

Article

Hydropedological Characterization of a Coal Mining Waste Deposition Area Affected by Self-Burning

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Abstract: Coal mining often produces severe environmental effects, including impacts on the soil system and, specifically, on hydropedological conditions that control the leaching of significant ions and Potentially Toxic Elements (PTEs). The research objective is to assess changes in the hydropedological conditions in an area with a coal mining waste pile that underwent self-burning. An integrative approach was implemented, starting with the definition of hydropedological zoning based on field observations of soil formation factors (namely, parent material, relief, biological activity, anthropic influence, and time). The soil profile in each hydropedological zone was characterized regarding morphological features. The upper mineral horizons were sampled and characterized in terms of mineralogy and PTE geochemistry. Field measurements of unsaturated hydraulic conductivity, soil water content, and hydrophobicity were performed. Afterwards, the hydrogeochemistry of leachates was determined, and the soil leaching potential was evaluated. The research outcomes express substantial differences regarding the hydropedological zones: development of different soil profiles, diverse mineralogy and PTE geochemistry, higher unsaturated hydraulic conductivity and leaching of major ions, and PTEs in soils affected by coal mining activities. Finally, a Principal Component Analysis confirmed the existence of significant contrasts according to hydropedological zoning.

Keywords: hydropedology; coal mining; soil leaching; soil and water pollution; coal waste self-burning



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1. Introduction

Mining activities, especially the operation and disposal of mining residues, usually produce severe environmental and social impacts, including changes in land use originating ecosystem disturbance, loss of biodiversity, as well as soil and groundwater and surface water bodies degradation, e.g., [1,2]. In many countries, current mining activities follow regulations that require and allow environmental protection [3]. However, past mining activities created environmental impacts that persist nowadays. Indeed, the exploitation of mineral resources may induce profound transformations in the local hydrological processes

as well as interrupt the regular pedological evolution, with long-term impacts on habitats and landscapes at both local and regional scales [4]. As a result, the hydrological and pedological features of the soil system often change dramatically. For example, mining frequently produces deforestation, which may disturb rainfall interception, overland flow, infiltration, and percolation. In contrast, the disposal of mining wastes in waste piles forms new soils—Technosols—frequently with different mineralogical and geochemical characteristics. In these environmental conditions, mining areas may develop new hydopedological characteristics, namely, the volume and velocity of water circulating in the upper unsaturated zone and the leaching potential of significant ions and Potentially Toxic Elements (PTEs). In this context, to understand how this type of environment functions, it is very useful to adopt a hydopedological perspective, which is the basis of an integrative scientific approach focusing on hydopedological zoning.

Coal mining activities have the potential to accumulate and release high concentrations of PTEs into nearby soils and water, contributing to environmental degradation [5–8]. Residues from coal mining pose environmental hazards and can potentially lead to human health issues [9,10], as several PTEs are frequent and abundant in coals [11]. Coal mining presents some specific hazards when compared with the exploitation of metals [5,12–14]. Spontaneous combustion and self-burning of coal in seams, stockpiles, and mining waste deposits is known worldwide as the cause of economic losses and environmental impacts, principally related to the emission of gases to the atmosphere and the alteration of the mode of occurrence of toxic compounds (including inorganic and organic compounds). Additionally, water percolation and acid drainage in coaly materials may also promote the leaching of compounds naturally occurring in coals, including PTEs and polycyclic aromatic hydrocarbons.

Coal mining in the Douro Coalfield (NW Portugal) occurred from the end of the 18th century until 1994. The thin and elongated shape of the coalfield explains the existence of various underground mines which stand out among others for their dimension and importance, the São Pedro da Cova and Pejão mines. The legacy of the coal mining in the Douro Coalfield is materialized today by the existence of dozens of waste piles. Five of them underwent self-burning after ignition caused by wildfires.

Previous studies investigated the waste piles in the Douro Coalfield [15–20] including: (i) the characterization of waste materials and identification of potential environmental impacts of coal waste piles; (ii) the identification of changes in mining waste caused by self-burning and the products generated by the combustion process in waste piles, as well as the associated potential impacts on the environment and human health; and (iii) the integrated monitoring of the combustion process ongoing in the São Pedro da Cova waste pile. Recently, the characterization of the residues deposited in the Fojo waste pile (in the Pejão area) was assessed by [21].

This research is part of a multidisciplinary project encompassing other subjects, namely ecotoxicology and environmental geochemistry (the latest is ongoing). The ecotoxicological study assessed the effects of soil leachates in seed germination and individual and subindividual parameters in *Lactuca sativa* [22], as well as the toxicity effects of soil leachates in aquatic species (*Allivibrio fischeri*, *Lemna minor*, and *Daphnia magna*)—[23]. In the ecotoxicological study, pedological zoning was defined, and the hydopedological zoning established in the present work (see Sections 2 and 3) is a development and upgrade of this preliminary zoning.

The research objective is to assess changes in the hydopedological conditions in an area with a coal mining waste pile that underwent self-burning. The assessment was based on an integrative approach encompassing hydrology, geology, pedology, mineralogy, geochemistry, and hydrogeochemistry and started with the definition of the hydopedological zoning, considering field observations related to soil formation factors (namely, parent material, relief, biological activity, anthropic influence, and time)—as described by [24,25]—and their relation with local hydrological conditions and processes (specifically, rainfall interception, infiltration, percolation, overland flow, and interflow). One of the

hydropedological zones represents conditions prior to coal mining influence, while others reflect anthropogenic influence, that is, the deposition of coal mining waste and, to a lesser extent, intensive forestry.

The study began with the observation of local hydrological conditions and processes, including rainfall interception, infiltration, percolation, overland flow, and interflow. Then, the soil profile was described in each hydropedological zone regarding morphological features, and the upper mineral horizons were sampled and characterized in terms of mineralogy and PTE geochemistry. Field measurements of unsaturated hydraulic conductivity (K), soil water content, and hydrophobicity were performed. Afterwards, the hydrogeochemistry of leachates was determined and the soil leaching potential was evaluated.

The research results revealed that coal mining waste disposal in the Fojo area originated new soil types with hydropedological characteristics different from the pre-depositional setting.

2. Materials and Methods

2.1. Study Area

The study site encompasses the Fojo coal mine waste pile, and the surrounding area and is located in the Pejão mining area, Douro Coalfield, NW Portugal (Figure 1). In the Pejão area, coal mining was carried out from 1920 until 1994 and originated a number of waste piles [15]. The ignition and consequent self-burning of the Fojo waste pile was caused by a wildfire in October 2017. Afterwards, between 2017 and 2019, an operation to control and extinguish the coal waste self-burning was conducted, comprising the remobilization of the coal waste and the application of water mixed with a cooling accelerator agent.

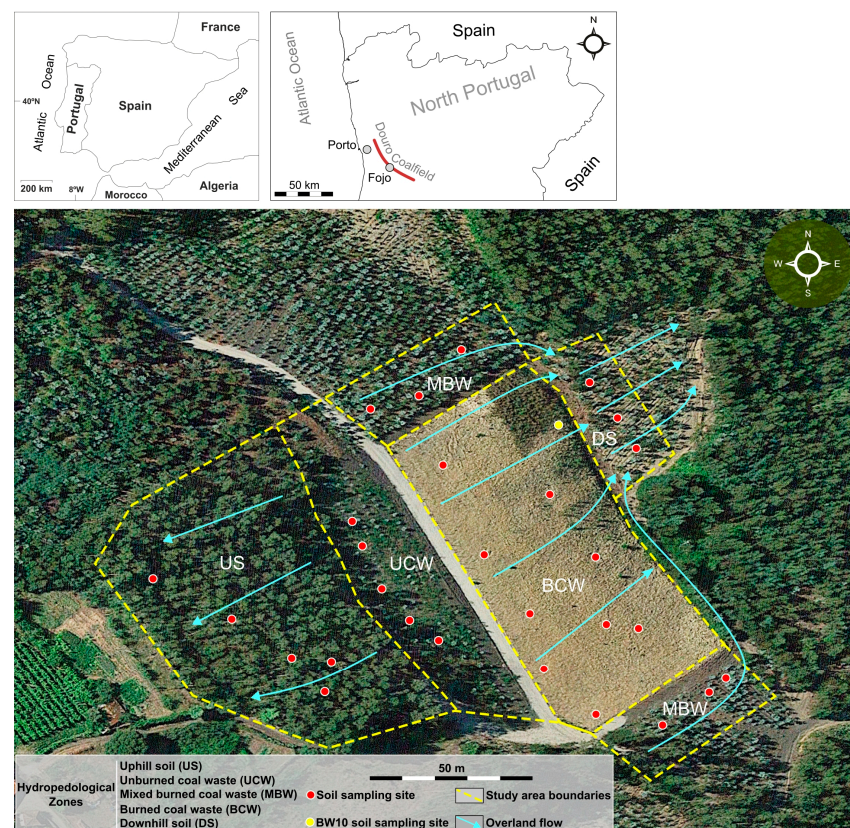


Figure 1. Fojo coal mine waste pile and the surrounding area and sampling sites (satellite image from Google Earth).

Due to the self-burning process and the fire control and extinction operation, significant changes occurred in the local pedological and hydrological conditions. These

alterations led to the development of new environmental features, allowing the definition of a hydropedological zoning comprising the waste pile and its surrounding area (Figure 1): Uphill Soil (US), Unburned Coal Waste Pile (UCW), Burned Coal Waste Pile (BCW), Mixed Burned Coal Waste (MBW), Downhill Soil (DS). Further descriptions of these hydropedological zones are provided in Section 3.1.

2.2. Field Methods

The hydropedological characterization of the Fojo coal mine waste pile and the surrounding area was carried out from May 2021 (first field survey) until July 2023 (last hydropedological field measurements). The hydropedological zoning of the study area was defined in accordance with the soil mapping of [26] and the World Reference Base for Soil Resources [27]. In each zone, the morphological description of the soil profile followed the FAO's guidelines [28], considering the following characteristics: (i) the formation of soil horizons, in the case of normal pedogenesis as well in the case of the influence of mine waste deposition and self-burning; (ii) the depth and thickness of the soil horizons; (iii) the type of soil horizon boundaries; (iv) the type of aggregation—structure; (v) soil texture; (vi) soil colour—described using the Munsell colour system; (vii) accumulation of humified organic matter; (viii) soil porosity; and (ix) biological activity.

Twenty-nine sites were selected in the study area for soil sampling and field measurement of unsaturated hydraulic conductivity (K), soil water content, and hydrophobicity (Figure 1). In all soil types (as detailed in Section 3), the uppermost mineral horizon was sampled to a depth of 20 cm. In the BCW zone, samples were taken from the cover layer and the waste itself, in both cases, to a depth of 20 cm. Unsaturated hydraulic conductivity (K) was assessed using a mini disk infiltrometer—e.g., [29–31]. All tests were performed with a suction rate of -1 cm. The volumetric water content was measured with a capacitance probe, specifically the ThetaProbe model ML3. Soil hydrophobicity was measured using the Water Drop Penetration Time (WDPT), using the procedure outlined by [32]. The hydropedological field measurements were carried out in March 2022 (wet season) and in July 2023 (dry season) in the A horizon of the US and DS zones, as well as in the C horizon of the UCW and the MBW zones and the C1 and C2 horizons of the BCW zone. An additional sample (BW10) from the deepest part of the burned waste pile was also collected close to the NE limit of the BCW hydropedological zone to provide a preliminary insight into the conditions prevailing in this environment.

Water from interflow in the self-burning waste pile, which may occur after periods of heavy rainfall, was sampled in March 2022.

2.3. Laboratory Methods

The soil geochemistry concerning PTEs was determined at the Bureau Veritas Mineral Laboratories (Vancouver, BC, Canada) via inductively coupled plasma mass spectrometry (ICP-MS) after ignition at 550°C and acid digestion using an acid solution of (2:2:1:1) H_2O -HF-HClO₄-HNO₃.

The soil mineralogy was characterized by X-ray diffraction (XRD). First, samples were dried at about 50°C and then disaggregated. The sedimentation method was applied to separate the fractions with particle size under $2\text{ }\mu\text{m}$. For the fractions under $63\text{ }\mu\text{m}$ and $2\text{ }\mu\text{m}$, the mineralogical analysis was carried out with a Panalytical X'Pert-Pro MPD, $\text{K}\alpha\text{ Cu}$ ($\lambda = 1.5405\text{ \AA}$) radiation on random-oriented powders (total sample) and oriented aggregates ($<2\text{ }\mu\text{m}$). The mineralogical composition was assessed using (hkl) peaks (on random powder mounts) for non-clay minerals and (00l) peaks (on oriented aggregates) for clay minerals; the mineral phases were identified through the criteria recommended by [33,34] and the Joint Committee for Powder Diffraction Standards. The semi-quantification of the mineralogical determinations was performed using the procedures described by [35,36].

The leaching of major ions, PTEs, and Fe in soils was assessed using the USGS Field Leach Test—USGS FLT, [37]. This leaching method is simple to apply and time-effective, allowing the simulation, prediction, and characterization of the water–soil geochemical

interaction during the percolation of rainwater in the upper soil profile. The pH, electrical conductivity (EC), and alkalinity were measured in unfiltered leachate subsamples. Leachates were then filtered using 0.45 µm pore-size nitrocellulose membrane filters and a glass vacuum filtration apparatus. Filtrates were collected and preserved for analysis, which was performed according to procedures outlined in [38,39].

The values of pH and EC were determined using a Crison MultiMeter MM 41. Total alkalinity and bicarbonate (HCO_3^-) were analysed by titration. Total organic carbon (TOC) was analysed using a Shimadzu TOC-V (TOC-ASI-V, Shimadzu Corporation, Kyoto, Japan); Potentially Toxic Elements (Cr, Mn, Ni, Cu, Zn, As, Al, Cd, and Pb), and Fe, were analysed in a Varian AA240 Atomic Absorption Spectrometer (Varian Inc., Palo Alto, CA, USA) and a Continuous Segmented Flow Instrument (CSF) (San-Plus Skalar, Skalar Analytical, Breda, The Netherlands), respectively. The major inorganic ions (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- , and SO_4^{2-}) were analysed by ion chromatography, CI (Dionex™ system DX-120/ICS-1000, Dionex Corporation, Sunnyvale, CA, USA).

As for water from interflow in the self-burning waste pile, the same parameters and components were analysed as in the case of soil leachates.

2.4. Statistical Analysis

A Principal Component Analysis (PCA) was performed to relate soil types in each hydropedological zone with the composition of soil leachates. Before conducting the multivariate analysis, the data underwent standardization to address the high variability in parameter values. Additionally, redundant variables were eliminated to streamline the analysis. A Principal Component Analysis (PCA) was then carried out using the software CANOCO for Windows version 4.5®.

3. Results and Discussion

The research outcomes reveal significant contrasts in the studied hydropedological features, as described in the following subsections. Indeed, the results highlighted apparent differences among the hydropedological zones defined in the study area, which are mainly driven by soil-forming factors: the type of parent material (in situ metasedimentary rock, unburned coal mining waste, burned coal mining waste, as well as a mixture of all these types of materials), topography both of the coal mining waste pile and the surrounding area, biological influence (type of vegetation cover), time, and anthropogenic influence (including the spatial distribution of coal mine waste accumulation and the self-burning process).

The observed hydropedological contrasts encompass the morphological characteristics of the soil profile, soil mineralogy and geochemistry, unsaturated hydraulic conductivity, soil water content, soil hydrophobicity, and hydrogeochemistry of soil leachates. These features are crucial for understanding the water–soil interaction and, consequently, comprehending the susceptibility of the coal waste pile and the surrounding soils to leaching.

Soil leaching also depends on other hydrological factors that influence the water available for infiltration and percolation, such as the volume of precipitation, interception, and evapotranspiration. Factors related to water movement in the porous media, namely K and hydrophobicity, are also relevant.

3.1. Hydropedological Zoning and Soil Morphology

In the study area, soils were classified as Regosols and Technosols, according to the criteria of the World Reference Base for Soil Resources [27]. Before the self-burning period (2017–2019), pedogenesis was driven by the regular functioning of the soil formation factors. However, self-burning disrupted this process in part of the waste pile, forming a distinct Technosol. Based on the environmental features after the self-burning process, hydropedological zoning was established, comprising the waste pile and its surroundings, in which every hydropedological zone corresponds to a specific environment (Figures 1 and 2):



Figure 2. Aspects of the Fojo coal mining waste pile and the surrounding area: (a) vegetation cover in the Uphill Soil; (b) soil profile in the Uphill Soil; (c) Unburned Coal Waste; (d) Mixed Burned Coal Waste; (e) sampling point of the Burned Waste layer (BW), and Cover Layer (CL); (f) Burned Waste layer; (g) Downhill Soil; (h) application of the mini disk infiltrometer in the Unburned Coal Waste.

(i) Uphill Soil (US): with a soil type representing the geological and hydropedological conditions before the deposition of the coal mining waste. This zone is situated in the highest part of the study area and is free from the influence of coal mining waste. The parent material consists of carboniferous metasedimentary rocks. The vegetation cover consists mainly of *Eucalyptus globulus*, *Acacia melanoxylon*, *Acacia dealbata*, and *Pinus pinaster*.

The soil profile is O-Ah-C-R. The analytical results and field measurements refer to the Ah horizon.

(ii) Unburned Coal Waste Pile (UCW): with a soil type composed of ordinary coal mining waste, in which self-burning did not take place. The vegetation cover is recent and consists mainly of *Acacia dealbata* and *Eucalyptus globulus*. The prevailing soil profile is O-A-C. The accumulation of humified organic matter in A horizon is very incipient and does not occur in part of the hydropedological zone. The analytical results and field measurements refer to the C horizon.

(iii) Burned Coal Waste Pile (BCW): with a soil type composed of coal mining waste influenced by self-burning (BW), covered by a 30–40 cm protective layer consisting of mixed material from the C horizon and especially the R horizon of nearby soils with several metasedimentary parent materials. The protective layer is referred to as the Cover Layer (CL). Vegetation is almost absent. The soil profile is C1–C2, with the C1 horizon corresponding to the CL protective layer and the C2 horizon to the BW layer. The analytical results and field measurements refer to both horizon C1 and horizon C2.

(iv) Mixed Burned Coal Waste (MBW): with a soil type consisting of a mixture of US, UCW, and BW material. The vegetation cover consists of *Eucalyptus globulus* planted in 2020. The soil profile is C-R. The R horizon consists of carboniferous metasedimentary rocks. The analytical results and field measurements refer to the C horizon.

(v) Downhill Soil (DS): with a soil type where the prevailing geological and pedological conditions are the ones before the deposition of the coal mining waste. However, since this zone is situated in the lowest part of the study, this soil type is influenced by the waste located uphill, namely, through the input of coal waste debris and water from overland flow and interflow. The vegetation cover consists mainly of *Eucalyptus globulus*. The soil profile is O-Ap-C-R. The analytical results and field measurements refer to the Ap horizon.

Regosols correspond to soils located uphill and downhill from the Fojo coal mining waste pile. In contrast, Technosols correspond to soils with all or part of the parent material composed of coal mining waste (Figures 1 and 2). According to the available soil mapping [26] and the criteria of the World Reference Base for Soil Resources [27], soil types from US and DS hydropedological zones have Regosol features, while soil types from UCW, BCW, and MBW hydropedological zones have Technosol features. Tables S1–S5 present selected morphological features of each soil type in the study area according to the FAO guidelines for soil description [28].

3.2. Hydropedological Field Measurements

Field tests were conducted at each soil sampling point (Figures 1 and 2). Unsaturated hydraulic conductivity (K) measurements were carried out using a mini disk infiltrometer (applying a suction rate of -1 cm), while the volumetric water content was measured using a capacitance probe, and the WDPT was applied to evaluate hydrophobicity. The results concerning K, volumetric water content, and hydrophobicity are presented in Table 1.

The mini disk infiltrometer test results indicate that, in all soils, the magnitude of K remains consistent between the wet season and the dry season, suggesting that the volumetric water content is not a key factor controlling this hydropedological feature. As for hydrophobicity, all soils are wettable throughout the year except for the soil from the US zone, which is severely water-repellent. In the Ah horizon (US zone), measured K is 0.00 cm/s in the wet and dry seasons, while most of the remaining K mean values are around 10^{-4} cm/s. In the UCW zone (C horizon), K values range from 1.39×10^{-4} cm/s to 1.79×10^{-3} cm/s. In the BCW zone, K values range from 3.05×10^{-5} cm/s to 1.90×10^{-3} cm/s in the C1 horizon (CL material) and from 1.76×10^{-4} cm/s to 5.50×10^{-3} cm/s in the C2 horizon (BW material). In the MBW zone (C horizon), K values range from 2.42×10^{-4} cm/s to 1.83×10^{-3} cm/s. In the DS zone (Ap horizon), K values range from 3.74×10^{-5} cm/s to 5.94×10^{-4} cm/s. Finally, the BW10 sample, composed of material from the deepest part of the burned waste pile, presents K in the same order of magnitude as the lowest values measured in the C2 horizon of the BCW zone (that is, 10^{-4} cm/s).

Table 1. Unsaturated hydraulic conductivity, volumetric water content, and hydrophobicity measured in soils from the Fojo coal mine waste pile and the surrounding area.

Hydropedological Zone/Soil Sample	Soil Horizon/ Number of Measurements	March 2022		July 2023		Hydrophobicity
		K (cm/s)	VWC (%)	K (cm/s)	VWC (%)	
US	Ah (<i>n</i> = 5)	0.00	8.5	0.00	6.5	Severely water-repellent
UCW	C (<i>n</i> = 5)	8.59×10^{-4}	15.6	7.47×10^{-4}	12.1	Wettable
MBW	C (<i>n</i> = 6)	8.12×10^{-4}	24.4	6.97×10^{-4}	10.3	Wettable
BCW	C1 (<i>n</i> = 9)	7.45×10^{-4}	19.2	5.90×10^{-4}	8.8	Wettable
	C2 (<i>n</i> = 9)	1.10×10^{-3}	34.2	1.10×10^{-3}	14.4	Wettable
DS	Ap (<i>n</i> = 3)	1.65×10^{-4}	25.3	6.78×10^{-4}	7.2	Wettable
BW10	C2 (<i>n</i> = 1)	9.19×10^{-4}	15.3	7.83×10^{-4}	5.4	Wettable

Mean values of unsaturated hydraulic conductivity (K) and volumetric water content (VWC); mini disk suction rate: −1 cm; hydrophobicity classification according to [32].

3.3. Soil Mineralogy

The analytical results highlight distinct mineralogical signatures within each hydropedological zone in the fine-earth and clay fractions.

The overall mineralogical composition of the fine-earth fraction (Table 2) is silicate, with an absolute predominance of Quartz, followed by phyllosilicates (essentially Muscovite and Kaolinite) and feldspars (potassic and calc-sodic). Iron oxides (Hematite and, in some samples, Goethite) and Titanium oxides (Anatase) are present in almost all the samples, as well as sulphates, namely, Jarosite and Alunite. As for carbonates, only Siderite was detected, which is relatively frequent but in small quantities.

The fine-earth fraction also reveals some mineralogical differences among hydropedological zones. The US soil is characterized by its almost monomineralic composition, given the predominance of Quartz (85.8%). The UCW soil is differentiated by some accessory minerals, namely, the higher values of Chlorite, Siderite, and Pyrite. The MBW soil shows an indistinct composition which reflects the mixture of US, UCW, and BCW material. In the case of the CL layer (C1 horizon of the BCW soil), Quartz is much less abundant than in the US soil (58%), offset by greater quantities of Muscovite, Kaolinite, and Chlorite; as accessory minerals, Goethite (instead of Hematite) and Siderite stand out. In addition to containing less quartz (55.8%), the BW layer (C2 horizon of the BCW soil) is noticeably enriched in Hematite, Jarosite, and Alunite. The presence of Siderite and Pyrite in the UW soil is related to the reducing environment in the coal mine rock massif, while the presence of Jarosite and Alunite in the BW layer reflects the oxidizing environment in the waste pile affected by self-burning. The DS soil, despite having a similar amount of Quartz to the US soil (82.5%), is characterized by some accessory minerals, namely because it is the only one in which the ubiquitous presence, although always discreet, of Opal C/CT, Zeolites, and Pyrophyllite has been identified. The fine-earth mineralogical composition of the BW10 sample is quite similar to that of the BW material.

Regarding the overall mineralogical composition of the clay fraction (Table 3), Illite is dominant in all soils, followed by Kaolinite. Smectite and Chlorite are also common, while Pyrophyllite is somewhat less abundant.

The clay fraction results also show distinctive aspects. The US soil is characterized by the very significant presence of Smectite at the expense of a relative decrease in Illite. The UCW soil shows a relative enrichment in Chlorite and Pyrophyllite. In addition to Illite and Kaolinite, the MBW soil is also characterized by the presence of Smectite. In the BCW soil, the CL layer is essentially distinguished by some of the accessory minerals, namely the ubiquitous presence of Smectite, Chlorite, and Pyrophyllite. An almost monomineralic composition characterizes the BW layer, such is the predominance of Illite.

However, the BW10 sample has more diversified clay mineralogy, including Smectite, Chlorite, and Pyrophyllite, like the DS soil, which is enriched in these minerals and depleted in Illite.

Table 2. Mean mineralogical composition (%) of the fine-earth fraction of soils from the Fojo coal mine waste pile and its surrounding area.

Minerals	Hydropedological Zones						BW10 (n = 1)
	US (n = 2)	UW (n = 2)	MBW (n = 2)	BCW		DS (n = 2)	
				CL (n = 5)	BW (n = 5)		
Quartz	85.8	52.8	69.0	58.0	55.5	82.5	55.0
K Feldspar	1.3	3.3	1.3	5.5	5.2	3.5	5.5
Plagioclase	4.3	7.3	5.0	5.6	5.8	3.0	4.5
Opal C/CT	0.0	0.0	0.0	0.0	0.0	traces	0.0
Zeolites	0.0	0.0	0.0	0.0	0.0	traces	0.0
Muscovite	4.5	13.0	9.5	12.9	12.4	4.3	13.5
Kaolinite	2.0	3.5	2.5	4.1	2.5	1.0	1.5
Chlorite	0.0	2.8	0.0	1.0	0.0	0.0	0.0
Pyrophyllite	0.0	0.0	0.0	0.0	0.0	traces	0.0
Hematite	0.0	1.5	3.8	0.9	6.5	0.0	8.0
Goethite	0.0	1.0	1.0	1.4	0.0	0.0	0.0
Anatase	2.3	4.5	2.5	3.7	3.6	2.0	3.5
Siderite	0.0	2.5	1.3	1.5	0.8	0.8	0.5
Pyrite	0.0	4.0	0.0	0.0	0.0	0.0	0.0
Jarosite	0.0	2.5	2.8	2.8	4.8	2.3	5.0
Alunite	0.0	2.0	1.5	2.8	3.3	1.0	3.5
Gypsum/Anhydrite	0.0	0.0	0.0	0.6	0.0	0.0	0.0

Table 3. Mean mineralogical composition (%) of the clay fraction of soils from the Fojo coal mine waste pile and its surrounding area.

Minerals	Hydropedological Zones						BW10 (n = 1)
	US (n = 2)	UW (n = 2)	MBW (n = 2)	BCW		DS (n = 2)	
				CL (n = 5)	BW (n = 5)		
Smectite	27.5	0.0	2.8	7.8	0.0	10.0	9.0
Chlorite	0.0	7.0	0.0	5.4	0.0	8.5	6.0
Illite	53.5	72.0	83.5	65.0	88.0	55.0	65.0
Pyrophyllite	0.0	5.0	0.0	1.8	0.0	15.5	10.0
Kaolinite	19.0	16.0	14.0	20.0	12.0	11.0	10.0

3.4. Hydrogeochemistry of Soil Leachates and Interflow

The results of the soil leaching tests showed that the water–soil interaction concerning major ions, Fe, and PTEs differs considerably according to the hydropedological zone. Similar contrasts were also observed in the pH and EC of leachates. In March 2022, after a rainy period, interflow was observed at the base of the waste pile, and a water sample was collected to carry out a hydrogeochemical characterisation similar to that of

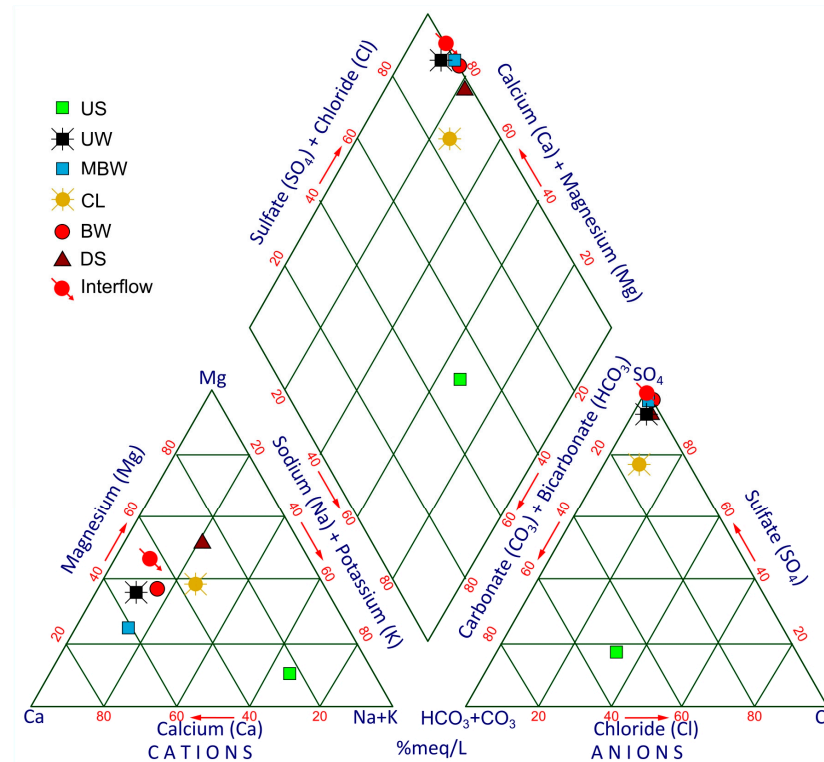


Figure 3. Piper diagram of soil leachates and interflow from the Fojo coal mine waste pile and the surrounding area.

The pH values are higher in samples without coal mining influence, specifically, 5.7 in US and 5.0 in CL. In the case of the samples with coal mining influence, pH values are more acidic, especially in materials with self-burning: 4.2 in BW and 4.1 in MBW. Soil electrical conductivity also reflects the coal mining influence since the lower values were measured in the US and CL samples (11 $\mu\text{S}/\text{cm}$ and 22 $\mu\text{S}/\text{cm}$, respectively). In comparison, the higher values were measured in UCW, BW, and MBW (67 $\mu\text{S}/\text{cm}$, 58 $\mu\text{S}/\text{cm}$, and 65 $\mu\text{S}/\text{cm}$, respectively). In the DS samples, intermediate pH and EC values were measured. The TOC in leachates is higher in soils with humified organic matter, particularly in the US soil, but also in the BCW soil, the BW layer of the BCW soil, and the DS soil.

Regarding major ion content, US and CL leachates show much lower mineralisation than the UCW, BW, MBW, and DS leachates, which is consistent with the EC results. The hydrogeochemical facies of leachates are Na- HCO_3 and Mg- SO_4 for US and CL, respectively, Ca- SO_4 in the case of UCW, BW, and MBW, and Mg-Ca- SO_4 in the case of DS. The BW10 leachate features are analogous to BW, except for the lower SO_4 content.

The results also revealed distinct distribution patterns of PTEs (Al, Mn, As, Cd, Ni, Cu, Cr, Zn, Pb) and Fe according to the hydrogeological zone. The concentration of PTEs and Fe in leachates is represented in Figure 4, showing higher values in soil samples influenced by coal mining (UCW, MBW, and BW) when compared with US and CL. Indeed, the UW and BW leachates have similar total concentrations of PTEs and Fe, with more significant differences observed in Al, Fe, Mn, and Zn. Compared to the BCW material, the BW10 sample contains more Fe (consistent with pyrite weathering in an environment with more intense self-burning) and Zn. However, this sample is relatively depleted in Al and, to a lesser extent, in Mn, Ni, and Cu.

The comparison of soil leachate hydrogeochemistry with soil geochemistry in Table 5 also highlights a different leaching potential in PTEs and Fe. In the case of Mn and Zn, higher hydrogeochemical concentrations correspond to higher geochemical concentrations, while in the case of Fe, Al, As, Cd, Ni, Cu, Cr, and Pb, this relation is not apparent.

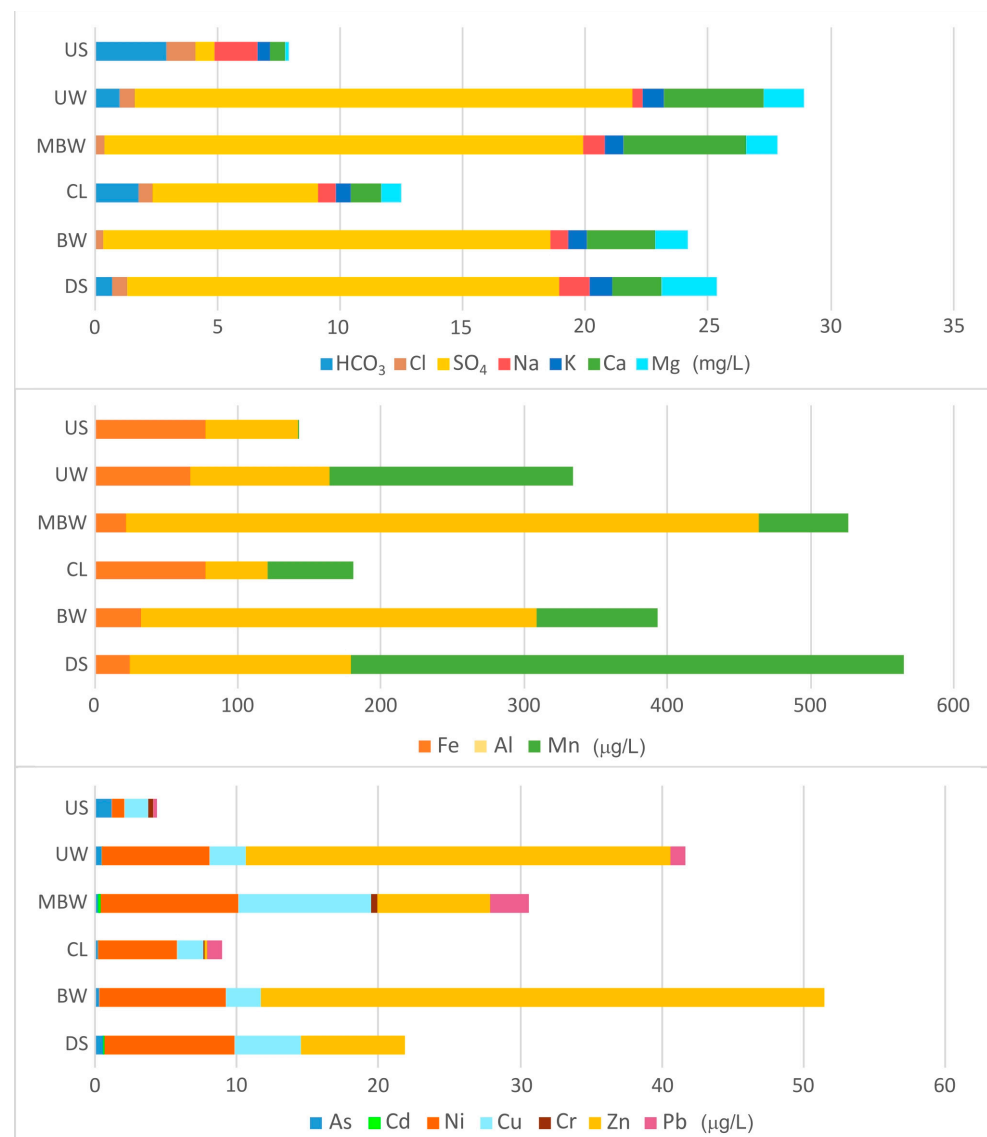


Figure 4. Mean contents of major ions, Potentially Toxic Elements, and Fe of soil leachates from the Fojo coal mine waste pile and the surrounding area.

The hydrogeochemistry of soil leachates reveals that the water–soil interaction in the upper unsaturated zone is more intense in the soils affected by coal mining, resulting in higher concentrations of readily soluble major ions and PTEs. Also, the DS soils show signs of coal mining influence (namely, the relatively high concentration of SO₄, Ca, Mg, Al, Mn, Ni, Cu, and Zn). This influence results from overland flow and interflow in the coal mine waste pile, which has probably been going on for decades since the waste was first deposited but has intensified since the self-burning event. Overland flow in the BCW and MBW hypopedological zones (Figure 1) was observed during heavy precipitation events. This process promoted the transport of solid particles and dissolved chemical compounds into the DS zone. Moreover, water from interflow emerging at the base of the waste pile, with a high concentration of major ions, PTEs, and Fe (see Tables 4 and 5), also reaches the DS material, contributing to the change in its geochemical and hydrogeochemical signature.

The hydrogeochemistry of interflow results from a longer and deeper flow path, in which the fluid becomes progressively more acidic due to the weathering of pyrite, promoting the interaction with the mine waste, resulting in a much more intense leaching of major ions, PTEs, and Fe. The pH and EC values are 3.7 and 2690 µS/cm, respectively. The mineralisation is two orders of magnitude higher than in the soil leachates, and the

hydrogeochemical facies is Ca-SO_4 . Likewise, the concentrations of Fe and several PTEs in interflow are more than one order of magnitude higher than in soil leachates, namely, in the case of Al, Mn, As, Cd, Ni, Cu, and Cr.

3.5. *Hydropedological Setting and Soil Leaching*

Field observations and measurements, along with mineralogy, geochemistry, and hydrogeochemistry results, pointed out that coal mining produced severe changes in the hydropedological conditions of the study area. The US hydropedological zone represents the conditions prior to the mining waste disposal, characterized by the least favourable setting for soil leaching. In this case, the rainfall interception caused by the abundant vegetation cover, which has existed in this location for decades, if not centuries, decreases the volume of water that reaches the ground surface and may originate infiltration. Additionally, the infiltration capacity of the Ah horizon is also reduced by its hydrophobic nature (originated by soil organic matter, e.g., [32]), which seems to persist during most of the year (see Table 1), increasing overland flow e.g., [40,41]. Under these conditions, the unsaturated hydraulic conductivity in the Ah horizon is very low or even negligible, and the water infiltration and percolation in the upper soil horizons primarily take place during the wettest events of the year, originating hydropedological conditions less favourable to leaching. Water percolation is also limited at greater depth, particularly from the R horizon downwards, due to the relatively low permeability of the fractured metasedimentary rock. Another relevant feature of the US zone is that the pedological evolution and the soil leaching have been going on for centuries or even longer. Consequently, the topsoil has become geochemically depleted in leachable compounds and enriched in minerals resistant to leaching, thus explaining the lower concentration of major ions, PTEs, and Fe in the soil leachates.

Moreover, the conditions in the hydropedological zones affected by coal mining, as well as in the DS zone, are more favourable to water infiltration/percolation in the upper horizons and may induce solute transport into the deepest part of the unsaturated zone and the unconfined aquifer. In the UCW and MBW hydropedological zones, the vegetation cover is recent and less dense than in the US zone, and the A horizon is incipient and very shallow (in part of the UCW zone) or absent (in the remaining UCW zone and all of the MBW zone). In these circumstances, not only is the interception much less effective than in the US zone, but the soil is much less hydrophobic as a result of the scarcity or lack of humified organic matter, allowing for higher infiltration and percolation in a more permeable porous medium, especially during the wet season, when most of the precipitation occurs, and evapotranspiration is lower. This situation is even more extreme in the BCW zone, where the vegetation is almost absent, the soil is hydrophilic, and K is one order of magnitude higher in the C2 horizon (see Table 1). In addition, the more permeable porous medium in the burned coal waste only gives way to the fractured medium at a greater depth than in the remaining hydropedological zones, originating a longer flow path with more favourable conditions for leaching.

Also, the mineralogical composition of the UCW and MBW soils reflects the incipient pedogenetic evolution and is more diversified and abundant in leachable compounds. In the case of the BW layer of the BCW soil, the self-burning process induced important mineralogical transformations, including oxidising processes leading to the destruction of Pyrite and Siderite followed by the formation of Hematite, Jarosite, and Alunite. As a result of the weathering of Pyrite, the water percolating through the BW material becomes progressively acidic and more able to promote leaching, resulting in highly mineralized interflow water.

The DS soil, which, before the coal mine waste deposition, was similar to the US, has been under the influence of the coal mine waste pile for decades. This influence includes the transport of solid particles (with size from clay to gravel), especially during overland flow in the BCW and MBW hydropedological zones, as well as dissolved chemical components from interflow through the deepest part of the burned waste pile in an acidic environment.

The hydrogeochemical signature of this influence includes higher contents of SO_4^{2-} , Ca^{2+} , Mg^{2+} , Al, Mn, Ni, Cu, and Zn than the US soil.

As confirmed by PCA statistical analysis, the chemical composition of soil leachates reflects the hydrogeological zoning. The PCA graph (Figure 5) clearly differentiates soil samples from the studied hydrogeological zones. The US samples are clustered regarding the pH of soil and leachates, TOC, HCO_3^- , Cl, Na, Fe, and As. Soils with self-burning influence (BW layer and MBW) are clustered in terms of SO_4 , Mg, Ca, Ni, Mn, Al, Cu, Zn, and Pb. On the other hand, the UCW samples appear dispersed (possibly because the coal waste pile is composed of somewhat heterogeneous material with different petrological features and weathering), while the CL samples are clustered close to the central part of the graphic. Nevertheless, self-burning, together with the waste mobilization during the fire control operation, seems to cause a process of homogenization with regard to leaching in the BW layer. A similar effect is observed in the MBW due to soil mobilization for planting eucalyptus. Finally, the DS samples define a boundary between the US and the burned material (BW and MBW).

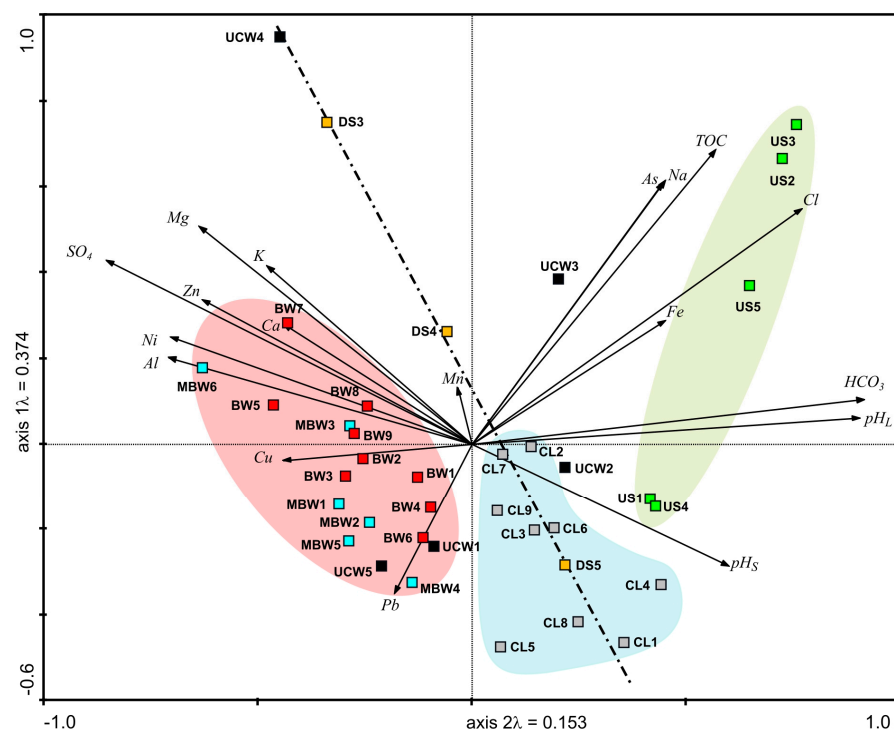


Figure 5. PCA analysis of chemical parameters in soil leachates from the Fojo waste pile and the surrounding area; Uphill Soil (US) cluster in green; Burned Waste layer (BW) and Mixed Burned waste (MBW) cluster in red; Cover Layer (CL) cluster in blue; the dashed line marks the boundary defined by the Downhill Soil (DS) samples; pH_L -leachates pH; pH_S -soil pH.

4. Concluding Remarks

The environmental impact of coal mining on soils and water bodies is a well-established fact. In coal mining areas, landscapes and ecosystems often undergo dramatic transformations, accompanied by changes in hydrological and pedological features and processes. The local water cycle is disturbed concerning rainfall interception, overland flow, infiltration, and percolation. Additionally, the local soil system is altered by waste disposal in piles, which are often large in volume and area, originating new soil types classified as Technosols.

A hydrogeological perspective (in the form of the definition of hydrogeological zoning) is valuable for understanding the water–soil interaction in this environment. It also provides a basis for an integrative scientific approach for assessing changes in processes and features in the upper unsaturated zone.

The research results showed clear contrasts between the hydropedological zones in all aspects studied, from soil morphology to soil leaching. Indeed, the hydropedological conditions favour rainfall infiltration, percolation, and leaching of major ions and PTEs in the upper soil horizons of hydropedological zones with mining influence compared to the US zone, which represents the pre-waste deposition setting. In addition, the leaching potential in the US zone is expected to be lower because of the soil mineralogy and the percolation into the deepest part of the soil profile (C horizon and, especially, R horizon), which takes place in a fractured medium corresponding to a material of lower permeability and lower specific surface than in the case of UCW, BCW, and MBW zones. Also, based on the morphological characteristics of the soil profile, hydropedological field measurements, and the structure of the unsaturated zone, it is to be expected that the transport of pollutants to greater depths and eventually to the unconfined aquifer will be more effective in the UCW, MBW, and BCW hydropedological zones.

The leachates from soils with mining influence are more acidic, especially those with self-burning, and have higher major ion content (with Ca-SO_4 hydrogeochemical facies) and higher PTE content. The influence of self-burning makes it possible to distinguish the soil in the UCW zone from the BW layer of the BCW zone. The BW layer is characterized by a higher K value, a somewhat different mineralogical composition (both in the fine soil fraction and the clay fraction), leachates with a slightly more acidic pH, and different concentrations of some PTEs.

Although, before the waste deposition, the DS soil was similar to the US soil, it presently reveals an apparent mining influence, as evidenced by leachates with a composition closer to that of mining-influenced soils.

In summary, the hydropedological setting in the mining-influenced hydropedological zones corresponds to soils more susceptible to major ion and PTE leaching and with a greater ability to disperse pollutants in the environment, namely in groundwater.

The study of the Fojo mine waste pile illustrates the interest in applying hydropedological concepts, methods, and techniques to assess the environmental impacts of coal mining. Such an approach can be of great value in decision-making related to the environmental management of coal mining areas and can be applied to the exploitation of many other geological resources.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/hydrology11050062/s1>, Table S1: Soil morphological characteristics of the Uphill Soil (US) hydropedological zone; Table S2: Soil morphological characteristics of the Unburned Coal Waste Pile (UCW) hydropedological zone; Table S3: Soil morphological characteristics of the Mixed Burned Coal Waste (MBW) hydropedological zone; Table S4: Soil morphological characteristics of the Burned Coal Waste Pile (BCW) hydropedological zone; Table S5: Soil morphological characteristics of the Downhill Soil (DS) hydropedological zone.

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