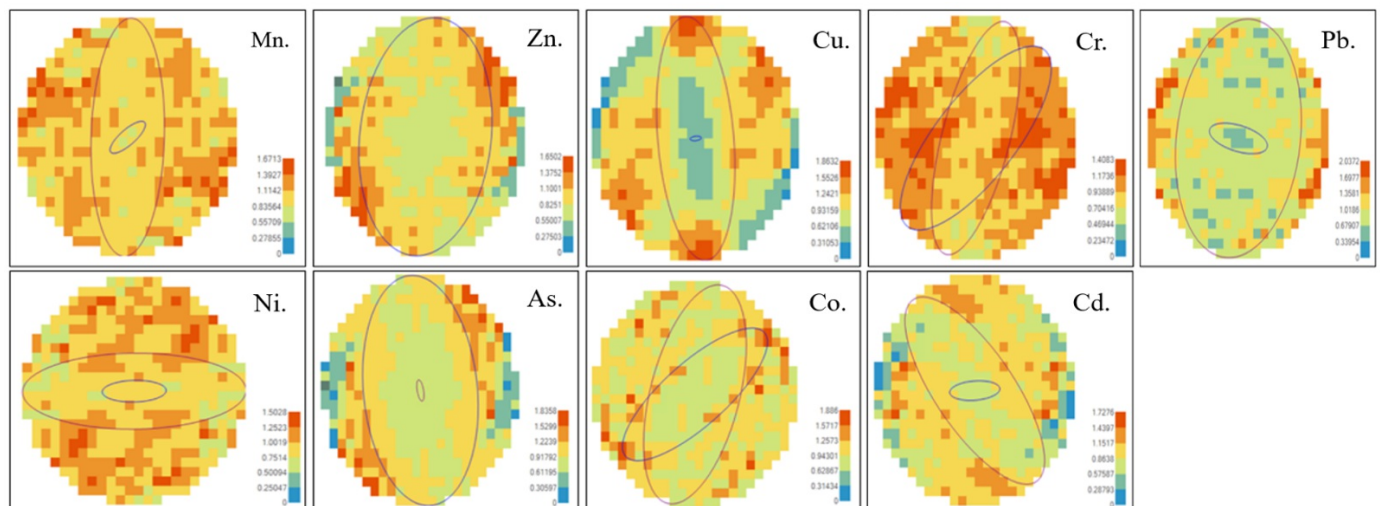
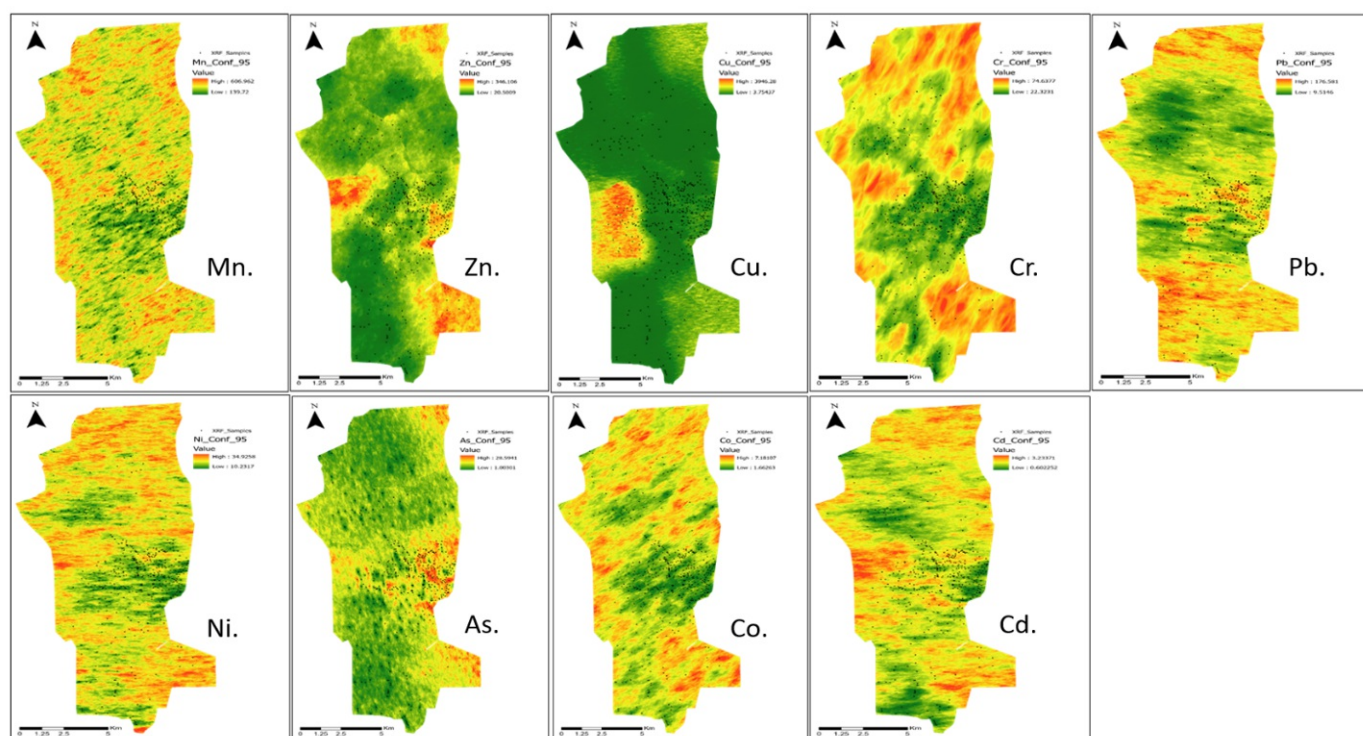


Fig. 3. Spatial continuity of the heavy metals

Fig. 4 shows that within the surveyed areas, yellow to red colored portions have a very high possibility (95%) of finding the given pollutants, and the light to dark green portions have less certainty that the pollutants will be found.



**Fig. 4.** Estimation uncertainty of the sequential simulation at the 95% confidence level

### 3.3. Relationships among the pollutant and trace elements

The Pearson correlation coefficients (Table 2) show possible sources, diffusion, adsorption, and absorption processes between the pollutant and trace elements. High positive correlations were observed between As and Pd (0.66), Cd and Mo (0.71), As and Zn (0.45), indicating a common source and spreading pattern. Previous research findings revealed that As is majorly attributed to agricultural activities while other elements are attributed by anthropogenic activities (Bhattacharya et al., 2007).

**Table 2.** Coefficients of correlations between pollutant and trace elements at  $p < 0.05$  significance



	As	Ca	Cd	Co	Cr	Cu	Fe	K	Mn	Mo	Ni	Pb	Ti	V	Zn	
As		0.12	0.16	0.28	-0.04	0.27	0.22	-0.04	0.23	0.16	-0.08	<b>0.66</b>	0.00	-0.01	<b>0.43</b>	
Ca	0.12		0.15	-0.04	-0.08	0.08	0.05	-0.07	0.06	0.12	-0.06	0.06	-0.07	-0.03	0.15	
Cd	0.16	0.15		-0.01	-0.25	0.06	-0.04	-0.38	-0.19	<b>0.71</b>	<b>-0.52</b>	0.11	-0.29	-0.29	0.12	
Co	0.28	0.04	0.01		0.18	0.25	0.19	0.05	0.33	-0.11	0.09	0.15	0.21	0.22	0.23	
Cr	0.04	-0.08	-0.25	0.18		0.07	0.17	0.24	0.15	-0.34	0.24	0.12	0.27	0.22	0.02	
Cu	0.27	0.08	0.06	0.25	0.07		0.12	0.04	0.22	0.07	-0.06	0.22	-0.03	-0.04	0.26	
Fe	0.22	0.05	0.04	0.19	0.17	0.12		0.15	0.27	0.02	0.12	0.20	0.15	0.05	0.13	
K	0.04	-0.07	-0.38	0.05	0.24	0.04	0.15		0.20	-0.34	0.37	-0.05	0.24	0.12	0.03	
Mn	0.23	0.06	-0.19	0.33	0.15	0.22	0.27	0.20		-0.14	0.25	0.16	0.14	0.19	0.26	
Mo	0.16	0.12	<b>0.71</b>	-0.11	-0.34	0.07	-0.02	-0.34	-0.14		<b>-0.43</b>	0.01	-0.32	-0.38	0.09	
Ni	-0.08	0.06	<b>-0.52</b>	0.09	0.24	-0.06	0.12	0.37	0.25	<b>-0.43</b>		-0.05	0.22	0.31	-0.09	
Pb	<b>0.66</b>	0.06	0.11	0.15	0.12	0.22	0.20	0.05	0.16	-0.01	-0.05		-0.03	-0.06	0.31	
Ti	0.00	0.07	-0.29	0.21	0.27	-0.03	0.15	0.24	0.14	-0.32	0.22	-0.03		0.35	0.01	
V	-0.10	0.03	-0.29	0.22	0.22	-0.04	0.05	0.12	0.19	-0.38	0.31	-0.06	0.35		-0.04	
Zn	<b>0.43</b>	0.15	0.12	0.23	-0.02	0.26	0.13	0.03	0.26	0.09	-0.09	0.31	0.01	-0.04		

Principal component analysis identified several linear combinations of fifteen metals to explain the variabilities among their concentrations and existences. Of these total factors, six components with eigenvalues  $\geq 1$  accounted for 62.931% variability and were extracted (Table 3).

**Table 3.** Pollutant and trace element characteristics in the top soil of Debrecen

PCA No's	Eigenvalue	%. Variance	%. Cumulation
1	2.61779	17.452	17.452
2	2.26137	15.076	32.528
3	1.26018	8.401	40.929
4	1.15344	7.690	48.619
5	1.11728	7.449	56.067
6	1.02959	6.864	<b>62.931</b>
7	0.867606	5.784	68.715
8	0.830428	5.536	74.251
9	0.719965	4.800	79.051
10	0.670079	4.467	83.518
11	0.647759	4.318	87.837
12	0.61567	4.104	91.941
13	0.509089	3.394	95.335
14	0.389908	2.599	97.934
15	0.309852	2.066	100.000

A factor analysis was performed to give further investigations of the potential sources and nature of the pollutants and trace elements in the area of Debrecen. Six factors accumulated a variance of 62.93% with eigenvalues  $\geq 1$ . The matrix of factor loadings is presented in Table 4. Six potential sources of these pollutants were identified, with the greatest variability (17.452%) attributed by Factor 1, indicating a high positive total loading (3.79) for As, Pb, and Zn with an eigenvalue of 2.618. Factor 2 loaded a total of 0.11 with Cd, Mo demonstrating high positive and Ni high negative loadings, respectively, accounting for 15.08% variability and an eigenvalue of 2.261. Factor 3 loaded with Cr, Ti, accounting for 8.4% variability, while Factor 4 loaded with Co and V, accounting for 7.69% variability. Factor 5 greatly loaded with Cu, accounting for 7.45% variation, and Factor 6 with a very strong negative loading of Ca, accounting for 6.86% variability (Table 4).

**Table 4.** Matrix of factor loading After Varimax rotation

Elements	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
As	<b>0.789912</b>	0.112526	0.0612384	-0.0319298	0.0885215	-0.0345144
Ca	0.0258761	-0.102559	0.0779222	0.059626	-0.150382	<b>-0.802839</b>
Cd	0.171891	<b>0.822564</b>	0.0654362	0.20623	-0.0130617	0.0470282
Co	0.40386	0.143389	0.0313407	<b>0.535107</b>	0.254273	-0.237766
Cr	0.1745	-0.198537	<b>0.621466</b>	-0.0642082	0.232587	-0.00286639
Cu	0.012317	-0.102026	0.182004	-0.0236237	<b>0.7633</b>	0.302608
Fe	0.437491	-0.0315251	0.416568	0.0530522	-0.218013	0.219782
K	0.00327703	-0.448046	0.323822	0.0269841	-0.56447	0.149306
Mn	0.40733	-0.381798	0.105571	0.447291	0.0302613	0.275173
Mo	0.201415	<b>0.74629</b>	-0.0309919	-0.0176618	0.00363914	0.2801
Ni	0.0881466	<b>-0.651409</b>	0.0973896	0.315854	-0.0298673	0.147328
Pb	<b>0.793851</b>	0.0621002	0.0574613	-0.128689	0.150094	-0.194327
Ti	-0.120009	0.104811	<b>0.786812</b>	0.0999461	-0.0673974	-0.130138
V	-0.24479	-0.04398	0.0125195	<b>0.753277</b>	-0.133453	-0.0311986
Zn	<b>0.650864</b>	0.0767387	-0.0829475	0.0734102	-0.210291	0.209805
Total	<b>3.79</b>	0.11	3.46	2.29	0.14	0.23
Eigenvalue	2.61779	2.26137	1.26018	1.15344	1.11728	1.02959
Variability %	17.452	15.076	8.401	7.690	7.449	6.864
Cumulative %	17.452	32.528	40.929	48.619	56.067	62.931

From the results, it is clearly shown that Factor 1 is the major contributor to pollution, mainly As, Pb, and Zn, due to mining and industrial activities (Li et al., 2023; Xu et al., 2022). The second factor shows a strong positive loading of Cd, Mo, and a strong negative load of Ni. This could be attributed to mining activities as well as surface runoff due to human activities and natural factors (Long et al., 2018). Factor 6 shows a very high extraction of Ca, which could be attributed to the mining of soil and wastes. This element exists in the form of  $\text{Ca}^{2+}$  in soluble forms which are easily leached away, thus exhibiting toxicity to the water system (Long et al., 2018). Some elements intersect in each factor, although in low quantities, due to natural occurrences and chemical bonding.

### 3.3. Heavy metal contamination in Debrecen urban and non-urban areas

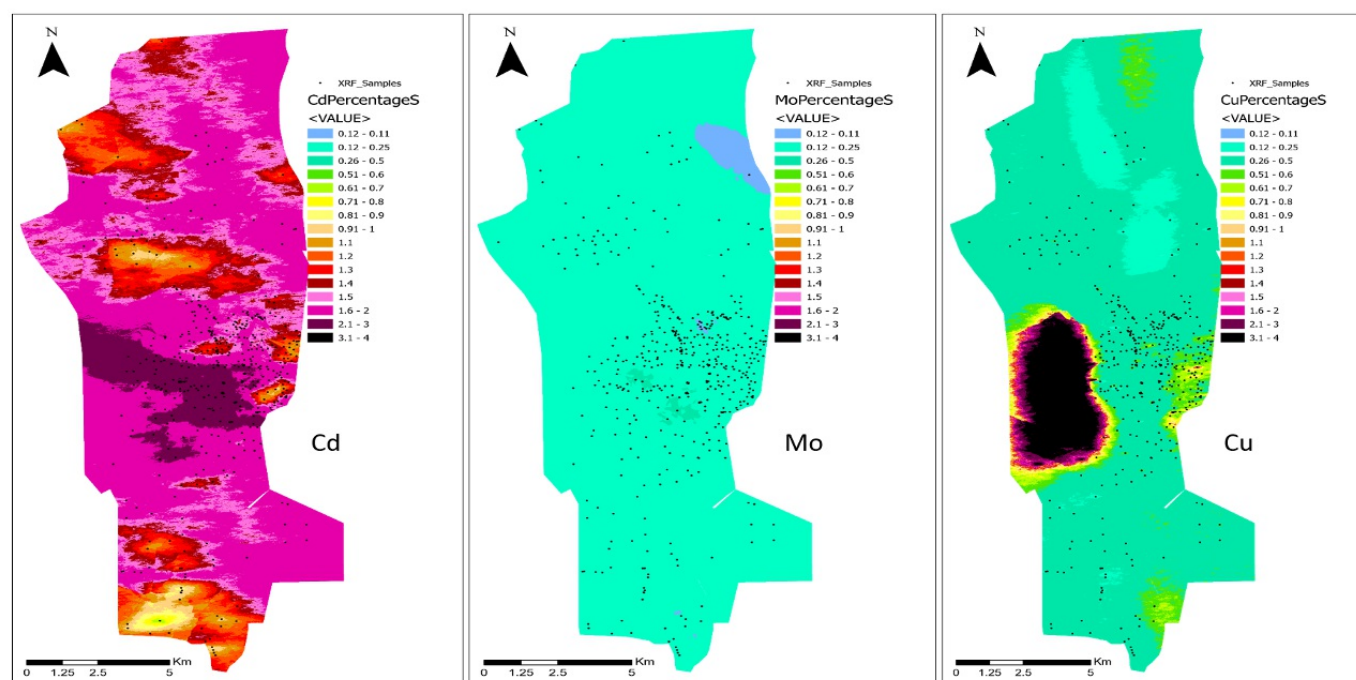
Several pollution indices were used to compute the extent of heavy metal contamination in the Debrecen area, such as the Pollutant Accumulation Index (PGI), Heavy Metal Enrichment Index (HMEI), Potential Risk Index ( $Y_r^n$ ), Environmental Risk Index (ERI), and Heavy Metal Pollution Load Index (HMPLI) (Table 5).

**Table 5.** Degree of contamination based on various pollution indices

Element	Mean (mg/kg)	Pollution limit value (Soil) of Debrecen (mg/kg organic dry matter compounds)	Pollutant accumulation index (PGI)	Heavy metal Enrichment Index (HMEI)	Toxicity coefficients of the elements	Potential risk index of each element ( $\gamma_r^n$ )
<b>Cd</b>	1.9	1	0.4	1.9	30.0	57
<b>Mo</b>	1.4	1	0.3	1.4	15.0	21.0
<b>As</b>	9.9	15	0.1	0.7	10.0	6.6
<b>Cu</b>	77.3	75	0.2	1.0	5.0	5.2
<b>Ni</b>	17.5	40	0.1	0.4	5.0	2.2
<b>Cr</b>	65.3	75	0.2	0.9	2.0	1.7
<b>Pb</b>	29.7	100	0.1	0.3	5.0	1.5
<b>Co</b>	7.7	30	0.1	0.3	5.0	1.3
<b>Zn</b>	89.1	200	0.1	0.4	1.0	0.4
<b>ERI</b>						<b>96.9</b>
<b>HMPLI</b>						<b>0.66</b>

Based on the computations of PGI, the Debrecen area is unpolluted to low polluted for all the pollutants. The heavy metal enrichment index indicates that the Debrecen region was moderately nourished with Cd, Mo, and Cu. The other elements (As, Ni, Cr, Pb, Co, and Zn) were deficient (Table 5).

For better analysis of the spatial distribution of the major pollutants, the mean concentrations of these elements (Cu=77.3 mg/kg, Mo= 1.4 mg/kg, and Cd=1.9) were compared against the permissible limits set out for the geological environment in Hungarian legislation 6/2009. (IV. 14.) KvVM-EüM-FVM, Appendix 1 as follows: Cu =75mg/kg, Mo= 1 mg/kg, and Cd = 1 mg/kg of organic dry matter compounds, whose ratios were then obtained in Fig. 5 for hotspot identification of those areas above the environmental limits.



**Fig. 5.** The ratio of the simulated element concentrations relative to the limit value for the region

The ecological environments of Debrecen can be noted to be considerably at risk of contamination, with high risks to flora and fauna (ERI = 96.9). The potential risk of the heavy metals is in the order of  $Cd > Mo > As > Cu > Ni > Cr > Pb > Co > Zn$ , with a pollution load of 0.66, which is at a baseline level for the pollutants.

The results reveal Cd, Mo, and Cu as the main toxic pollutants in Debrecen topsoils. These results are quite similar to studies on surface materials in other regions by (Xiao et al., 2021; Deng et al., 2020). The enrichment factors of Cd and Mo were moderate, with principal component analysis identifying a similar source (Table 4). These results are in line with the findings by Zhang et al. (2015) with regard to the Cd pollutant, whose main sources are majorly agricultural activities and waste substances.

## 4. Conclusion

The study, in conclusion, uses stochastic methods to identify the distribution of heavy metal pollutants and their uncertainties across Debrecen as the study area. Various pollution indices, together with multivariate statistical analysis, are employed for source identification and variability assessments of the pollutants in the topsoil.

Minor and major heterogeneities of pollutants were captured effectively across the study area by the stochastic model. The heavy metal concentration spatial continuity was revealed by the continuity maps generated by the model, which helped for site-specific interventions in the form of remediation and further analyses, saving time and costs involved in environmental quality monitoring of the study area.

The ecological pollution index revealed the Debrecen region as a hotspot area for considerable risk to the soil-water

system and life. The potential risk of pollutants to the environment is in the order of  $Cd > Mo > As > Cu > Ni > Cr > Pb > Co > Zn$ . Although the pollution load is at a baseline level, these pollutants need to be frequently monitored, and elements with concentrations above the threshold values, such as Cu, Cd, and Mo, need to be remediated in areas with high concentrations to mitigate their environmental risks.

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## References

- Abraham GMS, Parker RJ (2008) Assessment of heavy metal enrichment factors and the degree of contamination in marine sediments from Tamaki Estuary, Auckland, New Zealand. *Environ Monit Assess* 136:227–238
- Bhattacharya, P., Welch, A.H., Stollenwerk, K.G., McLaughlin, M.J., Bundschuh, J., Panaullah, G., 2007. Arsenic in the environment: biology and chemistry. *Sci. Total Environ.* 379, 109–120
- Brtnický, M., Pecina, V., Hladký, J., Radziemska, M., Koudelková, Z., Klimánek, M., Richtera, L., Adamcová, D., Elbl, V., Galiová, M.V., Baláková, L., Kynický, J., Smolíková, V., Houška, J., Vavřek, M.D., 2019. Assessment of phytotoxicity, environmental and health risks of historical urban park soils. *Chemosphere* 220, 678–686.
- Chen, L., Wang, G., Wu, S., Xia, Z., Cui, Z., Wang, C., Zhou, S., 2019. Heavy metals in agricultural soils of the lihe river watershed, east China: spatial distribution, ecological risk, and pollution source. *Int. J. Environ. Res. Publ. Health* 16. <https://doi.org/10.3390/ijerph16122094>, 2094
- Csorba, P. 2008. Landscape ecological fragmentation of the small landscape units (Microregions) of Hungary based on the settlement network and traffic infrastructure. *Ekológia (Bratislava)* Vol. 27. No.1.
- Deng, M., Yang, X., Dai, X.i., Zhang, Q.i., Malik, A., Sadeghpour, A., 2020. Heavy metal pollution risk assessments and their transportation in sediment and overlay water for the typical Chinese reservoirs. *Ecol. Ind.* 112, 106166
- Dey, S. S., Tripathy, B., Kumar, & Das, A. P. (2023). Ecotoxicological consequences of manganese mining pollutants and their biological remediation. *Environmental Chemistry and Ecotoxicology*, 5, 55–61. <https://doi.org/10.1016/j.enccco.2023.01.001>
- G. Darko, K.O. Boakye, M.A. Nkansah, O. Gyamfi, E. Ansah, M. Dodd, Human health risk and bioaccessibility of toxic metals in topsoils from gbani mining community in Ghana, *J. Heal. Pollut.* 9 (2019), 190602, <https://doi.org/10.5696/2156-9614-9.22.190602>.
- Gupta S, Satpati S, Saha RN, Nayek S (2013) Assessment of spatial and temporal variation of pollutants along a natural channel receiving industrial wastewater. *Int J Environ Eng* 5(1):52–69
- Hou, D., O'Connor, D., Nathanail, P., Tian, L., & Ying, M. (2017). Integrated GIS and multivariate statistical analysis for regional scale assessment of heavy metal soil contamination: A critical review. *Environmental Pollution*, 231, 1188–1200. <https://doi.org/10.1016/j.envpol.2017.07.021>



- Huang, Y., Li, T., Wu, C., He, Z., Japenga, J., Deng, M., & Yang, X. (2015). An integrated approach to assess heavy metal source apportionment in peri-urban agricultural soils. *Journal of Hazardous Materials*, 299, 540–549. <https://doi.org/10.1016/j.jhazmat.2015.07.041>
- Javed, M. T., Saleem, M. H., Aslam, S., Rehman, M., Iqbal, N., Begum, R., Ali, S., Alsahli, A. A., Alyemeni, M. N., & Wijaya, L. (2020). Elucidating silicon-mediated distinct morpho-physio-biochemical attributes and organic acid exudation patterns of cadmium stressed Ajwain (*Trachyspermum ammi* L.). *Plant Physiology and Biochemistry*, 157, 23–37. <https://doi.org/10.1016/j.plaphy.2020.10.010>
- Li, Q., Liao, L., Xu, R., Wu, Z., Yin, Z., Han, Y., Zhang, Y., Yang, Y., & Jiang, T. (2023). In situ preparation of a multifunctional adsorbent by optimizing the Fe<sup>2+</sup>/Fe<sup>3+</sup>/Mn<sup>2+</sup>/HA ratio for simultaneous and efficient removal of Cd(II), Pb(II), Cu(II), Zn(II), As(III), Sb(III), As(V) and Sb(V) from aqueous environment: Behaviors and mechanisms. *Journal of Hazardous Materials*, 444, 130389. <https://doi.org/10.1016/j.jhazmat.2022.130389>
- Liu, H., Xiong, Z., Jiang, X., Liu, G., & Liu, W. (2016). Heavy metal concentrations in riparian soils along the Han River, China: The importance of soil properties, topography and upland land use. *Ecological Engineering*, 97, 545–552. <https://doi.org/10.1016/j.ecoleng.2016.10.060>
- Long, J., Tan, D., Deng, S., & Lei, M. (2018). Uptake and accumulation of potentially toxic elements in colonized plant species around the world's largest antimony mine area, China. *Environmental Geochemistry and Health*, 40(6), 2383–2394. <https://doi.org/10.1007/s10653-018-0104-1>
- Lu, A., Wang, J., Qin, X., Wang, K., Han, P., & Zhang, S. (2012). Multivariate and geostatistical analyses of the spatial distribution and origin of heavy metals in the agricultural soils in Shunyi, Beijing, China. *Science of the Total Environment*, 425, 66–74. <https://doi.org/10.1016/j.scitotenv.2012.03.003>
- Muller G (1981) The heavy metal pollution of the sediments of Neckars and its tributary: a stocktaking. *Chem Zeit* 105:157–164
- Muller, G., 1969. Index of geoaccumulation in sediments of the Rhine River. *GeoJournal* 2, 108–118.
- O. Gyamfi, R.S. Wireko-Gyebi, E. Ansah, P.B. Sorenson, R.S. King, M.A. Nkansah, J. L. Bak, G. Darko, Assessment and awareness of health risks posed by mercury in artisanal gold mining in the Ashanti Region of Ghana, *Chem. Afr.* 5 (2022) 1765–1775, <https://doi.org/10.1007/s42250-022-00453-x>.
- Shi, T., Hu, Z., Shi, Z., Guo, L., Chen, Y., Li, Q., & Wu, G. (2018). Geo-detection of factors controlling spatial patterns of heavy metals in urban topsoil using multi-source data. *Science of the Total Environment*, 643, 451–459. <https://doi.org/10.1016/j.scitotenv.2018.06.224>
- Tomlinson, D. L., Wilson, J. G., Harris, C. R., & Jeffrey, D. W. (1980). Problems in the assessment of heavy-metal levels in estuaries and the formation of a pollution index. *Helgoländer meeresuntersuchungen*, 33, 566-575.
- Wang, H., Lu, S., 2011. Spatial distribution, source identification and affecting factors of heavy metals contamination in urban-suburban soils of Lishui city, China. *Environ. Earth Sci.* 64, 1921–1929.
- Wang, L., Cheng, W., Xue, Z., Xie, Y.X., Lv, X.J., 2023. Feasibility study of applying electrokinetic technology coupled with enzyme-induced carbonate precipitation treatment to Cu-and Pb-contaminated loess remediation. *J. Clean. Prod.* 401, 136734.
- Xiao, H., Shahab, A., Xi, B., Chang, Q., You, S., Li, J., Sun, X., Huang, H., Li, X., 2021. heavy metals pollution,

ecological risk, spatial distribution, and source identification in sediments of the Lijiang River, China. *Environ. Pollut.* 269, 116189.

- Xu, R., Li, Q., Yang, Y., Jin, S., Liao, L., Wu, Z., Yin, Z., Xu, B., Nan, X., He, Y., Zhu, B., & Jiang, T. (2022). Removal of heavy metal(loid)s from aqueous solution by biogenic FeS–kaolin composite: Behaviors and mechanisms. *Chemosphere*, 299, 134382. <https://doi.org/10.1016/j.chemosphere.2022.134382>
- Yang, S., Zhao, J., Chang, S.X., Collins, C., Xu, J., Liu, X., 2019. Status assessment and probabilistic health risk modeling of metals accumulation in agriculture soils across China: A synthesis. *Environ. Int.* 128, 165–174.
- Zhang, X., Chen, D., Zhong, T., Zhang, X., Cheng, M., Li, X., 2015. Assessment of cadmium (Cd) concentration in arable soil in China. *Environ. Sci. Pollut. Res. Int.* 22 (7), 4932–4941.
- Zhou, Q., Yang, N., Li, Y., Ren, B., Ding, X., Bian, H., & Yao, X. (2020). Total concentrations and sources of heavy metal pollution in global river and lake water bodies from 1972 to 2017. *Global Ecology and Conservation*, 22, e00925. <https://doi.org/10.1016/j.gecco.2020.e00925>