

Article

A Study on the Possible Relationship between Physico-Chemical Properties of the Covering Soil and the Mobility of Radionuclides and Potentially Toxic Elements in a Recultivated Spoil Bank

Márk Horváth ¹, György Heltai ^{1,*}, András Várhegyi ² and Lamlile Mbokazi ^{1,3,*}

¹ Institute of Environmental Sciences, Department of Environmental Analysis and Technologies, Hungarian University of Agriculture and Life Sciences, 2100 Gödöllő, Hungary

² Bányavagyon-hasznosító Nonprofit Közhasznú Kft (Mining Property Utilization Ltd.), 1126 Budapest, Hungary

³ Necsa, RadioAnalysis Department, South African Nuclear Energy Corporation SOC Limited, Madibeng Municipality 0240, South Africa

* Correspondence: heltai.gyorgy@uni-mate.hu (G.H.); lamlile.mbokazi@necsa.co.za (L.M.)

Abstract: This study is part of the ongoing environmental monitoring program of the abandoned Mecsek uranium mine. On the mine's recultivated spoil deposit No. I, anomalies that refer to possible migration alongside the slope were detected. The present study was conducted to supplement the ongoing monitoring study with a sampling strategy and analytical methods that can characterize the mobility of potentially toxic elements and radionuclides. A sampling strategy was developed: the vegetation and soil core samples were collected from the slope from top to bottom of the deposit, and nearby this spoil deposit, water samples were collected. Elemental analyses were conducted: the pseudo-total analysis, a total concentration of uranium in water, and the BCR sequential extraction analysis. The radionuclides were determined by gamma spectrometry and alphaGUARD. Additionally, the soil and plant moisture content, soil organic matter, pH, and cation exchange capacity (CEC) were determined. The Pearson correlation analysis and the principal component analysis, considering all possible influencing factors, verified that the elemental concentration increase from the top to the bottom direction of the deposit is strongly influenced by the soil pH, CEC, and Ca content. The mobility of Cd, Co, Mn, Pb, and U is relatively high and significantly migrates down the slope.

Keywords: radionuclides; potentially toxic elements; covering soil; uranium mine; multivariate statistical analysis



Citation: Horváth, M.; Heltai, G.; Várhegyi, A.; Mbokazi, L. A Study on the Possible Relationship between Physico-Chemical Properties of the Covering Soil and the Mobility of Radionuclides and Potentially Toxic Elements in a Recultivated Spoil Bank. *Minerals* **2022**, *12*, 1534. <https://doi.org/10.3390/min12121534>

Academic Editor: Tsutomu Sato

Received: 16 November 2022

Accepted: 26 November 2022

Published: 29 November 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Uranium mining and milling activities were stopped in Hungary due to the economic circumstances in 1997 after more than 35 years of operation [1]. Five mine works were in operation [2], which led to five spoil deposits. In 1998, clean-up of the uranium mining legacy started: closing of the underground mines and remediation of the rock heaps, the sedimentation ponds, and the contaminated water from the uranium mill. The key remediation activities at the Mecsek uranium mine were concluded in 2009, where 62 ha of land needed to be cleaned and 700,000 m³ of contaminated soil disposed of [3]. After closing measures were planned on the remediated site, there were plans and implementations of technical intervention for the continuous operation of the established radiological-hydrogeological-geodynamic monitoring system [2,4]. Mecsekérc Zrt [5] stated that regarding remediated waste rock dumps and tailings ponds, it is imperative that the performance of the radon barrier is enough and that the migration of radionuclides is constantly monitored. Since the groundwater had to be protected when uranium mining was completed, remediation and monitoring of the underground mines, waste rock heaps, and heap leaching sites

began immediately after the operation [6]. To follow the environmental protection criteria, the Mecsek uranium mine conducted a long-term land reclamation, which included the monitoring of air, groundwater and surface waters, soil, rocks, and vegetation as endangered and contaminated compartments in the period of mine closure, remediation, and post-closure operation [5]. The ongoing environmental monitoring program in the Mecsek uranium mine identified that spoil deposit No. I required further investigation on the mobility and vegetation uptake of PTEs and radionuclides. Due to the presence of numerous elements and radionuclides, mine tailings cause severe pollution problems and may pose risks to humans [7,8]. Spoil deposits may contain elevated concentrations of these elements and can often be prone to water and/or wind erosion, spreading the contamination to surrounding areas. These issues have risen over the last few decades [8]. The question of environmental contamination occurs when potentially toxic elements (PTEs) and radionuclides are mobilized from the deposits of uranium-containing waste (waste rock piles, tailings ponds, etc.) into the soil and absorbed by plants or transferred to groundwater [9,10]. Similarly, Sánchez-Donoso et al. [11] stated that the release of PTEs from waste deposits is particularly prone to contaminating drainage networks and groundwater ecosystems. As part of the remediation process, frequent monitoring of radioactivity and PTEs in groundwater near the spoil deposits, seepage water from the waste rock pile, mine water, and treated mine water was conducted. According to Mecsekérc Zrt. [5], this hydrogeological monitoring is to ensure that the Pellérd-Tortyogó and the northern karstic water resources are protected against any contamination and to predict any process indicating the distribution of contamination to be able to plan for any intervention.

The distribution of elements in the environment is determined by the properties of each element and by various environmental factors [12]. Soil properties are primarily grouped into physical, chemical and biological, microflora, and microfauna [13]. After radionuclides and PTEs deposition on the soil surface, the relocation and movement of these elements in the soil depend on the soil properties, i.e., pH, cation exchange capacity (CEC), texture, interchangeable calcium and potassium, clay content, grain size, as well as organic matter [10,14–16]. Similarly, these properties also contribute to the pollution of PTEs and radionuclides in soils and affect solubility [17]. Furthermore, the physico-chemical properties (pH, soil organic matter, cation exchange capacity, moisture content, clay content, nutrient status, and mineralogy) might influence the migration of these elements in soil [18]. Therefore, different factors need to be considered when studying the mobility of elements and radionuclides in soil. If mobility factors are very high, it indicates that anthropogenic radionuclides and PTEs have great potential to spread and be rapidly bioavailable in the environment if measures are not put in place [19]. There is a correlation between the CEC values and the values of the pH and organic matter (OM) content [20]. According to Bielicka-Giełdoń et al. [20], higher pH values and organic matter content result in higher values of the CEC measured. As a result, CEC is considered a good indicator of soil quality and productivity [21]. In addition, Agic et al. [22] state that when the pH, organic matter content, CEC, and clay increase, the percentage and availability of the metals reduce. As a consequence, it is of utmost importance to identify the factors that influence the bioavailability, leaching, and possible toxicity of elements in soils [23]. The transfer of trace elements between soil phases can be seen as the fundamental process regulating their behavior and bioavailability [24]. According to Popic [25], transfers of the radionuclides and trace elements will change over time due to various parameters and processes such as the ecosystem composition, the essential chemical composition of the elements, soil physical and chemical features, the temperature and hydrological conditions, element migration in the soil, changes in intake/uptake levels, and biological half-lives. The most critical problem in agricultural and environmental studies has been the bioavailability of trace elements and radionuclides [24,26].

Many studies that include the determination of total PTE concentrations have been conducted [27–33]. However, total concentrations might provide inadequate information about the potential mobilization and associated risk of PTEs in soils [34,35]. Although the

mobility, bioavailability, and eco-toxicity of PTEs depend more on their chemical speciation rather than on their total content [36], it is helpful to determine the total concentrations of PTEs. During the formation of the soil covering the process of spoil deposits in the Mecsek uranium mine, there was an erosion wounding occurrence in spoil deposit No. I. Consequently, there was a question of the adequacy of the 1-meter thick soil covering layer used to cover the spoil deposit. The lack of soil cover stability induces acute downward migration of radionuclides and PTEs [37]. The ongoing environmental monitoring program in the Mecsek uranium mine identified that spoil deposit No. I required further investigation on the mobility and vegetation uptake of PTEs and radionuclides. Previous research has revealed that the mobility of these elements depends on the forms in which they occur in the soils [20,34,38]. These forms, which can be distinguished by the BCR sequential extraction procedure, include [39]:

- (1) Exchangeable and acid-soluble fractions;
- (2) Bound to reducible species (e.g., Fe and Mn oxides, oxyhydroxides);
- (3) Oxidizable forms bound to organic matter or sulfides;
- (4) Strong oxidative acid-soluble residual contents (aqua regia and/or $\text{H}_2\text{O}_2/\text{HNO}_3$)

According to Bielicka-Giełdoń et al. [20], plants can readily access the first two types of forms, while the second two types are potentially accessible in the long term. A sequential extraction is an essential tool for knowing the conditions of these elements in soils and hence the possible mobility, bioavailability, and chemical nature of a given element that can thus offer a more accurate estimation of the actual environmental effect [40–42]. Thus, there was a need to include the BCR extraction technique in the monitoring program to provide the information needed for the effective planning and management of applications in the Mecsek uranium mine.

The present study is a supplementary part of the ongoing monitoring program of the Mecsek Uranium Mine remediation [5]. During previous routine monitoring at spoil deposit No. I., a high gamma dose rate was detected that was indicative of insufficiency of the 1-meter soil covering layer retarding the migration of PTEs, Rn-222, and radionuclides. Therefore, to spoil deposit No. I., an appropriate sampling strategy was elaborated following the vertical and along-the-slope migration of the above components in covering the soil layer and the vegetation uptake. Besides the "pseudo-total" [43], the determination of PTEs and uranium using the BCR sequential extraction procedure was utilized to evaluate the mobility of PTEs and U in the 1-meter-deep covering soil layer [44]. In addition, the U content of different types of water samples collected from the Mecsek mine during the ordinary monitoring program was conducted in parallel with this supplementary study. In previous publications, the plant uptake and the mobility of PTEs and U along the slope and vertical position, influenced by the pH and CEC of the covering soil, were reported using regression statistics [43–45]. In this paper, all interactions are evaluated by multivariate PCR method involving the non-published measurements of radionuclide migration and uptake by plants supporting the planning of improvement operations on the covering soil layer.

2. Materials and Methods

2.1. Geological Background

The mining site is located in the hilly countryside, and the main part of the milling site is a flat area [46]. Juhasz and Erdi-Krausz [46] further state that the geological formation of the mining site mainly consists of limestone, sandstone, and marl. According to René [47], the Upper Permian sandstones that make up the Mecsek deposit's uranium ore can reach a thickness of 600 m. Sandstones range in thickness from 15 m to 90 m and were folded into the Permian–Triassic anticline of the Mecsek mountains where uraninite, coffinite, pyrite, and marcasite represent the ore minerals [47].

2.2. Sampling and Sample Preparation

2.2.1. Sampling

Soil and covering plant samples were collected from four sampling locations in Mecsek uranium mine deposit No. 1 in Pécs, southwest of Hungary [44]: (1) at the top of the deposit—Rn-M11; (2) on the slope of the deposit—Rn-M12; (3) at the bottom field—Rn-M13; (4) at the bottom edge of the slope of the deposit—radioactive point. Figure 1 illustrates deposit No. 1 with gamma dose rates measured previously as part of the monitoring program [44]. The radioactive point was chosen based on the knowledge of its high gamma dose rate ranging between 150 and 450 nGy/h to indicate the behavior and type of radionuclides found in this location. Spoil deposit No. 1 was covered with different types of soils taken from various locations, mixed to form a soil covering layer, and it was also covered with different kinds of vegetation, mainly grass. Underneath the soil covering layer, there were natural rocks.

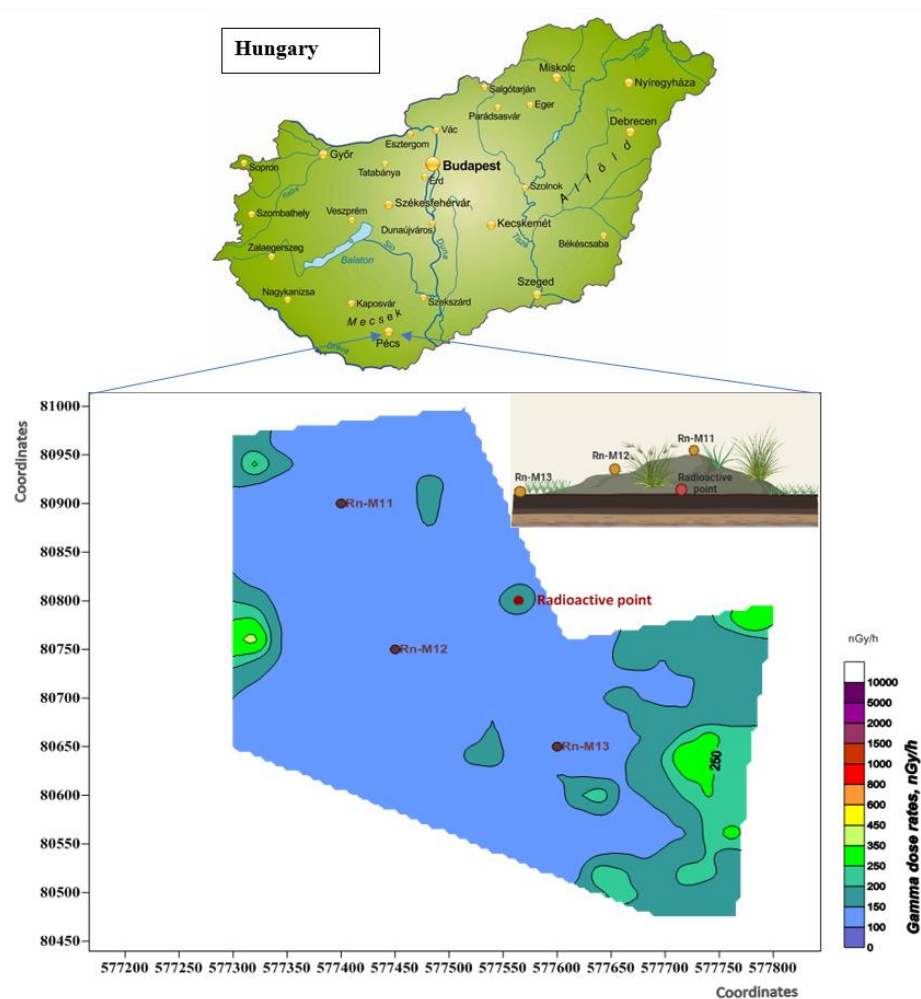


Figure 1. Site location map of Hungary downloaded from OrangeSmile.com [48] and map of Mecsek uranium mine spoil deposit No. 1, Pécs (2017), indicating soil sampling locations and the gamma dose rates distribution with an insert of spoil deposit No. 1 schematic diagram [44]. Reproduced with permission from Khumalo et al. [44], Ecological Chemistry and Engineering S; published by Sciendo, 2021.

2.2.2. Soil Sampling and Sample Preparation

Soil samples were collected using a hand auger instrument labeled with different measurements. Each soil core sample was taken from different depths: 0–25, 25–50, 50–75,

and 75–100 cm. For sample location Rn-M11, 75–100 cm depth could not be sampled as this was hard rock. Radioactive soil was possible to sample only from the top 0–25 cm layer.

All soil samples were air-dried for five days. After five days, the samples were physically homogenized and grinded using Retch SM 100 with a 0.25 mm sieve instrument. All soil samples were halved into two portions, half of each sample was used for the PTE analysis, and the other half was used for the radionuclide analysis. Approximately 30 g of homogeneous soil samples was weighed and airtight sealed in plastic containers for the gamma ray measurements. Samples were kept in storage for six weeks before gamma ray analysis took place; this incubation period allows Ra-226 and its short-lived progenies to achieve secular equilibrium, noting the exact dates and times from sealing being recorded.

2.2.3. Plant Sampling and Sample Preparation

Covering plant samples (a mixture of Asteraceae and Quackgrass—*Elytrigia repens*) were collected by cutting from the surface of the plants with a knife. Plant samples were collected from a 1.5 m² area of the exact locations where the soil samples were also collected (Rn-M11, Rn-M12, Rn-M13, and radioactive point) to determine any biological uptake of PTEs and radioactivity from the soil.

Only the radioactive plant sample was separated into two portions, half of the sample was not washed, and the other half was washed first with low- to medium-pressure water for five minutes to simulate the rain. This washing process was conducted on this sample to determine whether the radioactivity concentration is due to the contamination through air particles/dust or biological uptake through the soil.

After this process, all plant samples were air-dried for five days and grinded into a powder form. Approximately 8 g of grinded plant samples were weighed, airtight sealed in plastic containers, and kept for six weeks to allow the growth of Ra-226 and its short-lived progenies before gamma ray measurements.

2.2.4. Water Sampling and Sample Preparation

Water analysis results were not previously published, which is why this section is described in detail.

Water sampling sites were part of the overall Mecsek mine monitoring program. A total of eleven water samples were collected from various places around the Mecsek mine. Of these samples, six samples were groundwater samples, of which four samples: (1) Pk-29/1, (2) Pk-33/1, (3) Pk-44/3, and (4) 1504/1, were collected from the monitoring well near spoil deposit No. I and two samples: (5) P-2/5 and (6) P-2/6, were collected from the water pumping well at the former percolation area (spoil deposit No. II). One sample: (7) Északi-tározó (northern reservoir), was mixed water—mine water from spoil deposit No. III—and leaking water from precipitation collected from the gravitational effluent mine water (north mines). Two samples were seepage water; one sample: (8) CS-0, collected from spoil deposit No. II, and another sample: (9) IIIm. Gyűjtő (collector), collected from spoil deposit No. III. Another sample: (10) 6/11. Szint (level), was mine water from mine No. I collected from the water pumping well. The last sample: (11) Elfolyó (drain), was treated mine water collected from the mining water treatment plant. The samples were labeled based on the mine description.

2.3. Analytical Methods

2.3.1. Elemental Analysis

The total elemental analysis was conducted using a flexible multi-elemental method by Horiba Jobin Yvon ACTIVA M Inductively Coupled Plasma—Optical Emission Spectrometer (ICP-OES) (ACTIVA-M CCD ICP-Spectrometer, HORIBA France SAS, Palaiseau, France) with operational parameters proposed by the manufacturer for aqueous media optimized with matrix-matched calibration according to sample preparation and with the application of yttrium internal standard and appropriate Certified Reference Material (CRM) samples for Quality Control [45]. The detection limits for the multi-elemental method are

as follows: Ca— 1.30×10^{-5} mg/kg; Cd— 3.45×10^{-5} mg/kg; Co— 5.64×10^{-5} mg/kg; Cr— 5.59×10^{-5} mg/kg; Cu— 3.35×10^{-5} mg/kg; Fe— 3.81×10^{-5} mg/kg; K— 1.12×10^{-3} mg/kg; Mg— 1.15×10^{-5} mg/kg; Mn— 8.22×10^{-6} mg/kg; Na— 7.22×10^{-4} mg/kg; Ni— 6.74×10^{-5} mg/kg; P— 4.12×10^{-3} mg/kg; Pb— 2.21×10^{-4} mg/kg; U— 9.42×10^{-4} mg/kg; and Zn— 4.20×10^{-5} mg/kg [43,44].

(1) The pseudo-total elemental content in homogenous soil for all layers and plant samples was prepared in triplicate using a microwave digestion method conducted according to the Hungarian Standard MSZ 21470-50:2006 using a CEM Mars 5 Xtraction 230/60 Microwave Accelerated Reaction System 907501 (CEM Corporation, Matthews, NC, USA) and was determined by an ICP-OES using a yttrium internal standard for the determination of elements that are required in soil by plants in large quantities (macronutrients: Ca, K, Mg, P, and Fe), elements that are required in small amounts (micronutrients: Co, Cu, Mn, Na, Ni, and Zn), and toxic elements (Cd, Cr, Pb, and U). From the pseudo-total PTE concentrations, transfer factor (TF) values could be calculated. Detailed information about this section is published by Khumalo et al. [43].

(2) The uranium concentration in water analysis was conducted in collaboration with the accredited Mecsek uranium mine laboratory as an interlaboratory study to determine the reproducibility.

A HORIBA Jobin Yvon ACTIVA M Inductively Coupled Plasma–Optical Emission Spectrometer (ICP-OES) using operation parameters proposed by the manufacturer and yttrium internal standard was used to determine the uranium content in water. The operational parameters were as follows: incident RF-power—1200 W, outer gas flow (argon)—16 L/min, sheath gas flow (argon)—0.3 L/min, auxiliary gas flow (argon)—0.6 L/min, and nebulizer gas pressure (argon)—2.86 bar, nebulizer solution uptake (Meinhardt-cyclonic spray chamber)—0.85 mL/min. The detection limit for U measurements by ICP-OES is 9.42×10^{-4} mg/kg.

Water samples were prepared using the Hungarian Standard MSZ 1484-3: 2006 [45]. Water samples were filtered into a 40 mL centrifuge tube using Munktell filter discs grade 389. The samples were measured first before adding anything to determine if they will need dilution. Then, 1000 mg/L yttrium standard solution (YNO_3)₃ in HNO_3 0.5 mol/L was added into the samples as an internal standard. Further, 4.90 mL of each sample and 0.1 mL of yttrium standard solution were added into a 10 mL volumetric flask, and the sample solution was made up to 10 mL with distilled water.

To determine the uranium concentration in water samples, four blank solutions were prepared: 0 mL yttrium solution and 10 mL distilled water, 1 mL yttrium solution and 9 mL distilled water, 5 mL yttrium solution and 5 mL distilled water, and 10 mL yttrium solution and 0 mL distilled water. Three external standards were used:

- Uranium ICP standard (UO_2NO_3)₂ in HNO_3 2–3% 10 mg/L—U;
- Yttrium standard solution (YNO_3)₃ in HNO_3 0.5 mol/L – 1000 mg/L Y;
- Certified Elements Standard—Uranium; concentration: 1000 ± 3 µg/mL, 20 °C; matrix: 2.5% HNO_3 ; density: 1.0152 g/mL, 20 °C

(3) For the sequential extraction procedure, the 0–25 cm soil samples were prepared in triplicate using a three-step BCR sequential extraction procedure with an additional (+1) aqua regia extraction step proposed by the European Community Bureau of Reference in 1992 (the Standards Measurement and Testing Program). The Certified Reference Material BCR-701 was prepared in triplicate in parallel with the samples to ensure the accuracy of the analysis. The extractable contents of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, U, and Zn were determined by ICP-OES [45] using the BCR procedure as described in detail by Rauret et al. [39,49]. The results produced good recoveries for the Certified Reference Material BCR-701. In order to validate the BCR sequential procedure and the pseudo-total method, the sums of the cumulated concentrations for each element in Step 1 (Fraction 1) + Step 2 (Fraction 2) + Step 3 (Fraction 3) + aqua regia step (Fraction 4) were compared to the pseudo-total concentrations obtained from the same samples (0–25 cm depth) and given in mg/kg units. From the PTE concentrations obtained for the BCR se-

quential procedure, the mobility factor (MF) could be calculated. Detailed information about this section was published by Khumalo et al. [44].

2.3.2. Radiochemical Analysis

1. Gamma spectrometry analysis as described in detail in Section 2.4. for the determination of radionuclides: Ac-228, Pb-212, Pb-214, Th-232, Bi-214, U-235, U-238, K-40, Tl-208 using a CANBERRA HPGE high-purity semiconductor gamma detector.

2. Radon-222 (Rn-222) determination by AlphaGUARD. Radon-222 was measured for each soil sample for 24 hours using Genitron Instruments AlphaGUARD PQ2000/MC50 Multiparameter Radon Monitor. The detailed information about this section was published by Khumalo et al. [50].

2.3.3. Physico-Chemical Analysis

1. The soil pH was determined in 1 mol/l KCl (1:2.5 soil to KCl ratio) with the aid of a glass-electrode pH meter. The pH meter was calibrated with pH 7.0 and 4.0 buffer standards before use. The results were published by Khumalo et al. [44].

2. The CEC in soil was determined according to the Hungarian Standard MSZ 1484-3:2006 [51]. The detailed information was published by Khumalo et al. [44].

3. The soil organic matter (%SOM) was determined by weighing approximately 1 g of each homogenized, and the sieved soil sample was weighed in duplicate. Total carbon (% C) was determined using a Vario MAX cube CNS Analyzer instrument. Furthermore, the CaCO₃ content (%) was determined by employing the Lloyd Kahn procedure using LECO CR-412 Carbon Analyzer with an IR detector [52]. From the combination of these results, it was possible to determine the total organic carbon (%TOC). Then, the organic matter (% OM) was calculated from % TOC. Detailed information about this section was published by Khumalo et al. [44].

4. The soil moisture (%SM) was determined by weighing approximately 25 g of soil dried in an oven at 105 °C for 72 hours, cooled in a desiccator, and weighed for the determination of the soil moisture content. The detailed information was published by Khumalo et al. [43].

2.4. Gamma Spectroscopy

The gamma spectrometric results were not previously published; hence, this section is described in detail.

The gamma background was measured for 108,000 seconds. The indoor background spectrum within the collimator is assumed to be constant. The background was relatively low due to using a proper collimator. The background spectrum was normalized and then subtracted from the live-time and energy-calibrated observed spectra, obtaining a background compensated spectra channel as shown in Equation (1):

$$I_c = I - I_0 \quad (1)$$

where I_0 is background intensity, I is intensity, and I_c is background-compensated intensity.

Compensated spectra were processed, and the nuclide activities were determined from the predefined nuclide peaks using the total peak area method described in the ORTEC GammaVision 6 (5.2.1.1.) (CANBERRA HPGE high-purity semiconductor gamma detector, Mirion Technologies (Canberra), Inc., Meriden, CT, USA). The method was implemented in a Visual BASIC code running under an EXCEL environment. The minimum detectable activity (MDA) is a measure of how small activity could be present and not be detected by the analysis. The MDA calculation was completed by ORTEC Critical Level (GammaVision 6, 5.7.2.) (CANBERRA HPGE high-purity semiconductor gamma detector, Mirion Technologies (Canberra), Inc., Meriden, CT, USA).

The soil and plant samples were kept in storage for six weeks to attain the radioactive equilibrium between Ra-226 and the decay products with short half-lives [53]. All samples have had enough time for establishing secular equilibrium between decay series products;

thus, determining the activity of parent isotopes was possible by measuring daughter isotopes having significant gamma lines. The reference isotopes were used for quantitative analysis: actinium-228 (Ac-228) and Pb-212 for the Th-232 decay chain and Pb-214 and bismuth-214 (Bi-214) for U-238 (Ra-226) decay series.

Both homogenous soil and plant samples were measured for 3600 seconds each using CANBERRA HPGE high-purity semiconductor gamma detector. The instrument was calibrated for energy, full width at half maximum (FWHM), and efficiency (η) (geometry calibration and efficiency calibration function and calibration coefficients) before analysis to ensure the reliability of the instrument so that it can be trusted. Energy calibration was conducted using the following sources: Co-60, Ba-133, Cs-137, Na-22, and K-40. The same sources were used for specifying the efficiency calibration procedure and the calibration curve. The geometry calibration was completed by simulation using CANBERRA Geometry Composer v.4.2 software (CANBERRA HPGE high-purity semiconductor gamma detector, Mirion Technologies (Canberra), Inc., Meriden, CT, USA). The instrumental parameters for gamma measurements were as follows: outer diameter—60 mm; side wall—1 mm; bottom wall—0.5 mm; sample density— $\sim 1.7 \text{ g/cm}^3$ (sand/soil approximated); and sealed: foil— $\sim 0.3\text{--}0.4 \text{ mm}$; hermetic sealing.

The primordial radionuclides (U-238 and its decay products, Th-232 and its decay products, U-235, and K-40) were measured. The activity concentration for each radionuclide was determined per depth of the soil and plant samples. Measured radionuclides were compared to identify the changes in radionuclide activity concentrations in soil samples and to identify the trends of all the radionuclides as the depths and the slope of the deposit changed.

2.5. Calculations for the Soil/Plant Transfer Factor

All the TF values were calculated from the plant shoots.

From the previously published study [43], it was established that in the soil, the PTE concentrations for Ni and Cr were above the Hungarian limits in some sampling locations. However, the TF values for these elements were very low. This could be the result of the plant having low suitability for phytoextraction and phytoremediation [54]. Mirecki et al. [54] further explain that the availability of PTEs for plants is controlled by the plant's requirement for micronutrients and the capacity to absorb and eliminate toxic elements. Overall, the TF values for pseudo-total PTEs were below 1.

Transfer factor values for the radionuclides were determined on a mass basis; the activity concentration of plant samples (dry matter) was related to the radionuclide activity concentration in the first 25 cm of soil and calculated using Equation (2). The TF values obtained in this study were compared to the mean values for radionuclide TF ratios (grasses) in a temperate environment for all types of soil reported by the International Atomic Energy Agency on their Technical Reports Series no. 472 [4].

Soil-to-plant TFs have been commonly used in radioecology to measure the availability of radionuclides in soil for plant uptake using Equation (2) [13,54]. Likewise, the soil/plant TFs for radionuclides in this study were calculated using Equation (2) to determine the soil's effect for each radionuclide on the plants, consequently predicting the plant uptake.

$$\begin{aligned} \text{TF} &= \text{plant activity concentration (Bq/kg)} / \text{total soil activity concentration (Bq/kg)} \\ &\text{or} \\ \text{TF} &= \text{metal content in the plant (mg/kg)} / \text{metal content in soil (mg/kg)} \end{aligned} \quad (2)$$

The TF was calculated using the activity concentrations for each soil sample at 0–25 cm depth and the plant sample collected at the exact location to identify any biological uptake of radionuclides. The 0–25 cm depth of the soil sample was chosen because the grass does not have deep roots to reach a deeper level of the soil. The higher the TF value, the more mobile/available the element is [55,56].

2.6. Statistical Analysis

Table 1 indicates the summary of the methods and the soil samples used to determine the possibility of a relationship by statistical evaluation.

Table 1. Summary of methods used and samples for statistical evaluation.

Depth (cm)	Rn-M11	Rn-M12	Rn-M13	Radioactive Sample
0–25	2.3.1: 1 and 3;	2.3.1: 1 and 3;	2.3.1: 1 and 3;	2.3.1: 1 and 3;
	2.3.2: 1 and 2;	2.3.2: 1 and 2;	2.3.2: 1 and 2;	2.3.2: 1 and 2;
	2.3.3: 1, 2, 3, and 4	2.3.3: 1, 2, 3, and 4	2.3.3: 1, 2, 3, and 4	2.3.3: 1, 2, 3, and 4
25–50	2.3.1: 1;	2.3.1: 1;	2.3.1: 1;	Not enough soil cover
	2.3.2: 1 and 2;	2.3.2: 1 and 2;	2.3.2: 1 and 2;	
	2.3.3: 1, 2, 3, and 4	2.3.3: 1, 2, 3, and 4	2.3.3: 1, 2, 3, and 4	
50–75	2.3.1: 1;	2.3.1: 1;	2.3.1: 1;	
	2.3.2: 1 and 2;	2.3.2: 1 and 2;	2.3.2: 1 and 2;	
	2.3.3: 1, 2, 3, and 4	2.3.3: 1, 2, 3, and 4	2.3.3: 1, 2, 3, and 4	
75–100	Hard rock	2.3.1: 1;	2.3.1: 1;	
		2.3.2: 1 and 2;	2.3.2: 1 and 2;	
		2.3.3: 1, 2, 3, and 4	2.3.3: 1, 2, 3, and 4	

The statistical analysis was conducted using SPSS Statistics 28 for basic descriptive statistical analysis. Analyse-it for Microsoft excel 2010 version 5.80.2 software was used to determine the Pearson's correlation coefficients (r) conducted to verify the significance of the possible relationship between PTE and radionuclide concentrations and the soil characteristics variables in soil samples at a 95% confidence level ($p \leq 0.05$). When the r value is close to 1, it is considered that the two variables have a relationship, and $p \leq 0.05$ states that there is sufficient evidence to conclude that the correlation coefficient is significantly different from zero, and therefore, the null hypothesis is rejected [57,58]. Additionally, Analyse-it software was used to plot the principal component analysis (PCA) biplot to examine the common characteristics or the relationships between the PTEs, radionuclides, and physico-chemical properties in soil.

3. Results and Discussion

3.1. Distribution of PTEs and Measured Elements along the Slope Position and Vertical Direction in the Covering Soil Layer, Their Mobility and Influencing Soil Characteristics, and Plant Transfer

In previously published papers, the following relationships were earlier reported [43,44]:

- Pseudo-total PTE and other measured element content distribution vs. vertical position in the soil layer showed no significant trend.
- Pseudo-total PTE and other measured element content distribution vs. position on the slope showed an increasing tendency for certain PTEs along the top to bottom direction.
- PTE contents of the soil and uptake by plants were under the permissible limits of Hungarian and European regulations [59,60].
- PTE uptake by plants showed an increasing tendency in the top to bottom direction referring to migration along the slope.
- Soil pH and CEC had significant correlations with each other and decreased tendency vs. vertical position and top to bottom position.
- pH and CEC have shown different correlations with different mobility factors of elements determined by BCR fractionation of PTEs of 0–25 cm soil layer. The order of mobility was the following: $U > Mn > Pb > Co > Cd > Ni > Cu > Cr > Zn > Fe$.
- Co, Fe, and Ni mobility significantly decreased as the pH and CEC increased, while Cd, Cr, Pb, Cu, and U mobility increased with the decrease in pH and CEC.

The BCR sequential extraction of PTEs including uranium indicated that despite the relatively low pseudo-total concentration of PTEs, the sequential extraction proves

additional information on their mobility by water infiltration [44]. The BCR sequential extraction results indicated that the most mobile elements were U (100%), Mn (73.5%), Pb (55.1%), and Cd (36.8%). There was a high correlation ($p \leq 0.05$) among these elements, and they all move together in the direction of water flow. The mobility factor calculation results followed the order: $U > Mn > Pb > Co > Cd > Cu > Ni > Zn > Fe > Cr$. The MF values show what has already been established such that U was highly mobile in this study. The high concentration of U comes from the wounded area of spoil deposit No. I (the radioactive sample).

The results of the comparison between the sum of the accumulated BCR concentrations and the concentrations obtained from the pseudo-total were found to be acceptably close. There were some cases where the concentrations of the BCR were larger than the concentrations obtained by pseudo-total. This could be caused by the cumulative error from each extraction measurement [61]. These results indicated that these two methods are reproducible.

The physico-chemical properties results in the soil moisture content (%) [43], cation exchange capacity (CEC) (cmol(+)/kg) [44], as well as the pH [44] indicated that the distribution of PTE and radionuclide concentrations in the soil cover layer depends on the chemical character of an element and soil characteristics (pH, CEC, soil organic matter (SOM), soil moisture, etc.) and had shown different patterns for different sample collection areas, as can be seen in Table A1.

The possibility of migration of PTEs was confirmed using fractionation by sequential extraction for PTEs. The high average percentage of U, Mn, and Pb and a high percentage of U, Mn, Pb, and Cd in non-residual fractions indicates that there is a possibility that being released may become a threat to the environment by subsequently becoming available to be taken up by plants [62,63]. Although these elements exhibit high percentages in non-residual fractions, a large part of these percentages come from the radioactive sample, which is radioactive and highly contaminated with U. Therefore, the location where the radioactive sample was taken from should be considered as a potential hazard to the environment. The fractional distribution of the radioactive sample shows that the mobility, availability, and vertical transport of the metals are different [64]. The U, Cd, Co, Mn, Cu, Pb, and Zn fractional distribution in the radioactive sample indicates that some parts of the spoil deposit require additional steps to protect the environment.

3.2. Radiochemical Results

3.2.1. Distribution of Radionuclides in Cover Soil in Vertical and Slope Position

The soil activity concentrations for natural radionuclides measured were compared to the Hungarian mean value for the natural radionuclide content in the soil as specified by The United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) [65]. The activity concentrations for K-40 were presented separately from other radionuclides for better visuals in Figure 2.

The activity concentrations for U-238, Th-232, and U-235 radionuclides in the soil samples in each depth and the concentrations for the plant samples collected at the same location are shown in Figure 3. The activity concentrations for U-238 and Th-232 in soil were compared to the mean values for Hungary as reported by UNSCEAR [66]. The results for the radioactive sample are presented separately in Figure 4 to indicate the behavioral patterns for the U-238 and its progenies since U-238 had elevated concentrations in this location.

The activity concentrations for the radioactive soil sample and washed and unwashed radioactive plant samples were compared to other samples, as illustrated separately in Figure 4. While comparing the activity concentrations for the washed and unwashed plant samples, it was noted that the concentration difference was not significant. The difference in activity concentrations for both washed and unwashed plant samples was unnoticeable.

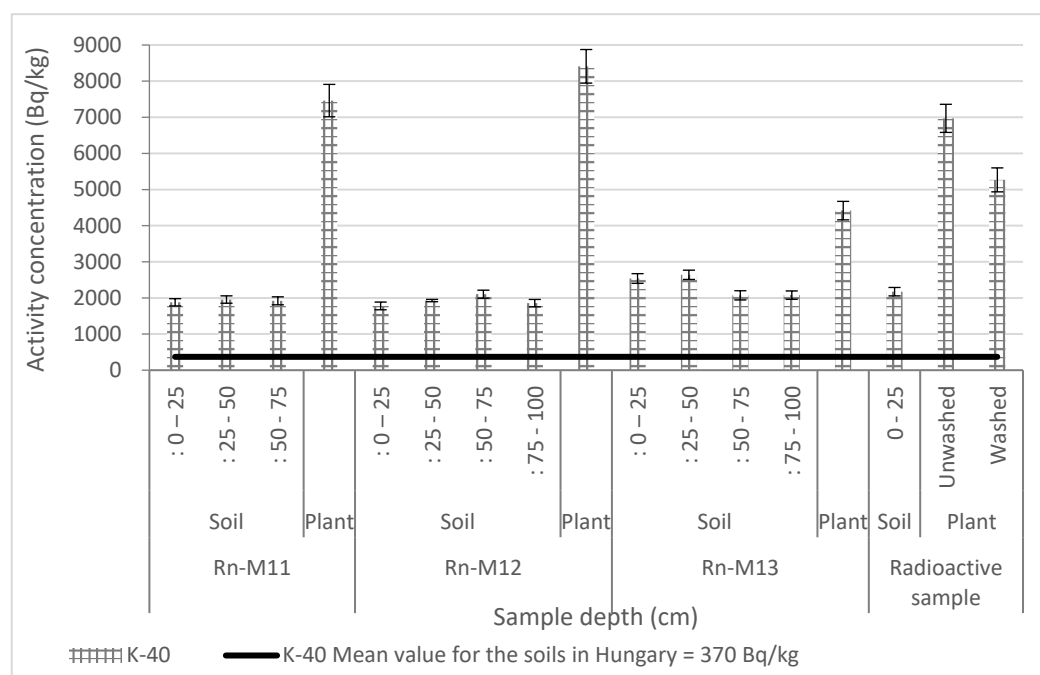


Figure 2. Activity concentrations for K-40 measured in soil and plant samples.

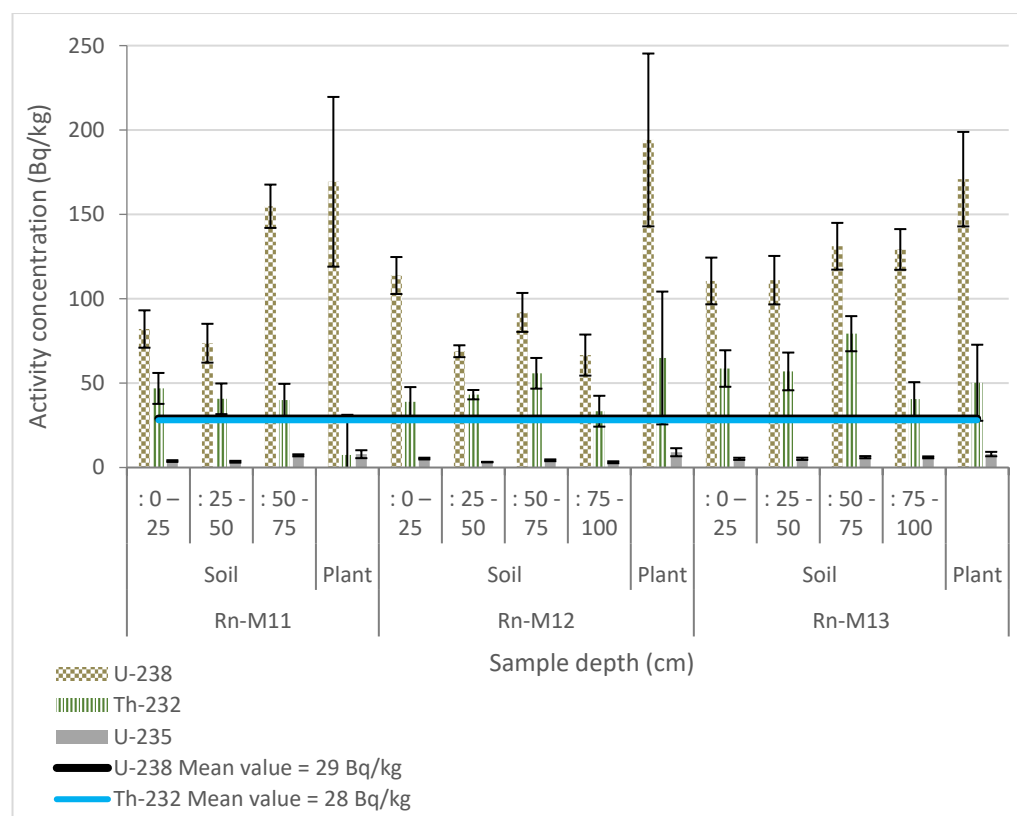


Figure 3. Activity concentrations for U-238, U-235, and Th-232 in soil and plant samples.

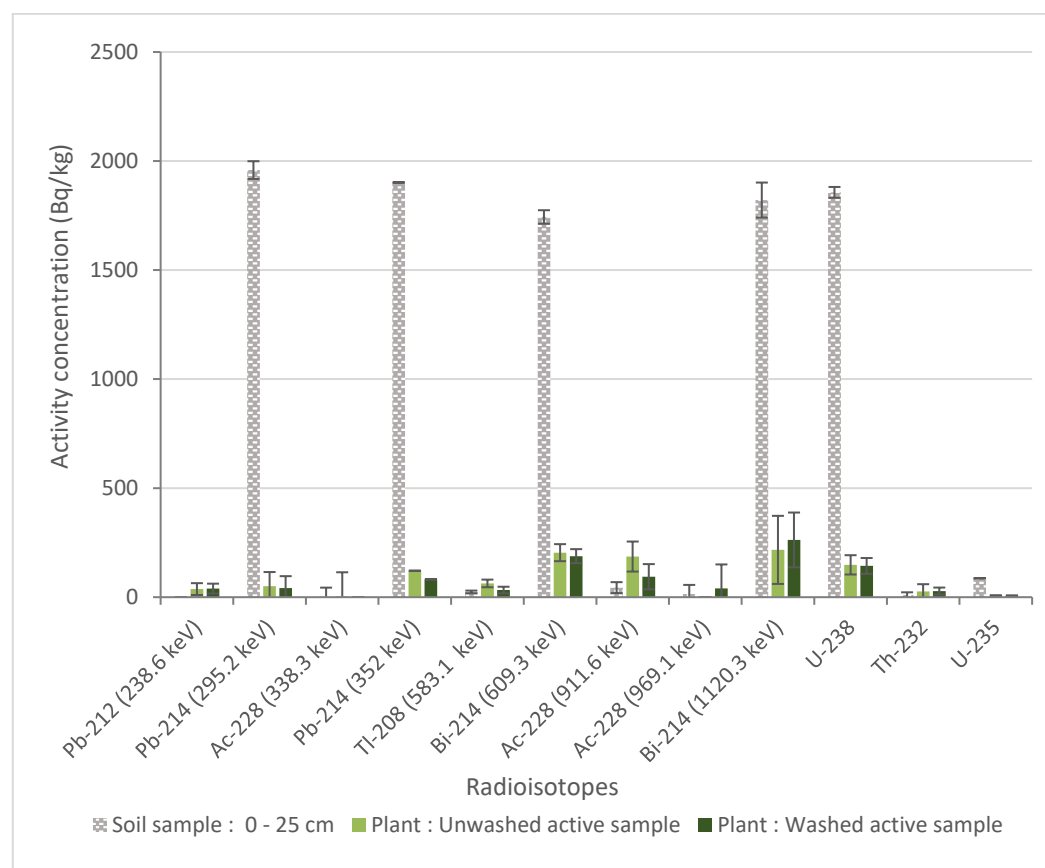


Figure 4. Radioactive sample—activity concentrations for radioactive soil and plant samples before and after washing.

3.2.2. Transfer Factors

Transfer factor values for the radionuclides were determined on a mass basis as indicated in Table 2. Rn-M11 and Rn-M12 indicated high TF ratios as compared to Rn-M13 and radioactive samples. Rn-M11 had the highest TF ratio of 7.95 ± 4.4 for Ac-228 (911.6 keV), followed by Tl-208 (583.1 keV) with a TF ratio of 6.40 ± 4.3 in sample Rn-M12.

The sequence for natural radionuclide TF ratios was as follows:

- K-40: Rn-M12 > Rn-M11 > radioactive sample > Rn-M13;
- U-238 and U-235: Rn-M11 > Rn-M12 > Rn-M13 > radioactive sample
- Th-232: radioactive sample > Rn-M12 > Rn-M13 > Rn-M11

It has been established that radioactivity should be controlled, and the limitation of discharges to the environment should ensure that the levels in the environment are below the limits derived from the ICRPs [67]. On the other hand, according to [68], there is no limitation to the concentration of naturally occurring radioisotopes in the soil [56]. However, the activity concentrations for the soil can be compared to the world median values reported by UNSCEAR [66].

It was observed that the activity concentrations of K-40, U-238, and Th-232 radionuclides indicated high activity concentrations in all soil and plant samples collected from the Mecsek uranium mine. The concentrations for these three natural radionuclides were above the Hungarian mean values and the world's median values as specified by UNSCEAR. The vertical distribution of activity concentrations for all the natural radionuclides in all depth levels did not follow any trend; the results varied throughout all sample locations. However, the soil samples collected from the bottom of the deposit (Rn-M13 and radioactive samples) had elevated activity concentrations as compared to the samples collected from the top and on the slope of the deposit. This increase in concentrations is due to the leaching of the spoil matter through the cover soil layer along

the slope of the deposit. The sequence for U-238 concentration in soil was as follows: radioactive > Rn-M13 > Rn-M11 > Rn-M12. The sequence for Th-232 activity concentrations was as follows: Rn-M13 > Rn-M12 > Rn-M11 > radioactive, and the sequence for U-235 activity concentrations was as follows: radioactive > Rn-M13 > Rn-M11 > Rn-M12.

Table 2. Transfer factors calculated from 0–25 cm soil samples.

Radionuclides	Rn-M11	Rn-M12	Rn-M13
Pb-212 (238.6 keV)	n.d.	1.25 ± 4.5	n.d.
Pb-214 (295.2 keV)	1.97 ± 4.9	3.27 ± 4.5	1.16 ± 2.0
Ac-228 (338.3 keV)	n.d.	1.56 ± 4.9	2.35 ± 2.1
Pb-214 (352 keV)	0.16 ± 4.4	2.57 ± 4.4	0.88 ± 2.0
Tl-208 (583.1 keV)	1.34 ± 4.8	6.40 ± 4.3	0.22 ± 2.2
Bi-214 (609.3 keV)	3.17 ± 4.4	1.72 ± 4.5	1.11 ± 2.0
Ac-228 (911.6 keV)	7.95 ± 4.4	1.68 ± 4.2	0.68 ± 2.4
Ac-228 (969.1 keV)	n.d.	n.d.	n.d.
Bi-214 (1120.3 keV)	2.30 ± 4.5	0.85 ± 4.7	2.44 ± 2.0
K-40	3.97 ± 4.5	4.73 ± 4.3	1.74 ± 1.9
U-238	2.06 ± 4.5	1.71 ± 4.7	1.55 ± 2.0
Th-232	0.16 ± 2.6	1.67 ± 4.5	0.86 ± 2.1
TF values for grasses [65]			
	Mean	Minimum	Maximum
Pb	0.31	0.11	1.0
K (in pasture grasses)	0.73	-	-
U	0.017	0.00020	5.5
Th	0.042	0.00074	0.65

* n.d. represents not detectable.

Notably, the activity concentration of K-40 in the unwashed plant samples was slightly higher than in the washed sample. This concludes that some of the activity concentration in plants is due to dust particles. Comparing the results for soil samples with plant samples collected at the same location indicated that the K-40 radioactivity concentrations of plant samples were more than double the soil activity concentrations. This implies that the plant samples might have taken up a large amount of K-40 from the soil. These results are in agreement with the study conducted by Manigandan [69], in which it was discovered that the K-40 activity concentrations were considerably higher than other radionuclides, which suggested higher levels of uptake of this radionuclide. Overall, the activity concentrations for all the natural radionuclides detected in plant samples were above the average concentrations found in soil samples collected from the same location, with an exception for Th-232. Thorium-232 displayed an average concentration that was less than the average concentration of the soil. This could be the indication that there was a biological uptake of these radionuclides by plants from the soil. However, for Th-232, the uptake was less than the uptake of other natural radionuclides.

Transfer factor results indicated a possibility of radionuclide uptake by plants. All samples were reported to have TF ratios that were very high for almost all radionuclides analyzed in this study (except for Pb-212 at 238.6 keV and Ac-228 at 969.1 keV).

3.3. Uranium Concentration in Water

The concentrations of uranium (U) in water were determined to evaluate the mobility of U from the surrounding spoil deposits into the groundwater and to determine the risks associated with its chemical effects. In addition, the levels of U in effluent water were determined to ensure that when the effluent water is released into the environment, it is within the regulatory limits to protect the environment [70]. Furthermore, the content of U in seepage water was determined to find out how much U could possibly seep into the groundwater. The U concentrations were measured on the groundwater effluent water and seepage water from the Mecsek uranium mine, and the results are recorded in Table 3.

The International Atomic Energy Agency (IAEA) [71] reported on the treatment of liquid effluents from uranium mines and mills during and after the operation. In this report, the concentrations for U in process water, pond water, seepage from the dams, and shallow groundwater measured in the Mecsek mine between 1996 and 2000 were reported and are listed in Table 3. In Hungary, research on the natural radioactivity of groundwater is an essential issue since both the drinking water supply and the bottled mineral water market rely almost 100% on groundwater [72]. Therefore, the groundwater concentrations obtained in this study were compared to the total uranium guideline value of 0.03 mg/L in drinking water set by the World Health Organization (WHO) [73]. In contrast, the effluent water and the seepage water results were compared to the U_{\max} limit of 2 mg/L, which is regulated by the Hungarian Ministerial Decree No. 15/2001 (VI. 6.) KöM [74]. All the water sample results obtained in this study were also compared to the results that were previously obtained in the Mecsek uranium mine and published by the IAEA [71]. Since the water analysis was an interlaboratory study, the results were also compared to the results obtained by the Mecsek uranium mine laboratory. The results obtained from both laboratories generated identical findings, which indicated that this method is reproducible.

Table 3. Uranium concentrations for water samples.

Results from the Current Study			Results from the IAEA Study [71]	
Sample ID	Sample Description	U Concentration (mg/L)	Sample Description	U Concentration (mg/L)
PK-33/1	Groundwater (No. I)	6.06 ± 0.03	groundwater	0.01–0.04
PK-44/3	Groundwater (No. I)	0.23 ± 0.001	pond water	0.03
PK-29/1	Groundwater (No. I)	1.87 ± 0.01	process water	<0.5
1504/1	Groundwater (No. I)	2.78 ± 0.01	seepage water	2–5
P-2/5	Groundwater (No. II)	1.90 ± 0.06		
P-2/6	Groundwater (No. II)	0.52 ± 0.003		
Elfolyó	treated mine water	0.32 ± 0.001		
6/11 Szint Északi-tározó	mine water from the spoil deposit No. I	2.46 ± 0.01		
	mixed water: mine water from the waste deposit No. III and leaking water from precipitation	6.72 ± 0.04		
IIIM. Gyűjtő	seepage water from the waste deposit No. III	6.99 ± 0.02		
Cs-0	seepage water from the waste rock pile No. II	0.84 ± 0.003		

In this study, the focus was on the groundwater samples collected near spoil deposit No. I, since it is the deposit that the entire study is based on. Groundwater sample PK-33/1 collected near spoil deposit No. I indicated an elevated U concentration of 6.06 ± 0.03 mg/L, which is above the World Health Organization (WHO) guideline value for U (0.03 mg/L) in drinking water [73]. All four groundwater samples collected near spoil deposit No. I (PK-33/1, PK-44/3, PK-29/1, and 1504/1) showed a large difference in concentrations (6.06 ± 0.03 , 0.23 ± 0.001 , 1.87 ± 0.01 , and 2.78 ± 0.01 mg/L, respectively). It was observed that all groundwater samples collected in this study were above the WHO guideline value. Elevated U concentrations in groundwater are of concern because they indicate active processes of uranium leaching from the spoil deposits. This increase also indicates the capability of elements to migrate into the groundwater. The elevated U levels in groundwater may be due to the seeping of water containing high concentrations of U from the process water. According to Abiye and Shaduka [75], if the tailings are not lined, the seepage from the processing water that is ponding on the tailing dams cannot be prevented from seeping into the groundwater. The comparison of U concentration in this study and the study conducted by the IAEA [71] indicated that U concentrations in groundwater for this study ranged from 0.23 to 6.06 mg/L, whereas the U concentrations from the

IAEA study ranged from 0.01 to 0.04 mg/L. In the Mecsek uranium mine, the groundwater contaminated with U is remediated by extracting it from the area and purifying it before being released to protect the drinking water aquifer [71]. The uranium decontamination of contaminated water involves ion exchange technology, in which uranium dissolved in water is bound by the anion exchange resin, and the U content of the purified water is reduced to below 1 mg/L to ensure compliance with the $U_{\max} = 2$ mg/L limit value [5]. This groundwater remediation process has been continuously operating since 2007.

The U concentration in the seepage water from spoil deposit No. III was very high (6.99 ± 0.02 mg/L) as compared to the U concentration range (2–4 mg/L) in the seepage water reported by the IAEA. Furthermore, it was observed that both the seepage water (IIIM. Gyűjtő) from spoil deposit No. III and the mixed water (Északi-táró) from the same deposit resulted in high levels of U (6.72 ± 0.04 and 6.99 ± 0.02 mg/L, respectively). Overall, the U concentrations in mine water for this study ranged from 0.32 ± 0.001 to 6.72 ± 0.04 mg/L, whereas the U concentrations from the IAEA study were <0.5 mg/L. According to Banik et al. [2], effluent often contains U, Ra-226, and other PTEs, often above regulatory requirements.

3.4. Statistical Analysis

3.4.1. Correlation Matrices and Comparison of Radionuclides, PTE Pseudo-Total, and Physicochemical Property Associations

The results of the correlation matrix are presented in Table A2. The outcome of the correlation relationship conducted was used to prove the null hypothesis, which states that the correlation coefficient is not significantly different from zero. When the r value is close to 1, it is considered that the two variables have a strong relationship, and $p \leq 0.05$ indicates that there is sufficient evidence to conclude that the correlation coefficient is significantly different from zero, and therefore, the null hypothesis is rejected [57,58]. To describe the correlation between the two variables, the following terms were used: weak correlation for $r = 0.20$ to 0.40 , moderate correlation for $r = 0.41$ to 0.60 , and strong correlation for $r > 0.60$ [76].

H₀ null hypothesis—the Pearson's correlation coefficient (r) is not significantly different from 0; the results are due to chance.

H₁ alternative hypothesis—the Pearson's correlation coefficient (r) is significantly different from 0; the r value is closer to 1.

The correlation matrix between radionuclides and PTEs indicated a significant relationship ($p \leq 0.05$) between the following pairs:

1. U-238–U-235 ($r = 1.00$), U-238–Rn-222 ($r = 0.73$) and U-238–Cu ($r = 0.97$);
2. Th-232–Fe ($r = 0.78$), Th-232–P ($r = 0.80$), Th-232–Na ($r = 0.79$), and Th-232–Mn ($r = 0.69$);
3. U-235–Rn-222 ($r = 0.73$) and U-235–Cu ($r = 0.97$);
4. K-40–K ($r = 0.84$) and K-40–Co ($r = 0.75$), K-40–Mn ($r = 0.60$), K-40–Zn ($r = 0.68$), K-40–Fe ($r = 0.57$), and K-40–P ($r = 0.54$).

whereas the observations among PTEs resulted in strong significant correlation matrices ($r > 0.60$; $p \leq 0.05$) between the following pairs:

- Fe–P, Fe–Co, Fe–Mn, Fe–Na and Fe–Zn and Zn;
- K–Co and K–Mn;
- P–Co, P–Zn, P–Mn, and P–Na;
- Co–Mn;
- Mn–Na.

Based on the correlation statistical analysis, a significant correlation between the pH and the CEC existed; therefore, it was concluded that these soil chemical properties have an impact on each other. Additionally, the pH had a significant relationship with Co, Fe, and Ni; and the CEC had a significant relationship with Co, Fe, and Ni; whereas the relationship

between the CEC and Cr was not significant. It was observed that the pH and CEC relationship with the radionuclides was not significant. However, soil moisture had a significant relationship with Th-232. This strong positive correlation between these radionuclides and PTEs suggests their common origin [77]. When considering the topography, it was observed that the SOM values were significantly different in all three depths that were considered for this analysis, whereas the CEC was only significantly different in 25–50 cm depth. In terms of depth, CEC and SOM were found to be significantly different in Rn-M11. There was a strong significant relationship between radionuclides and some PTEs.

3.4.2. Principal Component Analysis for PTE Pseudo-Total, Radionuclides, and Soil Characteristics

The correlation matrix for the PTEs in soil, radionuclides in soil, and soil characteristics were confirmed by the PCA correlation biplot (70.8%) in Figure 5. The correlation biplot indicated that most of the elements contribute to the positive side of PC 1 and the negative side of PC 2. PC 1 and PC 2 refer to the position of the samples on the slope of the deposit and the mobility of each element, respectively. In this biplot, it can be seen that the position on the slope and the depth of the soil layer are the main factors that determine the element concentration changes in the soil. Elements in this space can be classified according to their high mobility group. The mobility is strongly influenced by the pH, Ca, and CEC.

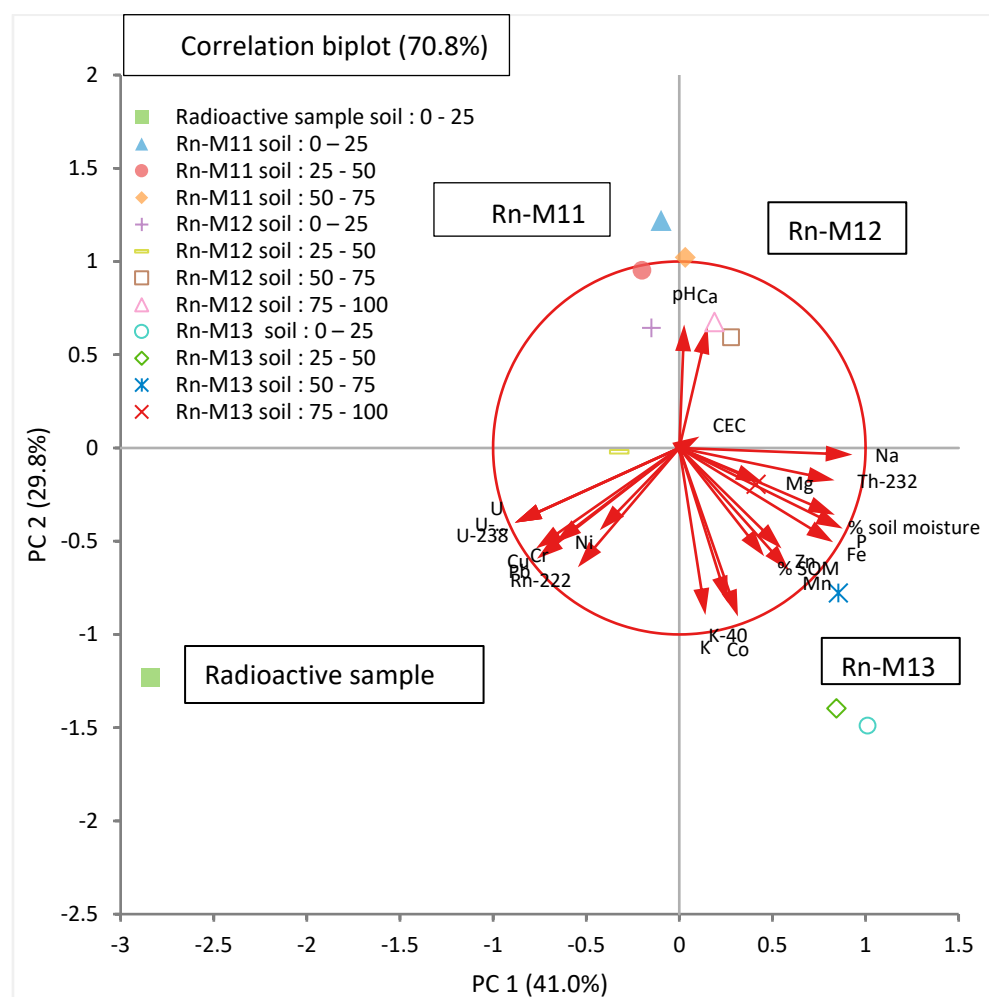


Figure 5. Principal component analysis plot for the soil characteristics, radionuclides, and PTEs in soil.

The principal component analysis biplot analysis for soil indicated that when the pH, CEC, and Ca are high, the mobility of U, U-235, U-238, Cu, Cr, Pb, Rn-222, and Ni decrease. Furthermore, there was a very strong relationship among Cd, Cr, Pb, U, and Cu, which is significant at a 95% confidence level. These results imply that where U is mobile, there is a high possibility that Cd, Cu, and Pb will also be available. These results show that two samples (Rn-M11 and Radioactive samples), which did not have sufficient (1 m) soil cover, showed significant differences in concentrations for some elements. Moreover, these results suggest that the insufficient cover layer affects the concentrations of these elements. The radioactive elements (U-238, U-235, and Rn-222) indicated a strong correlation with some PTEs (U, Ni, Pb, Cu, and Cr), which were all contributing to the negative side of PC 1 and PC 2. It could be observed that the CEC and the pH were diagonally opposite the U-238, U-235, and Rn-222, including all the PTEs that are correlated with these radionuclides (U, Ni, Pb, Cu, and Cr). This observation emphasizes that the diagonally opposite variables are negatively correlated; in this case, it can be pointed out that to minimize the mobility of these radionuclides, the pH and CEC should increase. Adding lime that contains calcium carbonate balances the pH by increasing it, consequently increasing CEC. Furthermore, Ca was observed to be strongly associated with pH. According to Panhwar et al. [78], when the Ca content increases in the soil, the pH will also increase. The CEC vector is short due to the large variance in the data.

The overall results suggest that the insufficient cover layer affects the concentrations of these elements from the spoil rock to the top layer of the deposit. If the soil cover layer is not sufficient, these elements can easily become mobile.

The BCR sequential extraction procedure has proven to be useful in providing information regarding the mobility of PTEs for the planning and management of recultivation applications [34]. Based on the plant radionuclidic and PTE uptake; and on the results from the BCR sequential extraction, it is apparent that one meter (1 m) of intact soil cover layer for spoil deposit No. I is enough for effective retardation of migration of PTEs and radionuclides. However, where the soil cover layer thickness is low (radioactive sample), it is not compelling enough. Therefore, the additional soil cover is needed to stabilize and protect the environment to ensure environmental safety. Additionally, since the sampling of the soil sample at the 75–100 cm depth in Rn-M11 and at 25–100 cm for the radioactive sample was not possible due to the rocks underneath, it is an indication that the cover layer was not 1 m in these locations as recommended by the OECD/NEA [79].

4. Conclusions

Radionuclide and PTE concentrations in the soil cover layer of deposit No. I take their origin from the soil's own matter and the spoil rock due to the leaching and migration by water infiltration vertically and along the slope. The distribution of PTE and radionuclide concentrations in the soil cover layer depends on the chemical character of an element and soil characteristics (pH, CEC, SOM, soil moisture, etc.) [80] and has shown different patterns for different elements. Correlation matrices and statistical analysis indicated the possible correlations between the PTEs, radionuclides, and physico-chemical properties; and the PCA determined the association of mobile elements with the samples collected from the area where there was an insufficient cover layer.

Using the pseudo-total soil concentrations for TF calculation, problem areas could be identified, and applying the BCR sequential extraction method helped to specify the elements prone to mobility and bioavailability according to environmental conditions in the Mecsek uranium mine. The combination of the BCR sequential extraction and pseudo-total methodologies discovered some problems regarding the efficacy of the recultivation soil in uranium mine areas.

Based on the high levels of U in the groundwater, it could be concluded that the soil cover layer requires an additional step to ensure that its integrity is intact. According to the IAEA [71], one of many techniques to monitor the integrity of the soil cover layer is to monitor the radiological and chemical leachate collected in the vault drainage system and in groundwater to provide an indication of degradation in cover performance.

It was proven that the soil cover layer satisfactorily retards the migration of the PTEs and radionuclides from the spoil leaching. However, when it is wounded, it may cause the release of these contaminants into the groundwater and surrounding environment.

Author Contributions: Conceptualization, L.M., G.H., A.V. and M.H.; Data curation, L.M.; Formal analysis, L.M. and M.H.; Funding acquisition, L.M., G.H. and M.H.; Investigation, L.M. and G.H.; Methodology, L.M., G.H. and M.H.; Project administration, L.M., G.H. and M.H.; Resources, L.M., G.H., A.V. and M.H.; Software, L.M. and A.V.; Supervision, G.H. and M.H.; Validation, L.M., G.H. and M.H.; Visualization, L.M. and A.V.; Writing—original draft, L.M.; Writing—review and editing, L.M. and G.H. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Tempus Public Foundation, grant number 238700, and by the South African Higher Education and Training.

Data Availability Statement: The data are contained within the article.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

Appendix A

Table A1. Physico-chemical properties that may affect the mobility of elements [43,44].

Sample Description	Depth (cm)	Soil Moisture Content (%)	Soil pH	CEC (cmol(+)/kg)	SOM (%)	Plant Moisture Content (%)
Rn-M11	0–25	9.24	6.22	52.9 ± 6.71	1.61	33.1
	25–50	7.44	6.12	20.2 ± 0.06	1.21	
	50–75	12.6	5.99	14.6 ± 4.55	2.56	
	75–100			Hard rock (not sampled)		
Rn-M12	0–25	9.47	5.79	33.0 ± 0.69	0.75	31.2
	25–50	8.99	5.50	8.23 ± 1.09	0.64	
	50–75	8.19	5.47	24.4 ± 1.31	0.96	
	75–100	8.43	5.38	33.0 ± 0.01	1.11	
Rn-M13	0–25	17.1	5.61	28.2 ± 0.44	5.27	25.0
	25–50	14.3	5.27	31.8 ± 4.61	3.34	
	50–75	14.2	5.38	28.1 ± 2.67	1.92	
	75–100	14.2	5.36	36.6 ± 0.01	1.76	
Radioactive sample	0–25	3.16	5.27	27.3 ± 0.01	1.31	60.3

Table A2. The correlation matrix (r) for the concentrations of the natural radionuclides, total PTEs, and the chemical properties of the soil.

Pearsons' (r)	U-238	Th-232	U-235	K-40	Rn-222	Ca	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	P	Pb	U	Zn	CEC	pH	% * SM	% * SOM
U-238	—																						
Th-232	−0.65	—																					
U-235	1.00	−0.65	—																				
K-40	0.13	0.31	0.13	—																			
Rn-222	0.73	−0.35	0.73	0.31	—																		
Ca	−0.30	−0.06	−0.30	−0.42	−0.54	—																	
Co	0.05	0.45	0.05	0.75	0.47	−0.57	—																
Cr	0.69	−0.43	0.69	0.16	0.62	−0.51	0.33	—															
Cu	0.97	−0.54	0.97	0.29	0.74	−0.30	0.18	0.67	—														
Fe	−0.55	0.78	−0.55	0.57	−0.05	−0.22	0.79	−0.23	−0.42	—													
K	0.26	0.22	0.26	0.84	0.40	−0.66	0.80	0.27	0.38	0.53	—												
Mg	−0.19	0.32	−0.19	0.34	−0.15	0.56	0.30	−0.34	−0.08	0.48	0.17	—											
Mn	−0.33	0.69	−0.33	0.60	0.18	−0.57	0.86	0.05	−0.22	0.88	0.62	0.10	—										
Na	−0.81	0.79	−0.81	0.19	−0.31	0.13	0.37	−0.61	−0.70	0.84	0.09	0.45	0.62	—									
Ni	0.39	−0.22	0.39	0.12	0.45	−0.50	0.39	0.94	0.38	−0.04	0.20	−0.35	0.23	−0.39	—								
P	−0.59	0.80	−0.59	0.54	−0.11	−0.11	0.70	−0.38	−0.44	0.98	0.48	0.54	0.80	0.89	−0.20	—							
Pb	0.97	−0.52	0.97	0.32	0.80	−0.42	0.26	0.70	0.98	−0.36	0.46	−0.12	−0.14	−0.69	0.42	−0.41	—						
U	1.00	−0.65	1.00	0.13	0.73	−0.30	0.05	0.69	0.97	−0.55	0.26	−0.20	−0.33	−0.81	0.39	−0.59	0.97	—					
Zn	−0.20	0.49	−0.20	0.68	−0.12	−0.05	0.50	−0.19	0.04	0.60	0.58	0.50	0.47	0.43	−0.16	0.66	−0.03	−0.20	—				
CEC	−0.03	0.05	−0.03	0.02	0.00	−0.11	−0.01	−0.32	−0.12	0.07	0.17	0.03	−0.01	0.18	−0.42	0.11	−0.01	−0.03	−0.25	—			
pH	−0.28	−0.05	−0.28	−0.44	−0.60	0.11	−0.71	−0.39	−0.37	−0.41	−0.36	−0.45	−0.46	−0.13	−0.38	−0.35	−0.38	−0.28	−0.26	0.28	—		
% *SM	−0.57	0.71	−0.57	0.50	−0.30	−0.13	0.51	−0.40	−0.39	0.81	0.46	0.38	0.64	0.74	−0.25	0.86	−0.39	−0.57	0.81	0.08	−0.10	—	
% *SOM	−0.11	0.38	−0.11	0.78	−0.15	−0.27	0.50	−0.12	0.07	0.53	0.78	0.33	0.46	0.26	−0.13	0.55	0.07	−0.11	0.86	0.08	−0.04	0.75	—

* SM, soil moisture; SOM, soil organic matter; the values highlighted in bold are Pearson's correlation coefficient (r) significant at 95% confidence level; $p \leq 0.05$.

References

- Juhasz, L.; Szerbin, P.; Lendvai, Z.; Csovari, M.; Benkovics, I. Planning for Uranium Mining and Milling Sites Environmental Restoration of in Central and Eastern Europe. In *Proceedings of the Planning for Environmental Restoration of Uranium Mining and Milling Sites in Central and Eastern Europe: Proceedings of a Workshop Held under the Technical Co-Operation Project RER/9/022 on Environmental Restoration in Central and Eastern Europe*; International Atomic Energy Agency: Vienna, Austria, 1996; pp. 102–116.
- Banik, J.; Csövári, M.; Németh, G. Uranium Ore Mining and the Remediation of the Site in Hungary. In *Proceedings of the The Uranium Mining Remediation Exchange Group (UMREG)*; IAEA: Vienna, Austria, 2011; pp. 125–137.
- Wallner, A.; Stein, P. *Uranium Mining in and for Europe*; Austrian Institute of Ecology: Vienna, Austria, 2012.
- IAEA. *Review of “Handbook of Parameter Values for the Prediction of Radionuclide Transfer in Terrestrial and Freshwater Environments”*; International Atomic Energy Agency (IAEA) Technical Reports Series No. 472. IAEA: Vienna, Austria, 2011; Volume 102.
- Mecsekérc, Z. Uranium Monitoring. Available online: <https://www.mecsekerc.hu/eng-uranipari-monitoring> (accessed on 10 May 2020).
- Erdi-Krausz, G. Problems and Solutions for Water Treatment at the Closed Hungarian Uranium Industry. In *Proceedings of the Recent Developments in Uranium Exploration, Production and Environmental Issues—IAEA-TECDOC-1463*; IAEA in Cooperation with the OECD Nuclear Energy Agency and DIAMO State Owned Enterprise; IAEA: Staz, Czech Republic, 2005; p. 87.
- Skipperud, L.; Strømman, G.; Yunusov, M.; Stegnar, P.; Uralbekov, B.; Tilloboev, H.; Zjazjev, G.; Heier, L.S.; Rosseland, B.O.; Salbu, B. Environmental Impact Assessment of Radionuclide and Metal Contamination at the Former U Sites Taboshar and Digmai, Tajikistan. *J. Environ. Radioact.* **2013**, *123*, 50–62. [[CrossRef](#)]
- Fernández-Ondoño, E.; Bacchetta, G.; Lallena, A.M.; Navarro, F.B.; Ortiz, I.; Jiménez, M.N. Use of BCR Sequential Extraction Procedures for Soils and Plant Metal Transfer Predictions in Contaminated Mine Tailings in Sardinia. *J. Geochemical Explor.* **2017**, *172*, 133–141. [[CrossRef](#)]
- Waggitt, P. Uranium Mining Legacies Remediation and Renaissance Development: An International Overview. In *Proceedings of the Uranium, Mining and Hydrogeology*; Merkel, B.J., Hasche-berger, A., Eds.; Saxon State Ministry of Environment and Agriculture: Freiberg, Germany, 2008.
- Shiva Kumar, D.; Srikantaswamy, S. Factors Affecting on Mobility of Heavy Metals in Soil Environment. *Int. J. Sci. Res. Dev.* **2014**, *2*, 201–203.
- Sánchez-Donoso, R.; García Lorenzo, M.L.; Esbrí, J.M.; García-Noguero, E.M.; Higuera, P.; Crespo, E. Geochemical Characterization and Trace-Element Mobility Assessment for Metallic Mine Reclamation in Soils Affected by Mine Activities in the Iberian Pyrite Belt. *Geosciences* **2021**, *11*, 233. [[CrossRef](#)]
- Jaishankar, M.; Tseten, T.; Anbalagan, N.; Mathew, B.B.; Beeregowda, K.N. Toxicity, Mechanism and Health Effects of Some Heavy Metals. *Interdiscip. Toxicol.* **2014**, *7*, 60–72. [[CrossRef](#)]
- Smčiklas, I.; Šljivić-Ivanović, M. Radioactive Contamination of the Soil: Assessments of Pollutants Mobility with Implication to Remediation Strategies. In *Soil Contamination—Current Consequences and Further Solutions*; Larramendy, M.L., Soloneski, S., Eds.; InTech: Rijeka, Croatia, 2016; pp. 268–276. ISBN 9789535128151.
- Salbu, B.; Lind, O.C.; Skipperud, L. Radionuclide Speciation and Its Relevance in Environmental Impact Assessments. *J. Environ. Radioact.* **2004**, *74*, 233–242. [[CrossRef](#)]
- Skipperud, L.; Salbu, B. Sequential Extraction as a Tool for Mobility Studies of Radionuclides and Metals in Soils and Sediments. *Radiochim. Acta* **2015**, *103*, 187–197. [[CrossRef](#)]
- Gupta, D.K.; Voronina, A. *Remediation Measures for Radioactively Contaminated Areas*; Springer International Publishing AG: Cham, Switzerland, 2019; ISBN 9783319733975.
- Igwe, J.C.; Nnorom, I.C.; Gbaruko, B.C. Kinetics of Radionuclides and Heavy Metals Behaviour in Soils: Implications for Plant Growth. *Afr. J. Biotechnol.* **2005**, *4*, 1541–1547. [[CrossRef](#)]
- Adesiji, N.E.; Ademola, J.A. Soil-to-Cassava Plant Transfer Factor of Natural Radionuclides on a Mining Impacted Soil in a Tropical Ecosystem of Nigeria. *J. Environ. Radioact.* **2019**, *201*, 1–4. [[CrossRef](#)] [[PubMed](#)]
- Ogundiran, M.B.; Osibanjo, O. Mobility and Speciation of Heavy Metals in Soils Impacted by Hazardous Waste. *Chem. Speciat. Bioavailab.* **2009**, *21*, 59–69. [[CrossRef](#)]
- Bielicka-Giełdoń, A.; Ryłko, E.; Zamojć, K. Distribution, Bioavailability and Fractionation of Metallic Elements in Allotment Garden Soils Using the BCR Sequential Extraction Procedure. *Polish J. Environ. Stud.* **2013**, *22*, 1013–1021.
- Ross, D.S.; Ketterings, Q. Recommended Methods for Determining Soil Cation Exchange Capacity. In *Plant Growth Regulators to Manipulate Oat Stands*; Rajala, A., Ed.; Springer: Berlin/Heidelberg, Germany, 2004; Volume 13, pp. 186–197.
- Agic, R.; Skopje, F.; Milenkovic, L.; Ilic, Z.S. Transfer Factor as Indicator. *Fresenius Environ. Bull.* **2015**, *24*, 4212–4219.
- Violante, A.; Cozzolino, V.; Perelomov, L.; Caporale, A.G.; Pigna, M. Mobility and Bioavailability of Heavy Metals and Metalloids in Soil Environments. *J. Soil Sci. Plant Nutr.* **2010**, *10*, 268–292. [[CrossRef](#)]
- Kabata-Pendias, A. Soil-Plant Transfer of Trace Elements—An Environmental Issue. *Geoderma* **2004**, *122*, 143–149. [[CrossRef](#)]
- Popic, J.M. *Environmental Impact of Radionuclides and Trace Elements in the Thorium Rich Fen Area in Norway*; Norwegian University of Life Sciences: Ås, Norway, 2014.
- Strok, M. Transfer of Natural Radionuclides from Hay and Silage to Cow’s Milk in the Vicinity of a Former Uranium Mine. *J. Environ. Radioact.* **2012**, *110*, 64–68. [[CrossRef](#)]

27. Opaluwa, O.D.; Aremu, M.O.; Ogbo, L.O.; Abiola, K.A.; Odiba, I.E.; Abubakar, M.M.; Nweze, N.O. Heavy Metal Concentrations in Soils, Plant Leaves and Crops Grown around Dump Sites in Lafia Metropolis, Nasarawa State, Nigeria. *Adv. Appl. Sci. Res.* **2012**, *3*, 780–784.
28. Baran, A.; Tarnawski, M. Assessment of Heavy Metals Mobility and Toxicity in Contaminated Sediments by Sequential Extraction and a Battery of Bioassays. *Ecotoxicology* **2015**, *24*, 1279–1293. [[CrossRef](#)] [[PubMed](#)]
29. Rosado, D.; Usero, J.; Morillo, J. Ability of 3 Extraction Methods (BCR, Tessier and Protease K) to Estimate Bioavailable Metals in Sediments from Huelva Estuary (Southwestern Spain). *Mar. Pollut. Bull.* **2016**, *102*, 65–71. [[CrossRef](#)]
30. Zhang, G.; Bai, J.; Xiao, R.; Zhao, Q.; Jia, J.; Cui, B.; Liu, X. Heavy Metal Fractions and Ecological Risk Assessment in Sediments from Urban, Rural and Reclamation-Affected Rivers of the Pearl River Estuary, China. *Chemosphere* **2017**, *184*, 278–288. [[CrossRef](#)]
31. Isimekhai, K.A.; Garelick, H.; Watt, J.; Purchase, D. Heavy Metals Distribution and Risk Assessment in Soil from an Informal E-Waste Recycling Site in Lagos State, Nigeria. *Environ. Sci. Pollut. Res.* **2017**, *24*, 17206–17219. [[CrossRef](#)]
32. Stevanović, V.; Gulan, L.; Milenković, B.; Valjarević, A.; Zeremski, T.; Penjišević, I. Environmental Risk Assessment of Radioactivity and Heavy Metals in Soil of Toplica Region, South Serbia. *Environ. Geochem. Health* **2018**, *40*, 2101–2118. [[CrossRef](#)] [[PubMed](#)]
33. Yun, S.W.; Kim, D.H.; Kang, D.H.; Son, J.; Lee, S.Y.; Lee, C.K.; Lee, S.H.; Ji, W.H.; Baveye, P.C.; Yu, C. Effect of Farmland Type on the Transport and Spatial Distribution of Metal(Loid)s in Agricultural Lands near an Abandoned Gold Mine Site: Confirmation of Previous Observations. *J. Geochem. Explor.* **2017**, *181*, 129–137. [[CrossRef](#)]
34. Sungur, A.; Soylak, M.; Ozcan, H. Investigation of Heavy Metal Mobility and Availability by the BCR Sequential Extraction Procedure: Relationship between Soil Properties and Heavy Metals Availability. *Chem. Speciat. Bioavailab.* **2014**, *26*, 219–230. [[CrossRef](#)]
35. Rinklebe, J.; Shaheen, S.M. Geochemical Distribution of Co, Cu, Ni, and Zn in Soil Profiles of Fluvisols, Luvisols, Gleysols, and Calcisols Originating from Germany and Egypt. *Geoderma* **2017**, *307*, 122–138. [[CrossRef](#)]
36. Soltani, N.; Keshavarzi, B.; Moore, F.; Sorooshian, A.; Ahmadi, M.R.; Sciences, A.; Ore, I.; Mining, G. Distribution of Potentially Toxic Elements (PTEs) in Tailings, Soils, and Plants around Gol-E-Gohar Iron Mine, a Case Study in Iran. *Env. Sci. Pollut. Res. Int.* **2017**, *24*, 18798–18816. [[CrossRef](#)]
37. Korychenskyi, K.O.; Laptev, G.V.; Voitsekhovych, O.V.; Lavrova, T.V.; Dyvak, T.I. Speciation and mobility of uranium in tailings materials at the u-production legacy site in ukraine. *Nucl. Phys. At. Energy* **2018**, *19*, 270–279. [[CrossRef](#)]
38. Nemati, K.; Bakar, N.K.A.; Abas, M.R.; Sobhanzadeh, E. Speciation of Heavy Metals by Modified BCR Sequential Extraction Procedure in Different Depths of Sediments from Sungai Buloh, Selangor, Malaysia. *J. Hazard. Mater.* **2011**, *192*, 402–410. [[CrossRef](#)]
39. Rauret, G.; López-Sánchez, J.F.; Sahuquillo, A.; Rubio, R.; Davidson, C.; Ure, A.; Quevauviller, P. Improvement of the BCR Three Step Sequential Extraction Procedure Prior to the Certification of New Sediment and Soil Reference Materials. *J. Environ. Monit.* **1999**, *1*, 57–61. [[CrossRef](#)]
40. Umoren, I.U.; Udoh, A.P.; Udousoro, I.I. Concentration and Chemical Speciation for the Determination of Cu, Zn, Ni, Pb and Cd from Refuse Dump Soils Using the Optimized BCR Sequential Extraction Procedure. *Environmentalist* **2007**, *27*, 241–252. [[CrossRef](#)]
41. Yang, Z.; Wang, Y.; Shen, Z.; Niu, J.; Tang, Z. Distribution and Speciation of Heavy Metals in Sediments from the Mainstream, Tributaries, and Lakes of the Yangtze River Catchment of Wuhan, China. *J. Hazard. Mater.* **2009**, *166*, 1186–1194. [[CrossRef](#)]
42. Saleem, M.; Iqbal, J.; Akhter, G.; Shah, M.H. Fractionation, Bioavailability, Contamination and Environmental Risk of Heavy Metals in the Sediments from a Freshwater Reservoir, Pakistan. *J. Geochem. Explor.* **2018**, *184*, 199–208. [[CrossRef](#)]
43. Khumalo, L.; Heltai, G.; Horváth, M. The Migration of Potentially Toxic Elements during the Recultivation of the Uranium Mining Deposit in Mecsek. *Acta Hydrol. Slovaca* **2020**, *20*, 210–217. [[CrossRef](#)]
44. Khumalo, L.; Heltai, G.; Várhegyi, A.; Horváth, M. Mobility of Potentially Toxic Elements from the Abandoned Uranium Mine's Spoil Bank. *Ecol. Chem. Eng. S* **2021**, *28*, 241–258. [[CrossRef](#)]
45. Heltai, G.; Győri, Z.; Fekete, I.; Halász, G.; Kovács, K.; Takács, A.; Khumalo, L.; Horváth, M. Application of Flexible Multi-Elemental ICP-OES Detection in Fractionation of Potentially Toxic Element Content of Solid Environmental Samples by a Sequential Extraction Procedure. *Microchem. J.* **2019**, *149*, 104029. [[CrossRef](#)]
46. Juhasz, L.; Erdi-Krausz, G. Consequences of the hungarian uranium mining and milling. In *Proceedings of a workshop held within the Technical Co-operation Project on Environmental Restoration in Central and Eastern Europe in Budapest, Hungary, 4–8 October 1993*; Planning for Environmental Restoration of Radioactively Contaminated Sites in Cent; International Atomic Energy Agency: Vienna, Austria, 1993; pp. 151–156.
47. René, M. History of Uranium Mining in Central Europe. In *Uranium—Safety, Resources, Separation and Thermodynamic Calculation*; Awwad, N.S., Ed.; IntechOpen: London, UK, 2018; Volume 1, pp. 1–20. ISBN 9781626239777.
48. OrangeSmile.com. Maps of Hungary. Available online: <http://www.https://www.orangesmile.com/travelguide/hungary/country-maps.htm> (accessed on 3 April 2021).
49. Rauret, G.; López-Sánchez, J.F.; Sahuquillo, A.; Rubio, R.; Davidson, C.; Ure, A.; Quevauviller, P. The Certification of the Extractable Contents (Mass Fractions) of Cd, Cr, Cu, Ni, Pb and Zn in Freshwater Sediment Following a Sequential Extraction Procedure—BCR-701; Belgium. 2001. Available online: <https://ec.europa.eu/jrc/en/publication/eur-scientific-and-technical-research-reports/additional-certification-pb-mass-fraction-bcr-320r-channel-sediment> (accessed on 17 April 2020).

50. Khumalo, L.H.N.; Heltai, G.; Horváth, M. Mobility of Radionuclides from the Spoil Deposit No. 1 of the Abandoned Uranium Mine in Pécs, Hungary. In *Proceedings of the 5th International Conference on Environmental Radioactivity ENVIRA 2019: Variations of Environmental Radionuclides*; Světlík, I., Povinec, P.P., Pachnerová Brabcová, K., Eds.; Czech Technical University in Prague: Prague, Czech, 2019; p. 159.
51. MSZ 1484-3:2006 Testing of Waters. Part 3: Determination of Dissolved, Suspended and Total Metals in Water by AAS and ICP-OES. Available online: <http://www.mszt.hu/web/guest/home> (accessed on 1 November 2020).
52. Bernard, B.B.; Bernard, H.; Brooks, J.M. Determination of Total Carbon, Total Organic Carbon and Inorganic Carbon in Sediments. Available online: https://www.tdi-bi.com/analytical_services/environmental/NOAA_methods/TOC.pdf (accessed on 24 April 2021).
53. Júnior, J.A.S.; Cardoso, J.J.R.F.; Silva, C.M.; Silveira, S.V.; Amaral, R.S. Determination of Radionuclides in the Environment Using Gamma-Spectrometry. *J. Radioanal. Nucl. Chem.* **2006**, *269*, 451–455. [CrossRef]
54. Gerzabek, M.H.; Strebl, F.; Temmel, B. Plant Uptake of Radionuclides in Lysimeter Experiments. *Environ. Pollut.* **1998**, *99*, 93–103. [CrossRef]
55. Intawongse, M.; Dean, J.R. Uptake of Heavy Metals by Vegetable Plants Grown on Contaminated Soil and Their Bioavailability in the Human Gastrointestinal Tract. *Food Addit. Contam.* **2007**, *23*, 36–48. [CrossRef]
56. Lațo, A.; Radulov, I.; Berbecea, A.; Lațo, K.; Crista, F. The Transfer Factor of Metals in Soil-Plant System Mp Ms. *Res. J. Agric. Sci.* **2012**, *44*, 67–72.
57. Statstutor Pearson's Correlation. 2015. Available online: <http://www.statstutor.ac.uk/resources/uploaded/pearsons.pdf> (accessed on 30 November 2020).
58. Althouse, A.D.; Soman, P. Understanding the True Significance of a P Value. *J. Nucl. Cardiol.* **2017**, *24*, 191–194. [CrossRef]
59. 6/2009. (IV. 14.) KvVM-EüM-FVM Common Order about the Standard Limits and Measurement of Contamination for the Protection of underground Water and Geological Medium; Budapest, Hungary. 2009. Available online: <https://net.jogtar.hu/jogszabaly?docid=a0900006.kvv> (accessed on 3 March 2021).
60. Rékási, M.; Filep, T. Fractions and Background Concentrations of Potentially Toxic Elements in Hungarian Surface Soils. *Environ. Monit. Assess.* **2012**, *184*, 7461–7471. [CrossRef]
61. Van Herreweghe, S.; Swennen, R.; Vandecasteele, C.; Cappuyns, V. Solid Phase Speciation of Arsenic by Sequential Extraction in Standard Reference Materials and Industrially Contaminated Soil Samples. *Environ. Pollut.* **2003**, *122*, 323–342. [CrossRef] [PubMed]
62. Pavlović, D.; Pavlović, M.; Čakmak, D.; Kostić, O.; Jarić, S.; Sakan, S.; Đorđević, D.; Mitrović, M.; Gržetić, I.; Pavlović, P. Fractionation, Mobility, and Contamination Assessment of Potentially Toxic Metals in Urban Soils in Four Industrial Serbian Cities. *Arch. Environ. Contam. Toxicol.* **2018**, *75*, 335–350. [CrossRef] [PubMed]
63. Perez-Moreno, S.M.; Gazquez, M.J.; Perez-Lopez, R.; Bolivar, J.P. Validation of the BCR Sequential Extraction Procedure for Natural Radionuclides. *Chemosphere* **2018**, *198*, 397–399. [CrossRef] [PubMed]
64. Fedotov, P.S.; Dzhendova, R.K.; Dampilova, B.V.; Doroshkevich, S.G.; Karandashev, V.K. Unexpected Behavior of Zn, Cd, Cu, and Pb in Soils Contaminated by Ore Processing after 70 Years of Burial. *Environ. Chem. Lett.* **2018**, *16*, 637–645. [CrossRef]
65. IAEA. *Handbook of Parameter Values for the Prediction of Radionuclide Transfer in Terrestrial and Freshwater Environments*; Elsevier Ltd.: Vienna, Austria, 2010; Volume 472, (accessed on 1 February 2021). [CrossRef]
66. United Nations. *Sources and Effects of Ionizing Radiation—United Nations Scientific Committee on the Effects of Atomic Radiation*; United Nations Publication: New York, NY, USA, 2000; pp. 1–659. ISBN 9211422388.
67. Valkovic, V. Determination of Radionuclides In Environmental Samples. In *Environmental Analysis: Techniques, Applications and Quality Assurance*; Barcelo, D., Ed.; Elsevier Science Publishers B.V.: Amsterdam, The Netherlands, 1993; pp. 311–356. ISBN 9781402095986.
68. Almeida, G.M.; Campos, S.S.S.; Gennari, R.F.; Souza, S.O. Determination of the concentration of radionuclides in soil and water next the uranium mine of caetité-ba. In *Proceedings of the International Nuclear Atlantic Conference; Nuclear Energy: New Jobs for a Better Life*, Belo Horizonte, Brazil, 24–28 October 2011.
69. Manigandan, P.K. Activity Concentration of Radionuclides in Plants in the Environment of Western Ghats. *Iran J. of Radiat. Res.* **2009**, *7*, 85–90.
70. Banik, J.; Baudu-Picquet, I.; Benkovics, I.; Csövari, M.; Csicsak, J.; Edwards, C.; Guler, H.; Hideg, J.; Holden, P.; Jarrell, J.; et al. *IAEA Safety Report Series No.35—Surveillance and Monitoring of Near Surface Disposal Facilities for Radioactive Waste*; IAEA: Vienna, Austria, 2004; pp. 1–65. ISBN 978-9201069191.
71. Bell, M.J.; Dayal, R.; Gera, F.; Green, T.H.; Han, K.W.; Holub, J.; Hubbell, J.; Hunter, G.; Kontic, B.; Kuèar-Dragičević, C.; et al. *IAEA Treatment of Liquid Effluent from Uranium Mines and Mills—Report of a Co-Ordinated Research Project 1996–2000*; IAEA: Vienna, Austria, 2004; pp. 145–167. ISBN 92-0-112304-3.
72. Erőss, A.; Csondor, K.; Izsák, B.; Vargha, M.; Horváth, Á.; Pándics, T. Uranium in Groundwater—The Importance of Hydraulic Regime and Groundwater Flow System's Understanding. *J. Environ. Radioact.* **2018**, *195*, 90–96. [CrossRef]
73. World Health Organization. *WHO Guidelines for Drinking Water Quality, Volume 1. Recommendations*, 3rd ed.; WHO: Geneva, Switzerland, 2008; Volume 1, ISBN 9789241547611.

74. Ministerial Decree, No. 15/2001 (VI. 6.) KöM Environment on Radioactive Discharges to the Atmosphere and into Waters during the Use of Atomic Energy and on Monitoring of the Discharge; Budapest, Hungary. 2001. Available online: <https://net.jogtar.hu/jogszabaly?docid=a0100015.kom> (accessed on 19 March 2021).
75. Abiye, T.; Shaduka, I. Radioactive Seepage through Groundwater Flow from the Uranium Mines, Namibia. *Hydrology* **2017**, *4*, 11. [[CrossRef](#)]
76. Gulan, L.; Milenkovic, B.; Zeremski, T.; Milic, G.; Vuckovic, B. Persistent Organic Pollutants, Heavy Metals and Radioactivity in the Urban Soil of Priština City, Kosovo and Metohija. *Chemosphere* **2017**, *171*, 415–426. [[CrossRef](#)]
77. Bai, H.; Hu, B.; Wang, C.; Bao, S.; Sai, G.; Xu, X.; Zhang, S.; Li, Y. Assessment of Radioactive Materials and Heavy Metals in the Surface Soil around the Bayanwula Prospective Uranium Mining Area in China. *Int. J. Environ. Res. Public Health* **2017**, *14*, 300. [[CrossRef](#)]
78. Panhwar, Q.A.; Naher, U.A.; Shamshuddin, J.; Othman, R.; Ismail, M.R. Applying Limestone or Basalt in Combination with Bio-Fertilizer to Sustain Rice Production on an Acid Sulfate Soil in Malaysia. *Sustainability* **2016**, *8*, 700. [[CrossRef](#)]
79. OECD/NEA. *Managing Environmental and Health Impacts of Uranium Mining*; Organisation for Economic Co-Operation and Development: Paris, France; OECD/NEA Publishing: Paris, France, 2014.
80. Golia, E.E.; Tsiropoulos, G.N.; Füleky, G.; Floras, S.; Vleioras, S. Pollution Assessment of Potentially Toxic Elements in Soils of Different Taxonomy Orders in Central Greece. *Environ. Monit. Assess.* **2019**, *191*, 106. [[CrossRef](#)] [[PubMed](#)]