Correlation analysis of heavy metals, radionuclides, and physicochemical properties in soil from Serbia

Emina Mrkalic[1], Biljana Nikic[1,*], Jelena M. Stajic[1]

[1] University of Kragujevac, Institute for Information Technologies, Department of Science, Jovana Cvijica bb, Kragujevac, Serbia; e-mail: bmilenkovic@kg.ac.rs, stajicjelena11052012@gmail.com emina.mrkalic@pmf.kg.ac.rs,

* Corresponding author

Abstract: This study investigates the correlations between physico-chemical properties, concentrations of heavy metals, and the presence of radionuclides in soil samples collected from various locations across Serbia. A total of 129 samples were analyzed to determine parameters such as pH, organic matter content, $CaCO_3$, and granulometric composition, along with concentrations of heavy metals (e.g. As, Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn) and radionuclides (e.g. ^{226}Ra, ^{232}Th, ^{40}K and ^{137}Cs). Correlation analysis was applied to explore potential relationships between the measured variables. The results reveal statistically significant correlations between certain soil properties and specific heavy metals. The observed correlations between certain metals and radionuclides suggest common sources and similar geochemical behavior. Additionally, moderate to strong correlations were observed between some radionuclides and soil characteristics, indicating possible environmental and geological influences. These findings contribute to a better understanding of soil contamination dynamics and may support future environmental monitoring and land use planning in the region.

Keywords: radionuclides, heavy metals, soil, correlation

1. Introduction

All living organisms have the ability to accumulate toxic heavy metals and naturally occurring radioactive isotopes. Radionuclides such as ^{226}Ra, ^{232}Th, and ^{40}K are naturally found in all rocks and soils [1]. However, their distribution is often heterogeneous, primarily due to variations in soil composition. Depending on their chemical forms, these radionuclides can enter biological systems via the food chain and may pose potential health risks to humans. In contrast, ^{137}Cs is one of the most prominent artificial radionuclides released into the environment through anthropogenic activities, with its major source being fallout from the Chernobyl nuclear accident.

Heavy metal (HM) contamination represents a significant environmental issue owing to the high toxicity, persistence, and bioaccumulative nature of these elements in

water, soil, and biota [2]. Although heavy metals occur naturally in all environmental compartments, additional inputs often originate from human activities such as fossil fuel combustion, traffic emissions, and various industrial and domestic processes. Several heavy metals—including cadmium (Cd), mercury (Hg), arsenic (As), chromium (Cr), and lead (Pb)—are recognized as highly toxic even at low concentrations, posing substantial threats to ecosystems and public health.

The objective of this study was to evaluate the relationships between selected physico-chemical characteristics of soil and the concentrations of specific heavy metals and radionuclides, with the aim of assessing their environmental behavior and potential risk to biota and human health.

2. Methodology

Surface soil samples (1–10 cm depth) were collected from 129 locations using the IAEA standard method, in order to capture a wide range of physico-chemical properties. Samples were cleaned, air-dried, ground, and sieved (2 mm).

For radioactivity analysis, subsamples were sealed in Marinelli beakers (450 mL) and stored for four weeks. Gamma spectrometry was performed using a HPGe detector (ORTEC GEM30-70), with calibration based on a certified multi-radionuclide solution (MBSS 2). Activity concentrations of ^{226}Ra, ^{232}Th, ^{40}K, and ^{137}Cs were determined via characteristic gamma lines.

Soil pH (in water and 1M KCl) was measured following ISO 10390:1994. Organic matter content was determined via sulfochromic oxidation (ISO 14235:1998), and particle size distribution by sieving and pipetting, classified per ISSS standards.

Total heavy metal content (Cd, Cr, Pb, As, etc.) was measured using ICP-OES after microwave-assisted digestion (USEPA Method 3051A). Mercury content was analyzed using DMA-80 (USEPA Method 7473). Certified reference materials were used for quality control, with recoveries within accepted ranges. Spearman correlation analysis was performed using SPSS 20.0 software.

3. Results and Discussion

Descriptive statistics of the physico-chemical soil properties, as well as concentrations of heavy metals and radionuclides, are presented in Table 1. These data provide insight into the range and variability of soil contamination and physicochemical conditions across the study area, serving as a basis for further correlation and spatial distribution analyses.

The concentrations of heavy metals and radionuclides showed high variability across the 129 soil samples, with elements like Pb, As, and Zn exhibiting extremely high maximum values and strong positive skewness, indicating localized contamination. Soil physico-chemical properties such as pH, organic matter, and texture also varied notably, influencing the distribution and mobility of the analyzed contaminants.

The resulting correlation coefficients are presented in Tables 2 and 3. Correlation analysis showed that heavy metal and radionuclide concentrations were significantly influenced by soil physico-chemical properties. Notably, Cd, Pb, and Zn exhibited positive correlations with organic matter and coarse particles, while Zn and Pb were negatively correlated with silt content. As and Cd showed weaker but still significant associations with several soil texture fractions. Among radionuclides, ^{226}Ra and ^{232}Th demonstrated strong negative correlations with pH and $CaCO_3$, but positive correlations with clay and silt, suggesting their affinity for finer soil fractions.

Table 1. Descriptive statistics of metals content (mg kg^{-1}), physicochemical characteristics and radionuclide specific activities (Bq kg^{-1})

Results	Min	Max	Median	Mean	SD	Skewness	Kurtosis
As	4.35	1551	14.42	46.60	171.50	7.161	57.000
Cd	n.d.	27.10	0.07	1.26	3.53	4.611	27.088
Co	5.51	36.33	13.98	15.78	6.21	1.032	1.144
Cr	27.46	300.40	85.80	91.09	43.77	1.679	4.955
Cu	11.52	491.00	39.63	60.82	79.90	3.915	16.585
Mn	146.70	4724	829.45	924.42	534.06	3.835	23.866
Ni	18.37	520.30	85.90	117.04	95.97	2.443	6.850
Pb	12.50	34160	41.32	785.35	3524.9	8.091	74.044
Zn	19.10	7389.0	103.60	280.55	814.12	7.139	56.439
pH	4.36	8.34	7.73	7.57	0.638	-2.543	8.789
$CaCO_3$	n.d.	58.80	2.35	5.40	9.14	3.707	16.861
OM	0.24	16.53	3.81	4.06	2.30	1.971	7.655
Coarse	0.36	55.67	11.60	15.275	11.67	1.338	1.454
Fine	20.67	57.41	32.07	33.63	8.51	-0.034	24.655
Silt	6.08	37.44	25.18	24.66	7.639	-0.0587	-0.420
Clay	2.28	50.68	28.38	26.44	10.91	-0.293	-0.541
^{226}Ra	9.70	91.10	30.95	31.13	11.43	1.696	7.157
^{232}Th	11.90	103.80	43.50	43.27	15.10	0.979	3.232
^{40}K	167.00	1148.70	423.50	463.26	171.61	1.445	3.080
^{137}Cs	0.46	385.00	16.25	30.85	52.35	5.516	35.228

*n.d. – not detected

Table 2. The Spearman correlation matrix of heavy metals and radionuclides with soil physicochemical characteristics

	pH	CaCO₃	OM	Coarse	Fine	Silt	Clay
As	0.008	0.079	0.022	0.214*	-0.109	-0.282**	0.041
Cd	0.089	0.265**	0.239**	0.175*	0.334**	-0.355**	-0.123
Co	0.015	-0.131	-0.031	-0.137	-0.421**	0.103	0.335**
Cr	0.055	-0.069	-0.244**	-0.042	-0.125	-0.126	0.218*
Cu	0.024	0.102	-0.074	0.076	0.055	-0.194*	0.048
Mn	-0.018	-0.114	-0.031	-0.275**	-0.270**	0.089	0.418**
Ni	0.147	0.067	-0.292**	0.072	-0.007	-0.220*	0.083
Pb	-0.040	0.119	0.346**	0.255**	0.030	-0.362**	-0.016
Zn	-0.150	0.071	0.215*	0.315**	-0.050	-0.386**	-0.057
²²⁶Ra	-0.296**	-0.402**	0.206*	-0.377**	-0.213*	0.312**	0.372**
²³²Th	-0.241**	-0.462**	0.005	-0.640**	-0.367**	0.527**	0.634**
⁴⁰K	-0.177*	-0.273**	-0.091	-0.185*	-0.077	0.115	0.247**
¹³⁷Cs	-0.215*	-0.131	0.290**	0.045	-0.052	0.101	-0.090

* Correlation is significant at the 0.05 level; ** Correlation is significant at the 0.01 level

The Spearman correlation analysis revealed that most heavy metals exhibited significant positive interrelationships, with particularly strong associations observed between Cr and Ni (r = 0.896), As and Pb (r = 0.647), and Pb and Zn (r = 0.638). Mn showed moderate positive correlations with most metals, while Cd and Cu displayed weaker and more selective associations. The radionuclides ²²⁶Ra and ²³²Th were strongly correlated (r = 0.707) and moderately associated with ⁴⁰K, whereas ¹³⁷Cs showed generally weak relationships with other parameters, except for moderate correlations with As, Pb, and Zn. The strong Ra–Th correlation reflects their common origin and similar soil behavior.

Table 3. The Spearman correlation matrix for heavy metals content and radionuclide activity concentrations

	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn	²²⁶Ra	²³²Th	⁴⁰K	¹³⁷Cs
As	1	0.145	0.534**	0.475**	0.156	0.408**	0.470**	0.647**	0.478**	-0.016	-0.042	0.152	0.358**
Cd		1	-0.274**	-0.012	0.417**	0.085	0.119	0.436**	0.175*	-0.194*	-0.339**	-0.091	-0.094
Co			1	0.601**	-0.309**	0.619**	0.492**	0.335**	0.137	0.120	0.243**	0.144	0.332**
Cr				1	0.161	0.344**	0.896**	0.215*	0.222*	-0.269**	-0.115	-0.081	0.035
Cu					1	0.117	0.305**	0.214*	0.396**	-0.090	-0.134	0.209*	-0.084
Mn						1	0.334**	0.355**	0.302**	0.191*	0.304**	0.281**	0.217*
Ni							1	0.251**	0.278**	-0.361**	-0.238**	-0.016	-0.004
Pb								1	0.638**	0.102	-0.015	0.081	0.383**
Zn									1	0.097	-0.099	0.149	0.382**
²²⁶Ra										1	0.707**	0.444**	0.284**
²³²Th											1	0.457**	0.211*
⁴⁰K												1	0.134
¹³⁷Cs													1

* Correlation is significant at the 0.05 level; ** Correlation is significant at the 0.01 level

4. Conclusions

The study showed considerable variability in soil physico-chemical properties, heavy metal concentrations, and radionuclide activities across 129 locations. Significant correlations indicated that soil texture and organic matter strongly influence contaminant retention, while the strong ^{226}Ra–^{232}Th relationship reflects their shared geological origin. The results underscore the combined impact of natural processes and anthropogenic inputs on soil contamination patterns.

Acknowledgment

References

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