






Article

Water-Rock Interaction and Potential Contamination Risk in a U-Enriched Area

Margarida Antunes ¹, Rui Teixeira ², Teresa Albuquerque ^{3,4,*}, Teresa Valente ¹, Paula Carvalho ⁵
and António Santos ⁶

¹ Department of Earth Sciences, Campus de Gualtar, ICT/University of Minho, 4710-057 Braga, Portugal; imantunes@dct.uminho.pt (M.A.); teresav@dct.uminho.pt (T.V.)

² Department of Geology and Pole of the Geosciences Centre (CGeo), University of Trás-os-Montes e Alto Douro, UTAD, Quinta de Prados, 5000-801 Vila Real, Portugal; rteixeir@utad.pt

³ CERNAS|QRural/Polytechnique Institute of Castelo Branco, 6000-084 Castelo Branco, Portugal

⁴ Institute of Earth Sciences, ICT/University of Évora, 7000-849 Évora, Portugal

⁵ MARE-Marine and Environmental Sciences Centre, Department of Life Sciences, University of Coimbra, 3001-456 Coimbra, Portugal; paula.carvalho@uc.pt

⁶ GeoBioTec, Department of Geosciences, University of Aveiro, 3810-193 Aveiro, Portugal; Antsantos@portugalmail.com

* Correspondence: teresal@ipcb.pt; Tel.: +351-96-814-1801

Abstract: The Picoto mining area is in the village of Vilar Seco (Viseu), central Portugal. Mineralization occurs mainly in quartz veins with meta-torbernite and uranophane and some U-bearing minerals, cutting a Variscan granite. Exploitation took place in two phases, between 1917 and 1953, and since the closure, the area has never been remediated. Water–rock interaction processes, including the mobility of potentially toxic elements through soil and water (surface and groundwater), were identified with the determination in situ of physicochemical parameters and selected anions and cations, by ICP-OES. The soils are contaminated with As (>44 mg/kg), Cu (>23 mg/kg), and U (>40 mg/kg) and cannot be used for agricultural or domestic purposes. The waters are generally weakly mineralized and have pH values ranging from acidic to neutral. However, some of them are contaminated with NO₂ (up to 2.3 mg/L), Fe (up to 1849 mg/L), Mn (up to 777 mg/L), Cu (up to 5.4 µg/L), As (up to 14.7 µg/L), and U (up to 66.2 µg/L) and cannot be used for human consumption or agricultural activities. The soil and water contamination are mainly related to the old mine activities and the subsequent human activities that have developed in the area.

Keywords: radium/uranium mines; soil; water; environmental risk; central Portugal



Citation: Antunes, M.; Teixeira, R.; Albuquerque, T.; Valente, T.; Carvalho, P.; Santos, A. Water-Rock Interaction and Potential Contamination Risk in a U-Enriched Area. *Geosciences* **2021**, *11*, 217. <https://doi.org/10.3390/geosciences11050217>

Academic Editors: Helder I. Chaminé and Jesus Martinez-Frias

Received: 13 April 2021

Accepted: 11 May 2021

Published: 15 May 2021

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



Copyright: © 2021 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

Minerals are the main repositories of chemical elements in the Earth's crust and are the main sources of elements that could affect global and local ecosystems. These elements are mainly released from minerals by anthropogenic activities such as mining [1] and can be transferred to other environmental compartments through water-rock interaction processes, promoting human exposure to potentially toxic elements, including metals and radioisotopes [2–4]. Particularly in mine areas, there are dumps containing tailings, waste-rock piles, and accumulated leach residues, which are subject to weathering processes and are the main reservoirs of potentially toxic elements.

Water-rock interaction processes are responsible for the transfer of toxic elements to soil and water (surface and groundwater) at high concentrations. Trace elements are persistent in the environment and can be accumulated in soils and waters through geochemical processes [5–7]. However, the different geochemical behavior of elements can lead to water geochemistry variations during water-rock interaction processes. In fact, during water-rock

interaction, a variety of geochemical reactions occur, such as weathering and dissolution, ion exchange, competitive adsorption, oxidation, and reduction processes [8–10].

In Portugal, between 1908 and 2001, about 60 deposits of radioactive ore were mined from the production of radium and uranium [11]. The exploration of uranium mines, ore treatments, and leaching of uranium from open pits, underground mines and dumps going towards streams and soils are causing significant contamination. The abandoned uranium mine areas with relatively high concentrations of uranium pose some risk to ecosystems and human health. The abandoned U mining sites contain the resulting tailings and discarded materials that have been deposited and discharged into the air and water since those years. After their closure, these mines were abandoned, and some of them were studied to evaluate the impact of environmental radioactivity and potentially toxic elements on human health, e.g., [11–19].

The main objective of the present research is to investigate and characterize water-rock interaction processes, and the resulting mobility of potentially toxic elements through environmental systems, particularly in abandoned mining areas. The identification of the geochemical characteristics of the mineralization of the area and the associated soil and water—both surface and groundwater—in the abandoned radium and uranium mining area will reveal the potential environmental risk and the associated contamination patterns. Nowadays, the integration of soil and water properties from the Picoto mine area obtained about seventy years after closure, and the resulting contamination, will be presented.

2. Study Area

The Picoto uranium mine area is located close to the Vilar Seco village (Nelas, central Portugal), within the autochthonous sector of the Central Iberian Zone of the Iberian Massif (Figure 1a). This sector contains granitic batholiths (Figure 1b) that intruded, during the last ductile deformation phase of the Variscan orogeny (late- to post-D3), into Precambrian to Cambrian phyllites and metagraywackes [20,21].

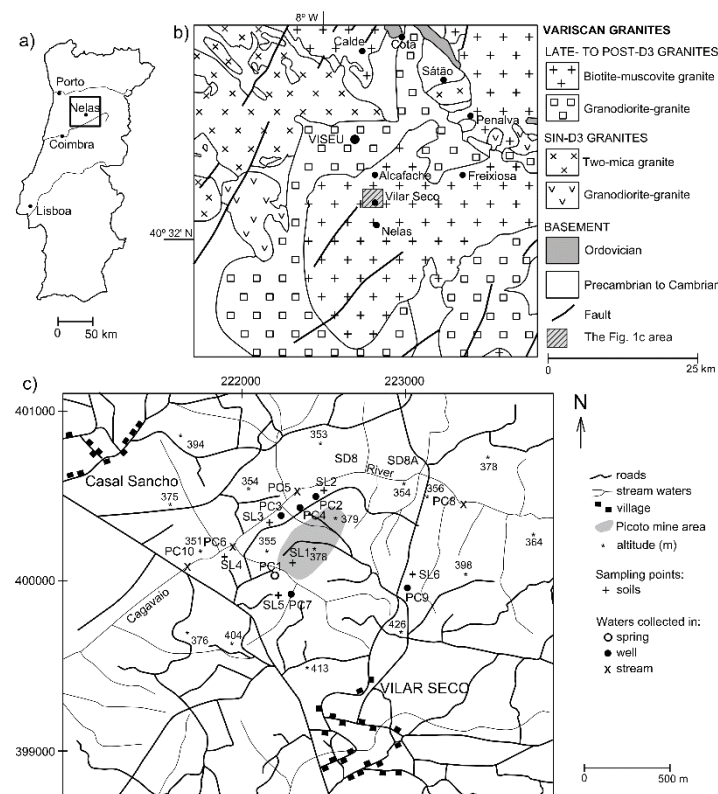


Figure 1. Study area: (a) geographical setting; (b) geological map; (c) location of the soil and water sampling points.

A medium- to coarse-grained porphyritic biotite-muscovite granodiorite-granite (300–295 Ma; [21]) crops out in the Picoto area and intruded into a coarse-grained porphyritic two-mica granodiorite-granite (306 Ma; [21]) (Figure 1b). The Picoto granite is peraluminous and contains 9–17 ppm U, hosted in U-bearing minerals such as uraninite, zircon, and monazite [22]. The granite is intersected by a brecciated, milky, and smoky quartz vein system, filling mainly 37° N–45° E, 50° N–70° E and, rarely, 5° N–20° E, trending fractures and faults [22].

Mineralization occurs mainly in quartz veins, which cross the granite. These quartz veins fill 37° N–45° E and 50° N–70° E orientation failures and fractures and are locally brecciated [22]. The quartz veins (50 m long, 5–10 m thick) contain torbernite, meta-torbernite and uranophane (Figure 2a), and other U-bearing minerals, such as muscovite, chlorite, and Fe- and Ti- and Mn-hydroxides (Figure 2b,c). Fe- and Mn-hydroxides contain nano inclusions of U-phosphates [23].

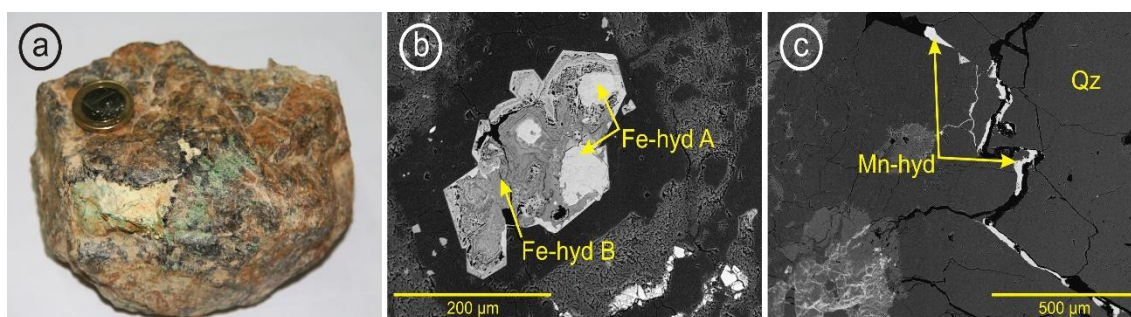


Figure 2. Mineralized quartz veins from Picoto mine: (a) Meta-torbernite (green mineral) and uranophane (yellow mineral); (b) Fe-hydroxides (Fe-hyd A and Fe-hyd B); (c) Mn-hydroxides (Mn-hyd) filling microfractures in quartz (Qz).

In adjacent areas of the fractures and faults, reddish altered rocks or “episyenites” occur because of hydrothermal alteration, involving alkali metasomatism, quartz dissolution, and the transformation of primary minerals [22,24]. Those fractures and faults cut across older NW-SW trending regional structures. The “episyenites” are alkali-rich metasomatic rocks that are commonly associated with U- and Th-enriched areas [25–29]. Metatorbernite was found associated with both alteration stages.

The Picoto granite is usually weathered, with feldspar kaolinization and oxidation of Fe in biotite. Locally, in the meteoric weathered zones, there are disseminated metatorbernite and Fe-hydroxides, filling the microfractures and spaces between grain boundaries. The secondary U-phases are associated with oxidizing conditions during solidification processes, with low-temperature hydrothermal fluids dissolving primary U-bearing minerals (e.g., uraninite) and carrying the uranyl ion (UO_2^{2+}). The U-bearing fluids ascend along fractures and faults, and precipitate as secondary epithermal uranyl minerals, such as oxyhydroxides, silicates, and phosphates, in structural traps [22,30,31].

In the area, mining activity was carried out in open pits and underground. In the first period, radium exploitation occurred in two open-pit mines (between 1917 and 1921) and after that, uranium was exploited (between 1950 and 1953), in underground galleries, about 150 m long. The exploitations ceased activity in 2001, and three waste heaps remain in the area (about 35,000 t; Figure 3a), without any intervention and rehabilitation processes.

The soils are occupied by local crops, with an emphasis on vineyards and agricultural products mainly for local domestic consumption (Figure 3b). The topography has a smooth slope (varying between 360 and 380 m, Figure 1c) and the area is included in the hydrographic basin of the Cagavaio river, with dominant NE-SW drainage (Figure 3c).



Figure 3. Topographic features from the study area: (a) the mine’s dump; (b) local crops; (c) Cavaio river.

3. Materials and Methods

Representative samples from Picoto granite, episyenite rocks, and quartz veins were collected by transmitted and reflected-light microscopy and scanning electron microscopy studies. A total of six samples of soils were collected in the study area. Five samples were collected on the mine influence area; one sample (SL6; Figure 1c) was from outside the mine influence area and represents the natural background. The soil samples were collected at a depth between 20 cm and 30 cm, were transported to the laboratory in polyethylene bags, dried at 40 °C, disaggregated with a rubber hammer, and sieved through a 2 mm nylon sieve. The pH was measured in a solid-water suspension with a liquid/solid ratio of 2.5 [32], while for electrical conductivity (EC) a liquid/solid ratio of 1/5 was used [33]. Only the <250 μm fraction of soil samples were digested with aqua regia (3:1 HCl-HNO₃), filtered through a 2 μm filter, and analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES), using a Horiba Jobin Yvon JY 2000 2 spectrometer with a monochromator (operating in a plasma Ar flow rate) to determine metals and metalloids. The certified sewage sludge amended soil BCR 143R was used to validate an internal reference soil (Table 1), prepared with aqua regia. Duplicate blanks and a laboratory standard were included at the beginning and the end of the analyzed samples. Detection limits were obtained using a blank signal, and dispersion estimated by a sampling signal in the 0.5 s interval following the ICP-OES [34]. The detection limits in mg/kg for soils were 1.30 for Al, 1.45 for Mn, 1.76 for Zn, 2.1 for Cu, 2.4 for W, 2.5 for Pb and Co, 2.6 for Ni and Sr, 2.7 for Cd, 2.9 for Th, 3.0 for Cr, 3.3 for Sb and U, 3.5 for As and 4.9 for Fe. The conversions from mg/L to mg/kg were estimated using the following equation:

$$DL \text{ (mg/kg)} = (X * 0.1) / m \tag{1}$$

where *X* is the DL at (mg/L) given by the ICP-OES, and *m* is the average of the heavy masses of the samples in kg.

Table 1. References for accuracy and precision for routine analysis.

	Accuracy	Precision
Concentration relative to detection limit (DL)	$\overline{\Delta \lg C} = \lg \bar{C}_i - \lg C_s $	$\lambda = \sqrt{\frac{\sum_{i=1}^n (\lg C_i - \lg C_s)^2}{n-1}}$
Soils		
<3 DL	≤0.024	0.031
>3 DL	≤0.015	0.018
Water		
<3 DL	≤0.022	0.033
>3 DL	≤0.017	0.023

C_i—Values of BCR_i for soils and Relacre for water. *C_i*—Standard average values of BCR and Relacre. *C_s*—Value recommended for standards for BCR and Relacre. *n*—Total samples included in the batch.

In the mining area of Picoto, ten sampling points, for surface water (PC5, PC6, PC8, PC10; Figure 1c) and groundwater (spring: PC1; well: PC2, PC3, PC4, PC7, PC9; Figure 1c)

were selected and collected, twice in a hydrological year, representative of the dry (summer) and rainy period (winter).

Temperature, pH, Eh, dissolved oxygen, electrical conductivity (EC), and alkalinity were determined in situ. The cations were determined by ICP-OES, using a Horiba Jovin Yvon JV2000 2 spectrometer with a monochromator, and the anions by ion chromatography with a Dionex ICS 3000 Model, on the water samples filtered through 0.45 µm pore size membrane. Duplicate blanks and a laboratory water standard were analyzed for quality control. The accuracy and precision of the water analyses were obtained by inserting 2 subsamples of an external standard (Relacre, report EAA.2007 Fev. V0) within each batch of 10 water samples (Table 1).

The validation of the determinations was carried out according to the methodologies of [35,36]. The analytical data show ion balance errors within $\pm 10\%$ for most water samples, and the measurement precision was within a relative standard deviation of 5%. All determinations were carried out in the Department of Earth Sciences, University of Coimbra, Portugal.

4. Results and Discussion

The abandoned mining area of Picoto is in a rural area, close to Vilar Seco, and some of the waters are used for irrigating agricultural land.

4.1. Geochemistry of Soils

The physical–chemical parameters and concentration of selected metals and As from soils of the Picoto mine area are presented in Table 2. The soil sample PL6 represents the natural background of the area, and the soil samples collected under the influence of mine activities are represented by the minimum and maximum range values.

Table 2. Physical–chemical parameters and concentration of selected metals and As from soils of the Picoto mine area.

	Soils from Picoto Mine Area		
	Background	Mining Area influence	
		Minimum	Maximum
pH	4.9	4.3	5.0
EC	25.0	17.0	47.0
Al	21,840.5	12,711.6	35,047.4
As	56.5	43.8	93.2
Co	-	2.9	3.4
Cr	-	4.7	8.6
Cu	97.2	22.8	163.5
Fe	18,680.2	15,658.2	25,210.2
Mn	255.9	149.0	437.2
Pb	32.7	18.1	37.8
Sn	21.0	17.9	43.4
Sr	11.1	5.9	14.5
Th	78.2	60.5	122.5
U	80.1	39.8	95.4
W	6.3	4.1	8.1
Zn	82.4	57.0	91.0

Cd, Ni, and Sb contents are below the detection limit. EC = electrical conductivity (µS/cm). Trace element content is expressed in mg/kg.

The acid pH of soils from the Picoto area influences the capacity for the adsorption of metals and metalloids. The soil located in the influence of the mining activities contain higher electrical conductivity values and maximum concentrations of analyzed trace elements than the natural background of the area. These trace elements were released from the mineralization, mainly due to intensive mining activities, and retained in the soil. The weathering of host granite and mineralized veins will also have some contribution to the U and Th concentrations in soils because these elements occur in the accessory minerals, like monazite, apatite, and U-bearing minerals, as have been found in other U-mine abandoned areas from Portugal [4]. However, the highest maximum values are found in the soil samples located downstream of the mine influence area.

In general, soils from the Picoto mine area present higher contents for As, Cu, Fe, Th, U, and Zn than the median values recorded in the Geochemical Atlas of Europe (As = 6 mg/kg, Cu = 13mg/kg, Fe = 1960 mg/kg, Th = 7.24, U = 2.03, and Zn = 48 mg/kg [37]).

The soil from the Picoto uranium mine area is contaminated with As, Cu, and U, and cannot be used for agricultural or residential uses (Figure 4) according to Ontario's soil standards [38]. However, almost all soil samples present adequate contents that could be used in commercial or industrial applications.

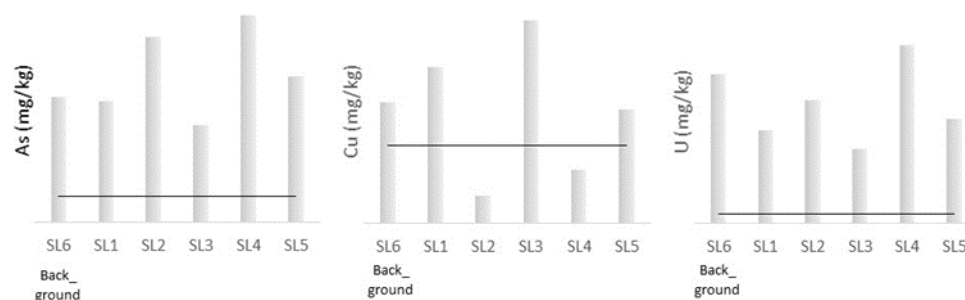


Figure 4. Projection of the soils from the Picoto mine area. Black solid line: parametric values for agricultural and residential uses [38].

4.2. Hydrochemistry and Water Quality

The Piper diagram shows the characteristics of the water (Figure 5). The dominant hydrochemical facies of most water samples is of undefined type, (Na + K)-Cl or locally Ca-HNO₃ type, according to Piper's classification.

The hydrochemical processes that control chemistry in the study area could be expressed by the contribution of major ions to the water mineralization (expressed through the EC). However, the water has lower mineralization, and the correlations found between EC and major ions are lower (EC-HCO₃⁻ = 0.4805; EC-SO₄²⁻ = 0.2253; EC-Ca = 0.498; EC-Na = 0.3912), suggesting the influence of water-rock interaction processes, including the weathering of minerals and the agricultural activity in this area, which could be responsible for the low correlations found.

There is no significant difference between the composition of the waters collected outside the mine's area of influence, representing the natural water composition (PC8st and PC9w; Figure 6), and the water located within the area of influence of the Picoto mine. In general, the waters are acidic or near neutral, with pH values varying between 4.7 and 6.3; the most acidic value was found in the surface water receiving influence from the mining area (PC6st; Figure 6) and the groundwater background associated with granitic rocks (PC9w; Figure 6).

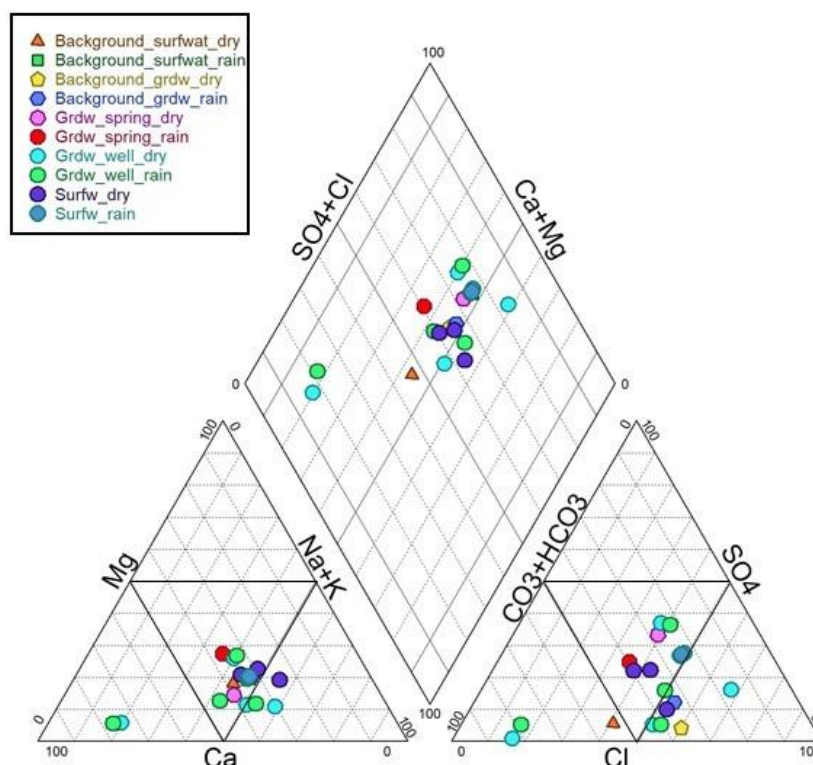


Figure 5. Hydrochemistry classification (Piper diagram) of the water from the Picoto mine area. Surfwat—Surface water; Grdw—Groundwater. Diagrammes software was used for computation purposes [39].

Most waters are poorly mineralized ($EC = 44\text{--}190 \mu\text{S}/\text{cm}$), which is supported by the low values of total dissolved solids ($TDS = 49\text{--}137 \text{ mg}/\text{L}$). In the summer, the waters tend to be more acidic and have higher EC values, particularly groundwater (springs and wells). The more acidic waters result from the oxidation of sulfides from mineralized veins and, consequently, from tailings and heaps, which makes the water more aggressive, promoting the leaching of potentially toxic elements from the embedding rock [40,41].

Generally, in the dry period, lower values of pH and higher levels of EC, NO_2 , Fe, Mn, Cu, As, and Th occur than in the rainy period (Figure 6), probably due to the concentration effect due to the loss water flow. However, in the groundwater from the spring (PC1sp; Figure 6) the contents of Fe, Mn, As and U tend to be higher during the rainy period, probably due to dissolution in pH-Eh conditions. Uranium content observed in surface water does not show significant temporal variation.

Most waters are contaminated with NO_2 , Fe, Mn, Cu, As, and U, and should not be used for human consumption or agricultural activities. Fe and Cu water contamination occurs preferentially in the dry period (lower pH values), which promotes an increase of chemical species dissolution with the release of the metals.

The results of external radiation (gamma) show high values, particularly close to the heaps ($0.61 \mu\text{Gy}\cdot\text{h}^{-1}$), exceeding the regional background value for the Oliveira do Hospital region, being an indicator of radiological contamination resulting from mining activity [42].

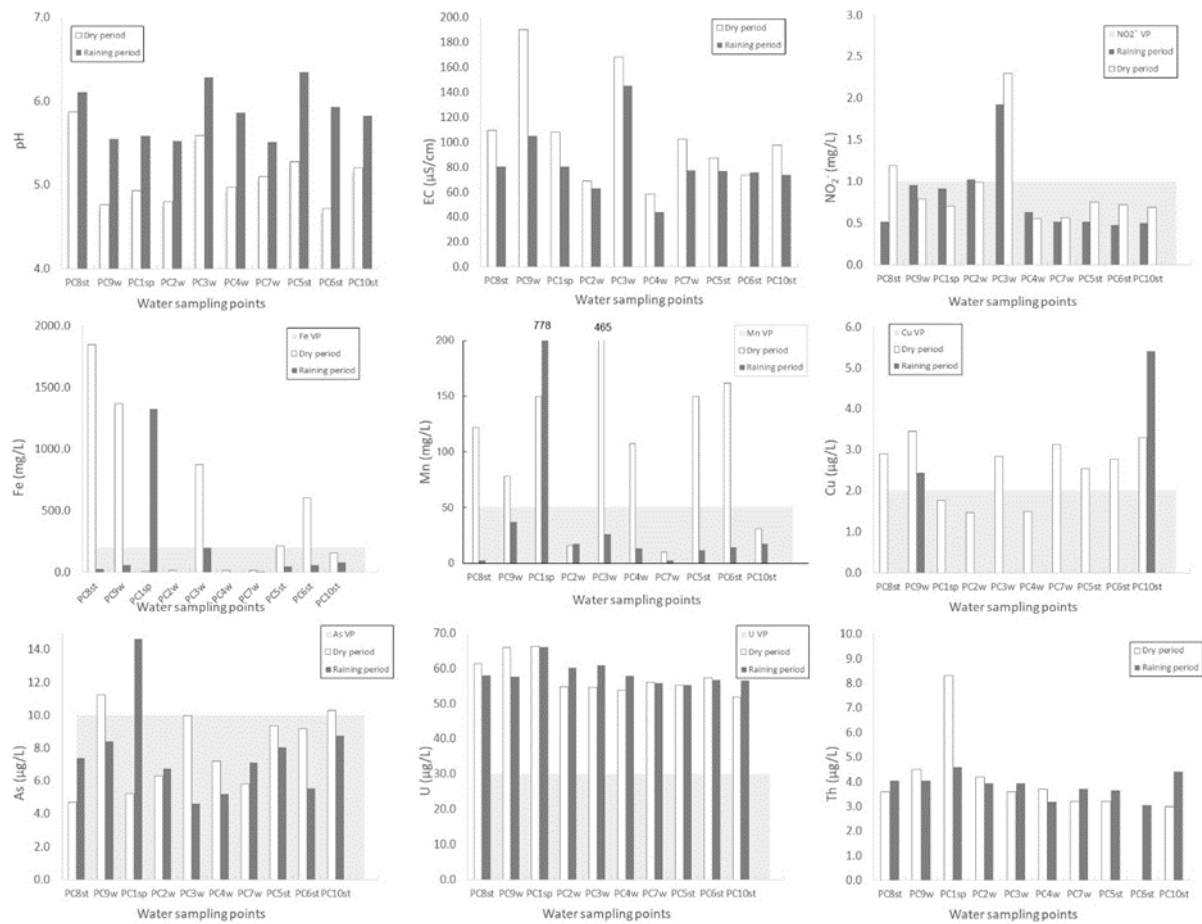


Figure 6. Diagrams of seasonal variation for the waters of the Picoto area. Water sampling points: st—stream; w—well; sp—spring; VP—parametric value [43–45].

5. Conclusions

The present study characterized the soil, surface, and groundwater from an old radium and uranium mining area, and its associated water-rock interaction processes. The mine activities ceased and are abandoned, and the local cultivated area is developed.

The soil from the Picoto mine area presents higher contents for selected metals (Cu, Fe, Th, U, and Zn) and As than the median values recorded in the Geochemical Atlas of Europe. These trace elements were mainly released from the mineralization and mining activities and retained in soils. However, it can be expected that the host granite and mineralized veins’ weathering will also contribute to the U and Th concentrations in soils, as these elements occur in the accessory minerals. The soil from the area suggests a geogenic and mining influence. These soils are contaminated with As, Cu, and U, and should not be used for agricultural or residential uses.

Water-rock interactions were identified by the hydrochemistry and water quality assessment through groundwater and surface water samples collected in the area. There is no significant difference between the composition of the water collected outside (background) and inside the mine area, suggesting the direct influence of water–rock interaction processes, including the weathering of minerals and the agricultural activity in this area. Most waters are poorly mineralized; however, they are contaminated with NO₂, Fe, Mn, Cu, As, and U and should not be used for human consumption or agricultural activities.

The obtained results from the geochemistry of soil, surface, and groundwater from this abandoned mine area reinforce the association between environmental risk and human health if adequate remediation processes are not implemented. Accordingly, it is essential to define and apply appropriate remediation and/or rehabilitation actions, considering the

potentially toxic elements' spatial mobility associated with water-rock-interaction processes. The present study intended to work as a pilot-scale project, aiming at future extensions in similar abandoned mining areas, and, therefore, helping decision-making on water and soil resources management.

Author Contributions: Conceptualization, M.A. and R.T.; methodology, M.A., R.T., T.V., and A.S.; validation, M.A., R.T., T.A., T.V., P.C.; data curation, M.A., R.T., T.A., and P.C.; writing—original draft preparation, M.A.; writing—M.A., R.T., and T.A.; review and editing—M.A., R.T., T.A., T.V., P.C., and A.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by FCT—Fundação para a Ciência e a Tecnologia, through projects UIDB/04683/2020 UIDB/00073/2020, UIDP/00073/2020 and Nano-MINENV 029259 (PTDC/CTA-AMB/29259/2017).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors thank FCT—Fundação para a Ciência e a Tecnologia, I.P., through the project's reference UIDB/04683/2020, UIDP/04683/2020 and Nano-MINENV 029259 and UIDB/MAR/04292/2020 (MARE—Marine and Environmental Sciences Centre).

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Brown, G.E., Jr.; Calas, G. Environmental mineralogy—Understanding element behavior in ecosystems. *C. R. Geosci.* **2011**, *343*, 90–112. [[CrossRef](#)]
2. Brugge, D.; de Lemos, J.L.; Oldmixon, B. Exposure pathways and health effects associated with chemical and radiological toxicity of natural uranium: A review. *Rev. Environ. Health* **2005**, *20*, 177–193. [[CrossRef](#)] [[PubMed](#)]
3. Costa, M.R.; Pereira, A.J.S.C.; Neves, L.J.P.F.; Fererira, A. Potential human health impact of groundwater in non-exploited uranium ores: The case of Horta da Vilariça (NE Portugal). *J. Geochem. Explor.* **2017**, *183 Pt B*, 191–196. [[CrossRef](#)]
4. Neiva, A.M.R.; Carvalho, P.C.S.; Antunes, I.M.H.R.; Albuquerque, M.T.D.; Santos, A.C.T.; Cunha, P.P.; Henriques, S.B.A. Assessment of metal and metalloid contamination in the waters and stream sediments around the abandoned uranium mine area from Mortórios, central Portugal. *J. Geochem. Explor.* **2019**, *202*, 35–48. [[CrossRef](#)]
5. Ke, X.; Gui, S.F.; Huang, H.; Zhang, H.J.; Wang, C.Y.; Guo, W. Ecological risk assessment and source identification for heavy metals in surface sediments from the Liaohe River protected area, China. *Chemosphere* **2017**, *175*, 473–481. [[CrossRef](#)]
6. Zhang, P.Y.; Qin, C.Z.; Hong, X.; Kang, G.H.; Yang, D.; Pang, B.; Li, Y.Y.; He, J.J.; Dick, R.P. Risk assessment and source analysis of soil heavy metal pollution from lower reaches of Yellow River irrigation in China. *Sci. Total Environ.* **2018**, *663*, 1136–1147. [[CrossRef](#)]
7. Yang, T.; Chen, J.; Xiaoping, L.; Wu, T.; Hu, Z.; Wang, S. Ecological risk by heavy metal contents in sediments within the Wei River Basin. *Environ. Earth Sci.* **2019**, 78–101. [[CrossRef](#)]
8. Cutter, G.A.; Cutter, L.S.; Featherstone, A.M.; Lohrenz, S.E. Antimony and arsenic biogeochemistry in the western Atlantic Ocean. *Deep Sea Res. Part II Top. Stud. Oceanogr.* **2001**, *48*, 2895–2915. [[CrossRef](#)]
9. Elgano, L.; Kannan, R. Rock–water interaction and its control on chemical composition of groundwater. In *Developments in Environmental Science*; Sarkar, D., Datta, R., Hannigan, R., Eds.; Elsevier: Amsterdam, The Netherlands, 2007; Volume 5, Chapter 11; pp. 229–243.
10. Redwan, M.; Abdel Moneim, A.A.; Amra, M.A. Effect of water–rock interaction processes on the hydrogeochemistry of groundwater west of Sohag area, Egypt. *Arab. J. Geosci.* **2016**, *9*, 111. [[CrossRef](#)]
11. Carvalho, F.P. The National Radioactivity Monitoring Program for the Regions of Uranium Mines and Uranium Legacy Sites in Portugal. *Proc. Earth Planet. Sci.* **2014**, *8*, 33–37. [[CrossRef](#)]
12. Pinto, M.M.S.C.; Silva, M.M.V.G.; Neiva, A.M.R. Pollution of water and stream sediments associated with the Vale de Abrutiga uranium mine, Central Portugal. *Mine Water Environ.* **2014**, *23*, 66–75. [[CrossRef](#)]
13. Antunes, I.M.H.R.; Albuquerque, M.T.D. Using indicator kriging for the evaluation of arsenic potential contamination in an abandoned mining area (Portugal). *Sci. Total Environ.* **2013**, *442*, 545–552. [[CrossRef](#)] [[PubMed](#)]
14. Carvalho, P.C.S.; Neiva, A.M.R.; Silva, M.M.V.G.; Antunes, I.M.H.R. Metal and metalloid leaching from tailings into stream water and sediments in the old Ag-Pb-Zn Terramonte mine, northern Portugal. *Environ. Earth Sci.* **2013**, *71*, 2029–2041. [[CrossRef](#)]
15. Neiva, A.M.R.; Carvalho, P.C.S.; Antunes, I.M.H.R.; Silva, M.M.V.G.; Santos, A.C.T.; Cabral Pinto, M.M.S.; Cunha, P.P. Contaminated water, stream sediments and soils close to the abandoned Pinhal do Souto uranium mine, Central Portugal. *J. Geoch. Explor.* **2014**, *136*, 102–117. [[CrossRef](#)]

16. Neiva, A.M.R.; Antunes, I.M.H.R.; Carvalho, P.C.S.; Santos, A.C.T. Uranium and arsenic contamination in the former Mondego Sul uranium mine area. Central Portugal. *J. Geoch. Explor.* **2016**, *162*, 1–15. [[CrossRef](#)]
17. Antunes, I.M.H.R.; Neiva, A.M.R.; Albuquerque, M.T.D.; Carvalho, P.C.S.; Santos, A.C.T.; Cunha, P.P. Potential toxic elements in stream sediments, soils and waters in an abandoned radium mine (central Portugal). *Environ. Geochem. Health* **2018**, *40*, 521–542. [[CrossRef](#)]
18. Antunes, I.M.H.R.; Albuquerque, M.T.D.; Roque, N. Spatial Environmental risk evaluation of Potential Toxic Elements in stream sediments. *Environ. Geochem. Health* **2018**, *40*, 2573–2585. [[CrossRef](#)] [[PubMed](#)]
19. Antunes, I.M.H.R.; Santos, A.C.T.; Valente, T.M.F.; Albuquerque, M.T.D. Spatial Mobility of U and Th in a U-enriched Area (Central Portugal). *Appl. Sci.* **2020**, *10*, 7866. [[CrossRef](#)]
20. Oliveira, J.T.; Pereira, E.; Ramalho, M.; Antunes, M.T.; Monteiro, J.H. *Geological Map of Portugal, 1/500 000*, 5th ed.; SGP: Lisboa, Portugal, 1992.
21. Azevedo, M.R.; Valle Aguado, B.; Nolan, J.; Martins, M.; Medina, J. Origin and emplacement of syn-orogenic Variscan granitoids in Iberia the Beiras massif. *J. Virtual Explor.* **2005**, *19*, 1–18. [[CrossRef](#)]
22. Coteló Neiva, J.M. Jazigos portugueses de minérios de urânio e sua génese. In *Engineering Geology and Geological Resources. Book in Honour to Prof. J.M. Coteló Neiva*; Ferreira, M.R.P.V., Ed.; Coimbra University Press: Coimbra, Portugal, 2003; Volume 1, pp. 15–76.
23. Cabral Pinto, M.M.S.; Silva, M.M.V.G. The Vale de Abrutiga uranium phosphates mine, central Portugal (short communication). *Chem. Erde* **2007**, *67*, 251–252. [[CrossRef](#)]
24. Jaques, L.; Bobos, I.; Noronha, F. Study of fluids related to hydrothermal alteration of biotite granites from Gerês and Guarda (Portugal). *Comum. Geol.* **2010**, *97*, 81–98.
25. Leroy, J. The Margnac and Fanay uranium deposits of the La Crouzille district (western Massif Central, France): Geologic and fluid inclusion studies. *Econ. Geol.* **1978**, *73*, 1611–1634. [[CrossRef](#)]
26. Costi, H.T.; Dall’Agnol, R.; Borges, R.M.K.; Minuzzi, O.R.R.; Teixeira, J.T. Tin-bearing sodicepisyenites associated with the Proterozoic, A-type Água Boa Granite, Pitinga mine, Amazonian craton, Brazil. *Gondw. Res.* **2002**, *5*, 435–451. [[CrossRef](#)]
27. Condomines, M.; Loubeau, O.; Patrier, P. Recent mobilization of U-series radionuclides in the Bernardan U deposit (French massif central). *Chem. Geol.* **2007**, *244*, 304–315. [[CrossRef](#)]
28. Cuney, M.; Emetz, A.; Mercadier, J.; Mykchaylov, V.; Shunko, W.; Yuslenko, A. Uranium deposits associated with Nametasomatism from central Ukraine: A review of some of the major deposits and genetic constraints. *Ore Geol. Rev.* **2012**, *44*, 82–106. [[CrossRef](#)]
29. Martins, L.M.O.; Gomes, M.E.P.; Teixeira, R.J.S.; Pereira, A.J.S.C.; Neves, L.J.P.F. Indoor radon risk associated to post-tectonic biotite granites from Vila Pouca de Aguiar pluton, northern Portugal. *Ecot. Environm. Saf.* **2016**, *133*, 164–175. [[CrossRef](#)] [[PubMed](#)]
30. Murphy, W.M.; Shock, E.L. Environmental aqueous geochemistry of actinides. In *Uranium: Mineralogy, geochemistry and the environment*. *Rev. Min.* **1999**, *38*, 221–253.
31. Cabral Pinto, M.M.S.; Silva, M.M.V.G.; Neiva, A.M.R. Geochemistry of U-bearing minerals from the Vale de Abrutiga uranium mine area, Central Portugal. *Neues Jahrb. Mineral.* **2008**, *185*, 183–198. [[CrossRef](#)]
32. British Standard (BS) 7755. Soil Quality, part 3. Chemical methods, section 3.2. In *Determination of pH. ISO 10390*; ISO: Geneva, Switzerland, 1995.
33. British Standard (BS) 7755. Soil Quality, part 3. Chemical methods (BS) 7755, section 3.4. In *Determination of Specific Electrical Conductivity. ISO 11265*; ISO: Geneva, Switzerland, 1994.
34. User Manual. Jobin Yvon ICP Spectrometers, Version 3.0; Reference: 321088486, January 2001; pp. 20–23.
35. Xuejing, X. Analytical requirements in international geochemical mapping. *Analyst* **1995**, *120*, 1497–1504. [[CrossRef](#)]
36. Min, L.; Xiaohuan, X.; Guiyi, X.; Hangxin, C.; Zhongfang, Y.; Guohua, Z.; Jiayu, Y.; Zhonghui, L. National multi-purpose regional geochemical survey in China. *J. Geoch. Explor.* **2014**, *139*, 21–30. [[CrossRef](#)]
37. Salminen, R.; Batista, M.J.; Bidovec, M.; Demetriades, A.; De Vivo, B.; De Vos, W.; Duris, M.; Gilucis, A.; Gregorauskiene, V.; Halamić, J.; et al. *FOREGS Geochemical Atlas of Europe, Methodology and Maps*; Geological Survey of Finland: Espo, Finland, 2005; Part 1, p. 526; Part 2, p. 690.
38. Canadian Environmental Quality Guidelines (CCME). *Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health—Diisopropanolamine*; Canadian Council of Ministers of the Environment: Winnipeg, MB, Canada, 2017; summary tables 1–6.
39. Antunes, I.M.H.R.; Neiva, A.M.R.; Albuquerque, M.T.D.; Santos, A.C.T. Spatial Surface and groundwater interaction in an abandoned radium-bearing mine (Guarda, central de Portugal). *Proc. Earth Planet. Sci.* **2017**, *17*, 618–621. [[CrossRef](#)]
40. *Software Diagrammes*, Version 6.73; Laboratoire d’Hydrogéologie d’Avignon: Avignon, France, 2003.
41. Antunes, I.M.H.R.; Gomes, M.E.P.; Neiva, A.M.R.; Carvalho, P.C.S.; Santos, A.C.T. Potential risk assessment in stream sediments, soils and waters after remediation in an abandoned W>Sn mine (NE Portugal). *Ecot. Environm. Saf.* **2016**, *133*, 135–145. [[CrossRef](#)] [[PubMed](#)]
42. Empresa de Desenvolvimento Mineiro (EDM). *Mina do Picoto—Relatório Interno*; EDM: Lisboa, Portugal, 2007.
43. Diário da República. *Decreto-Lei 236/98—Legislação Portuguesa de Qualidade da água*; Diário da República I-A: Lisboa, Portugal, 1998; pp. 3676–3722.

-
44. Diário da República. *Legislação Portuguesa de Qualidade da água*; Diário da República I-A: Lisboa, Portugal, 2017; pp. 5747–5765.
 45. World Human Organization. *Guidelines for Drinking Water Quality*, 4th ed.; World Human Organization: Geneva, Switzerland, 2011; Available online: http://Whqlibdoc.Who.int/publications/2011/9789241548151_eng.pdf (accessed on 13 April 2021).