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Changes Induced by Self-Burning in Technosols from a Coal Mine Waste Pile: A Hydropedological Approach

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Abstract: Coal mining originates environmental impacts on soil and water bodies, including the leaching of Potentially Toxic Elements (PTEs) and Polycyclic Aromatic Hydrocarbons (PAHs) in mine waste piles. This research aims to identify and characterize changes induced by self-burning in Technosols from a coal mine waste pile by means of a comprehensive hydropedological assessment encompassing geochemical, mineralogical, and hydrological data, bearing in mind the potential leaching of PTEs and PAHs. The soil profile from two contiguous areas (an area with normal pedological evolution vs. an area affected by self-burning) was characterized in terms of morphological features. Each soil horizon was sampled and analyzed for geochemical and mineralogical characterization. The unsaturated hydraulic conductivity (K_i) was also measured in all soil horizons. Finally, the leaching potential of PTEs and PAHs in water was evaluated. Several changes induced by self-burning were identified in the studied Technosols: development of specific soil horizons; destruction of humified organic matter; contrasting geochemical composition, especially in the deeper horizons; mineralogical modifications, pointing to clay minerals with higher ion exchange capacity and higher specific surface by sulphates of lower structural order; diverse K_i values in the intermediate and lower part of the soil profile; and specific susceptibility to leaching of PTEs and PAHs. The research demonstrated that self-burning causes severe changes of hydropedological relevance, with influence on the leaching of PTEs and PAHs.

Keywords: coal mining pollution; coal waste combustion; potentially toxic elements; polycyclic aromatic hydrocarbons; soil leaching

1. Introduction

The exploration of mineral resources usually originates a great diversity of environmental impacts, namely on soil and water bodies, with major socioeconomic relevance, e.g., [1–3]. Some of the most critical and widespread mining impacts are related to the pollution of soil and the aquatic environment by metals and metalloids, due to the severity of the negative effects on ecosystems and on human health [4–6]. The environmental degradation resulting from the leaching of Potentially Toxic Elements (PTEs) and compounds, such as Polycyclic Aromatic Hydrocarbons (PAHs) from mine waste piles, as well as from acid mine drainage, is considered a major concern by governmental agencies, mining companies, and citizens [7,8].

Coal mining activities originate waste piles, often of great volume, containing PTEs, that is, metals and metalloids, including Al, Mn, As, Cd, Ni, Cu, Cr, Zn, Fe, and Pb in concentrations frequently higher than background values [9–12]. PAHs are chemical compounds consisting of fused aromatic rings, which constitute a global concern for the environment and human health. The 16 PAHs defined as priority pollutants by the United States Environmental Protection Agency and by the European Commission are also present in coal waste piles [13].

Soil leaching is found to be one of the primary pathways for PTEs and PAHs entering into the environment [14,15], namely, in industrial facilities, such as those related to coal mining. Through the process of leaching, PTEs and PAHs may disperse in the environment and cause significant damages to a large number of living organisms, including humans. Specifically, the exposition of human beings to PTEs and PAHs in soil and/or water may have carcinogenic, mutagenic, teratogenic, neurological, and endocrine disruption consequences [15–17].

The susceptibility to the leaching of PTEs and PAHs of materials in a given coal waste pile may vary according to a number of features, such as granulometry, geochemistry, mineralogy, pedological evolution, and the occurrence of self-burning. In particular, the leaching of PTEs and PAHs may pollute the meteoric water, which infiltrates into the soil, percolates through the unsaturated zone, and recharges the aquifer [18].

Soil pedogenesis influences the physical, chemical, and mineralogical properties of mine waste piles, and, a few decades after the waste deposition, the pedological differentiation of soil horizons may become noticeable [19]. In particular, the pedological evolution of Technosols from coal waste piles depends on the way soil formation factors transform the original materials [20] and may influence water circulation and pollutants transport in these porous materials. The occurrence of subsequent processes, such as coal waste self-burning, may induce severe changes in the normal soil profile evolution and originate zones with distinct hydropedological features. As a result, the soil from coal waste piles may present high spatial contrast concerning the leaching of pollutants.

Coal mining has been carried out in Portugal for centuries, in a variety of locations and geological frameworks. Of these, the mining operations in Douro Coalfield (N Portugal) were the most noteworthy. The exploitation of anthracite A in the Douro Coalfield was carried out between 1795 and 1994 and originated more than 20 waste piles in the abandoned mining areas. During the last few decades, several waste piles have been burning and the resulting geochemical processes and mineralogical transformations have been investigated [10,13,21].

The Douro Coalfield integrates the terrestrial Carboniferous basin (Upper Pennsylvanian (Lower Stephanian C)) in Portugal and outcrops along a strip with 53 km of length and width, ranging from 30 to 250 m (Figure 1). Besides the two principal centers of mining operations (São Pedro da Cova and Pejão), the elongated shape of the basin made the exploitation spread in small mining operations, and therefore the waste piles are also dispersed all over the area of the basin. The exploited coal was, for decades, principally used for power generation, and the mining activities had a significant role in the social and economic sectors of the region.

Consequently, the existence of coal waste piles close to old mining areas is significant and of environmental concern. In the Douro Coalfield, previous studies identified 20 coal waste piles [11], all located in forested areas. From those, three started self-burning in 2005 (including the São Pedro da Cova waste pile, which is still burning now) and two started self-burning in 2017, in all cases with ignition caused by wildfires.

The objective of this research is to identify and characterize changes induced by self-burning in Technosols from a coal mine waste pile by means of a comprehensive hydropedological assessment, encompassing geochemical, mineralogical, and hydrological data, bearing in mind the potential leaching of pollutants (PTEs and PAHs).

The research was carried out in Technosols from a coalmine waste pile (São Pedro da Cova mine, Douro Coalfield—41°09'25" N; 08°30'11" W). For that purpose, a comparative

study was carried out encompassing the soil horizons from two contiguous areas: an area with normal pedological evolution vs. an area affected by self-burning.

2. Materials and Methods

The field research methods encompassed the morphological description of the soil profile and the in-situ measurement of the unsaturated hydraulic conductivity (K_i). The geochemical and mineralogical analysis of collected soil samples was also performed, as well as leaching tests for the determination of PTEs and PAHs concentration in leachates.

Two contiguous locations in the São Pedro da Cova mine waste pile were selected: one representing the waste with normal pedological evolution and the other representing the waste that has been affected by self-burning. In each location, samples were collected from each soil horizon.

The soil profile description adopted the FAO's guidelines [22] and the World Reference Base for Soil Resources classification [23] and was carried out in terms of the following field features: (i) the development of soil horizons resulting from the normal influence of soil formation factors, as well as soil horizons resulting from self-burning; (ii) soil horizon boundary; (iii) texture; (iv) structure; (v) volumetric water content (measured with a capacitance probe—ThetaProbe model ML2x); (vi) colour; (vii) presence of humified organic matter content; (viii) porosity; and (ix) biological activity. Hydrophobicity was assessed through the Water Drop Penetration Time (WDPT), as described by [24]. The in-situ measurement of the unsaturated hydraulic conductivity was carried out using a mini disk infiltrometer, e.g., [25–27].

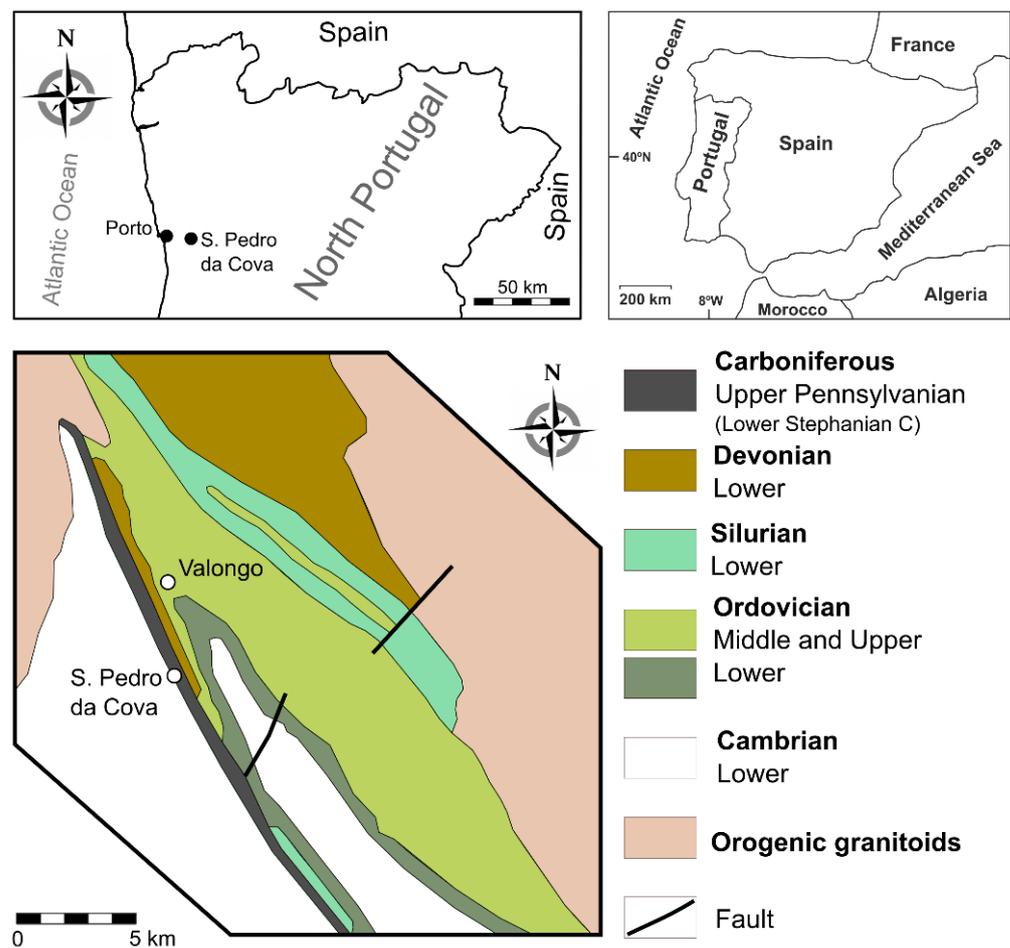


Figure 1. São Pedro da Cova location and geological framework (modified from [28]).

The geochemical analysis of soil samples, for the determination of concentration of major and trace elements, was performed through inductively coupled plasma mass spectrometry (ICP-MS) by Bureau Veritas Mineral Laboratories (9050 Shaughnessy St, Vancouver, British Columbia V6P 6E5, Canada) after ignition at 550 °C, followed by acid digestion, with an acid solution of (2:2:1:1) H₂O-HF-HClO₄-HNO₃.

Mineralogical composition was assessed by X-Ray diffraction (XRD). Samples were dried at about 50 °C and gently disaggregated before testing. Fine fractions (<2 µm particle size) were obtained by sedimentation, according to Stokes Law. Mineralogical analyses of fractions under 63 µm and 2 µm were carried out by X-Ray diffraction, using a Panalytical X'Pert-Pro MPD, Kα Cu (λ = 1.5405 Å) radiation on random-oriented powders (total sample) and oriented aggregates (<2 µm). The oriented aggregates were treated with glycerol and exposed to heat-treatment at 500 °C. 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 identification of the different mineral phases followed the criteria recommended by [29,30] and the Joint Committee for Powder Diffraction Standards. The mineralogical semi-quantification of the identified minerals was made through peak areas determination of the diagnostic reflections and recalculated following the “reflective powers method”, according to [31,32].

The USGS Field Leach Test (USGS FLT, [33]) was used for PTEs and PAHs chemical analysis. It is a fast (5-min), effective, and simple leach test that allows to simulate, predict, and characterize the geochemical interactions between percolating water and the geologic and environmental matrices. The procedure performs an extraction ratio of 20:1 to ensure that the readily soluble components of the samples are taken into that solution without exceeding leachate saturation limits and to provide sufficient leachate to all desired measurements and elemental analyses.

To leach, 50 g of each prepared sample was weighed and carefully transferred to a 1L wide-mouthed borosilicate glass bottle. Next, 1 L of deionized water (pH 5.7) was slowly added, so that no dust was lost. The bottle was then capped and vigorously shaken on a bench-top horizontal shaker for 5 min. After shaking, contents were allowed to settle for 10 min. After settling, unfiltered subsamples of the leachates were dispensed into disposable plastic beakers and measured for pH, conductivity, and alkalinity. Leachates were then filtered using 0.45 µm pore-size nitrocellulose filters. Filtrates were collected and preserved for analysis, which were performed according to procedures outlined in [34,35]. Electrical conductivity (EC) and pH were determined in a Crison MultiMeter MM 41. Total alkalinity, bicarbonate (HCO₃⁻), and oxidability were analyzed by titration. The major inorganic ions (Na⁺, K⁺, Mg²⁺, Ca²⁺, Li⁺, Cl⁻, NO₃⁻, F⁻, and SO₄²⁻) were analyzed by ion chromatography, CI (Dionex™ system DX-120/ICS-1000, Dionex Corporation, Sunnyvale, CA, USA), and the heavy metals (Cr, Mn, Ni, Cu, Zn, As, Cd, and Pb) in a Varian AA240 Atomic Absorption Spectrometer (Varian Inc., Palo Alto, CA, USA). Other components, such as Al, Fe, NO₂⁻, NH₄⁺, and SiO₂ were analyzed and put in a Continuous Segmented Flow Instrument (CSF) (San-Plus Skalar, Skalar Analytical, Breda, The Netherlands).

PAHs were analyzed by dispersive liquid–liquid microextraction coupled to gas chromatography/mass spectrometry (DLLME–GC/MS) methodology in a Shimadzu GCMS-QP2010 gas chromatograph mass spectrometer equipped with an auto injector AOC5000 (Shimadzu Corporation, Kyoto, Japan). Analytical standards were supplied by Sigma–Aldrich (Steinheim, Germany) and Merck (Darmstadt, Germany). The reference standard mixture, containing the 16 EPA PAHs (naphthalene, Nap; acenaphthylene, Acy; acenaphthene, Ace; fluorene, Flu; phenanthrene, Phe; anthracene, Ant; fluoranthene, Flt; pyrene, Pyr; benz[a]anthracene, BaA; chrysene, Chr; benzo[b]fluoranthene, BbF; benzo[k]fluoranthene BkF; benzo[a]pyrene, BaP; dibenz[a,h]anthracene, DahA; benzo[ghi]perylene, BghiP; and indeno [1,2,3-cd]pyrene, Ind) were supplied by Sigma–Aldrich (Steinheim, Germany). Methanol, dichloromethane, and acetonitrile were high-purity SupraSolv solvents and were supplied by Merck (Darmstadt, Germany). Ultrapure water was highly purified by a Milli-Q gradient system (18.2 mΩ/cm) from Millipore (Milford, MA, USA).

3. Results

The hydropedological assessment was carried out in a slope of the São Pedro da Cova coal mine waste pile, where the Technosol with normal pedogenesis was adjacent to the Technosol affected by self-burning (Figure 2). The results express substantial contrasts regarding most of the assessed features, as described in the next subsections.



Figure 2. Some aspects of the studied Technosols: (a) view of the coal mine waste pile in 2004, before the wildfire; (b) view of the coal mine waste pile in 2019; (c) waste pile slope with normal pedogenesis; (d) waste pile slope affected by self-burning; (e) soil profile representing the waste pile with normal pedogenesis (A horizon and C horizon); (f) soil profile representing the waste pile affected by self-burning (C1, C2, and C3 horizons). \triangle stands for Technosol with normal pedogenesis; \square stands for Technosol affected by self-burning. Satellite images from *Google Earth* (21 March 2004; 3 April 2019).

3.1. Soil Profile Description

The studied soils are Spolic Technosols, with technogenic diagnostic materials (that is, parent materials consisting of coal mine waste), according to the criteria of the World Reference Base for Soil Resources [22]. Before the occurrence of self-burning, the studied slope of the waste pile was under the normal influence of soil formation factors (parent material, climate, topography, biological influence, time, and anthropogenic influence). Since the waste deposition ceased around 50 years ago, the soil became gradually covered with vegetation dominated by *Acacia melanoxylon*, *Acacia dealbata*, *Pinus pinaster*, and *Quercus suber* (Figure 2a,c), and this cover originated a superficial organic layer (O horizon)

consisting of weakly decomposed litter. With time, the topsoil became progressively enriched with humified organic matter up to 20 to 40 cm in depth. As a result, a weakly developed soil profile was formed, which included two mineral horizons (Figure 2e): an incipient A horizon (the most superficial layer, with perceptible accumulation of humified organic matter); a C horizon, with none to very low humified organic matter content (Table 1).

Table 1. Soil Characteristics in the Coal Mine Waste Pile with Normal Pedogenesis ¹.

Soil Feature	A Horizon	C Horizon
Colour	5Y3/1 (very dark grey)	5Y2.5/1 (black)
Texture	sandy loam	sandy loam
Structure	blocky subangular, weak to moderate, medium	apedal
Thickness	20–40 cm	>1 m
Lower boundary (distinctness/topography)	clear to gradual/wavy	–
Humified organic matter (presence/abundance)	present/moderately abundant	mostly absent/none to very scarce
Porosity (size/abundance)	fine/common, medium/very few	fine/common, medium/few
Biological activity (roots: diameter/abundance)	fine/few, medium/common, coarse/very few	fine/none, medium/very few, coarse/very few

¹ According to [22] guidelines.

In the summer of 2005, a wildfire caused the ignition of the waste pile and triggered the self-burning process. After that, self-burning moved along the SW slope of the waste pile (Figure 2b), relatively fast and with higher temperatures in the first years (principally until 2010). Since 2013, the burning process seems to have occurred at lower temperatures and is static in the same area. This indicates that the combustion process is being very heterogeneous along the waste pile and, therefore, the waste material was differently affected, both laterally and in depth.

According to [10], the mineralogical composition of the mine waste affected by self-burning points out that the combustion temperature reached at least 1000 °C, very close to the surface (\approx 10–20 cm of depth). Measurements with an optical fiber system have shown temperatures higher than 800 °C, at 1 to 2 m in depth [21]. The variability of the attained temperatures is explained by the fact that the combustion process differs along the waste pile. The resulting near surface temperature gradient has originated three soil layers that correspond to three differentiated C horizons (C1, C2, and C3), with distinct physical, geochemical, and mineralogical features (Figure 2f and Table 2). In fact, self-burning has obliterated the pedological features observed in the Technosol with normal evolution, namely, the accumulation of humified organic matter and the formation of structural aggregates.

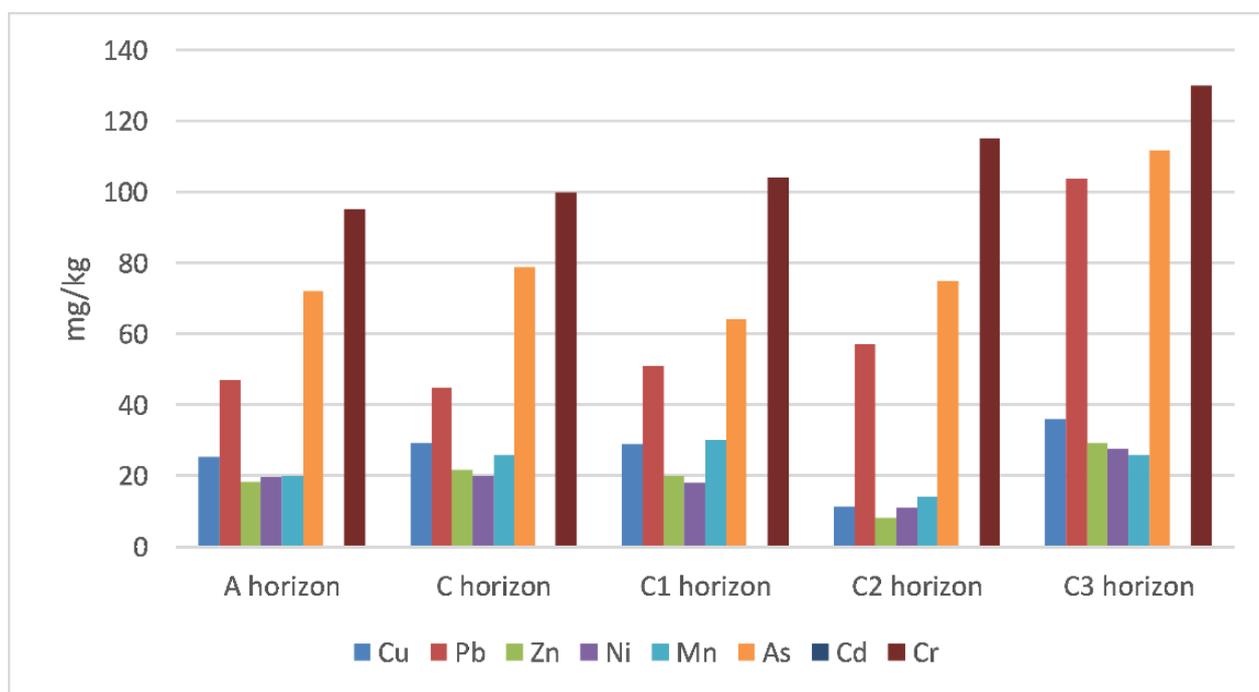
3.2. Soil Geochemistry

The geochemical study encompassed the horizons identified in the São Pedro da Cova waste pile Technosols (see Section 3.1), that is, in the waste pile with normal pedogenesis (A horizon and C horizon) and in the waste pile affected by self-burning (C1, C2, and C3 horizons). Table 3 presents the concentration of major and trace elements hosted by the Technosol samples, and Figure 3 represents the geochemical distribution of the PTEs analyzed in leaching tests (see Section 3.5).

Table 2. Soil Characteristics in the Coal Mine waste Pile Affected by Self-burning¹.

Soil Feature	C1 Horizon	C2 Horizon	C3 Horizon
Colour	5Y2.5/1 (black)	5Y8/4 (pale yellow)	10R5/8 (red)
Texture	loamy sand	clay loam	loamy sand
Structure	apedal	apedal	apedal
Thickness	10–20 cm	10–30 cm	>1 m
Lower boundary (distinctness/topography)	clear/wavy	clear/wavy	–
Humified organic matter	absent	absent	absent
Porosity (size/abundance)	fine/common, medium/few	fine/common, medium/few	fine/few, medium/common, coarse/few
Biological activity (roots)	none	none	none

¹ According to [22] guidelines.

**Figure 3.** PTE concentrations in soil horizons from São Pedro da Cova mine waste pile.

The most abundant elements present in the waste pile samples were Al (up to a maximum of 14.09 wt.% in the C3 horizon), followed by Fe (with a maximum of 4.83 wt.% in the C2 horizon), and K (with a maximum 3.06 wt.% in the C3 horizon).

The overall geochemical features of the A horizon and C horizon were similar to the C1 horizon, and the upper layer in the soil was affected by self-burning. The more intensively combusted C2 and C3 horizons showed an increase in Al, Fe, and K when compared to the less burned C1 horizon and A and C horizons, due to mineral changes during combustion and also to the loss of fossil organic matter. Additionally, the horizons affected by self-burning showed an increase of S, especially the C2 horizon. Previous studies [10] have shown similar results, that is, the burned material from the Douro Coal Basin generally presents an increase in Al, Fe, K, and Ti.

Regarding trace elements, some contrasts between the coal waste material with normal pedogenesis and the material affected by self-burning have been identified (see Table 3).

The C3 horizon had higher concentrations in several trace elements in comparison with the A and C horizons: Ba, with 866 mg/kg (versus 512 and 523 mg/kg in the A and C horizons, respectively); Pb, with 103.7 mg/kg (while the A and C horizons registered 47.0 and 44.9 mg/kg, respectively); As, with 111.8 mg/kg (whereas the A and C horizons showed 72.0 and 78.9 mg/kg, respectively); Sr, with 202 mg/kg (while horizons A and C

presented concentrations of 126 and 125 mg/kg, respectively); V, with 205 mg/kg (versus 124 and 123 mg/kg in the A and C horizons, respectively). The elements Ni, Cr, Cu, and Zn also showed a slight increase in the C3 horizon, with 27.7 mg/kg Ni, 130 mg/kg Cr, 36.1 mg/kg Cu, and 29.4 mg/kg Zn when compared to the unburned samples from the A and C horizons. On the other hand, Mn concentrations did not show a significant difference between the C3 horizon (26 mg/kg) and the A and C horizons (20 mg/kg and 26 mg/kg, respectively). Regarding Cd, the concentrations found in all samples were below the detection limit, with the exception of the C3 horizon, with a concentration of 0.23 mg/kg.

Table 3. Concentrations of major (wt.%) and trace elements (mg/kg) in soil horizons from São Pedro da Cova mine waste pile.

Elements ¹	Normal Pedogenesis		Affected by Self-Burning		
	A Horizon	C Horizon	C1 Horizon	C2 Horizon	C3 Horizon
<i>Al</i>	9.72	9.96	10.06	12.53	14.09
<i>Ca</i>	0.01	0.02	0.02	<0.01	0.02
<i>Fe</i>	3.44	3.93	2.85	4.83	4.41
<i>K</i>	1.98	2.08	2.30	3.06	2.96
<i>Mg</i>	0.12	0.13	0.14	0.12	0.11
<i>Na</i>	0.40	0.43	0.46	0.59	0.53
<i>P</i>	0.07	0.07	0.05	0.04	0.08
<i>S</i>	0.30	0.25	0.43	1.66	0.67
<i>Ti</i>	0.34	0.34	0.40	0.46	0.62
<i>Ag</i>	201	227	184	201	201
<i>As</i>	72.0	78.9	64.2	74.8	111.8
<i>Ba</i>	512	523	739	232	866
<i>Be</i>	4	4	4	3	6
<i>Cd</i>	<0.02	<0.02	<0.02	<0.02	0.23
<i>Co</i>	2.1	2.2	2.4	0.9	3.7
<i>Cr</i>	95	100	104	115	130
<i>Cu</i>	25.2	29.4	28.9	11.4	36.1
<i>Cs</i>	53.5	54.3	51.5	67.5	78.3
<i>Ga</i>	28.1	29.3	30.3	39.4	38.4
<i>Hf</i>	3.04	3.07	3.50	2.81	1.84
<i>Li</i>	253.4	260.1	212.5	88.3	149.2
<i>Mo</i>	3.6	3.5	3.8	5.0	4.6
<i>Mn</i>	20	26	30	14	26
<i>Nb</i>	11.1	10.8	15.0	15.5	18.4
<i>Ni</i>	19.6	20.1	18.1	11.1	27.7
<i>Pb</i>	47.0	44.9	50.9	57.2	103.7
<i>Rb</i>	145.2	151.2	167.2	207.7	205.4
<i>Re</i>	0.005	0.005	0.004	0.003	0.022
<i>Sb</i>	6.3	6.2	5.5	4.6	8.3
<i>Se</i>	2.7	2.5	5.3	14.8	1.6
<i>Sn</i>	4.2	4.6	5.6	5.8	28.7
<i>Sr</i>	126	125	164	199	202
<i>Ta</i>	0.8	0.8	1.1	1.1	1.3
<i>Te</i>	0.08	0.07	0.09	0.69	0.40
<i>Th</i>	15.8	16.9	17.6	13.1	24.4
<i>Tl</i>	1.1	1.1	1.2	1.6	1.7
<i>U</i>	5.9	5.9	5.6	4.4	4.5
<i>V</i>	124	123	135	184	205
<i>Zn</i>	18.2	21.6	20.1	8.1	29.4
<i>Zr</i>	111.2	113.0	125.6	102.2	63.9
Σ LREE ²	204.6	216.1	248.7	112.0	382.5
Σ HREE ³	43.5	44.7	44.8	30.1	45.4

¹ Major elements highlighted in italic; ² LREE: Low Rare Earth Elements; ³ HREE: Heavy Rare Earth Elements.

Samples affected by combustion showed a decrease in Zr, with the C3 horizon presenting 63.9 mg/kg, as the A and C horizons registered 111.2 and 113 mg/kg. Similarly,

previous studies conducted by [10] indicate that the burned samples, collected from the coal mine waste pile in the past, showed an increase in As, Ba, Cr, Li, Ni, Pb, Rb, Sr, and V and a decrease in Zr concentrations, possibly due to volatilization. The only exception seems to be Li, showing that, at present, results seem to be suffering a decrease in burned samples, with just 149.2 mg/kg in the C3 horizon and a minimum of 88.3 mg/kg registered in the C2 horizon.

The geochemical results from the coal waste pile affected by self-burning showed other relevant contrasts and trends concerning the distribution of elements in the soil profile (see Table 3 and Figure 3, which focuses on PTEs).

In fact, the concentration of some elements tended to increase with depth and reach of the maximum values in the C3 horizon, specifically, As (111.8 mg/kg), Cr (130.0 mg/kg), Cs (78.3 mg/kg), Pb (103.7 mg/kg), Rb (205.4 mg/kg), and V (205.0 mg/kg). The C2 horizon showed depletion in some elements, namely, Ba (232.0 mg/kg), Co (0.9 mg/kg), Cu (11.4 mg/kg), Li (88.3 mg/kg), Mn (14.0 mg/kg), Ni (11.1 mg/kg), Th (13.1 mg/kg), and Zn (8.1 mg/kg). Additionally, the C2 horizon was enriched in other elements in comparison to the C1 and C3 horizons: S (1.66 wt.%), Mo (5.0 mg/kg), Se (14.8 mg/kg), and Te (0.7 mg/kg).

As for the total concentration in Light Rare Earth Elements (LREE), the A horizon, C horizon, and C1 horizon presented similar values (between 204.6 mg/kg and 248.7 mg/kg); the C2 horizon was depleted (112.0 mg/kg) and the C3 horizon was enriched (382.6 mg/kg)—see Table 3. With respect to the total concentration in Heavy Rare Earth Elements (HREE), all horizons presented similar values (between 43.5 mg/kg and 45.4 mg/kg), except for the C2 horizon, which showed depletion (30.1 mg/kg).

In general terms, the concentrations of Cu, Pb, Zn, Ni, and Cd found in the studied soil profiles from São Pedro da Cova mining waste piles are below the reference value for contaminated soils provided by the Portuguese Environmental Agency (APA) [36]. The most concerning elements are As and Cr, which showed concentrations significantly higher than the reference values provided. Specifically, APA proposes a reference value for As, ranging from 11 mg/kg to 18 mg/kg, depending on the land use, while the mine waste pile samples range from 64.2 mg/kg to 111.8 mg/kg, that is, more than 10 times higher than the reference. Regarding Cr, the proposed reference values range from 67 mg/kg to 70 mg/kg, depending on the land use, whereas the waste dump samples range between 95 mg/kg and 130 mg/kg.

3.3. Soil Mineralogy

The mineralogical composition of the studied samples collected in the waste pile (fine earth fraction), in material from soil profiles, with normal pedogenesis and affected by self-burning, can be found in Table 4.

Table 4. Mineralogical composition (%) of the fine earth fraction of soil horizons from São Pedro da Cova mine waste pile.

Minerals	Normal Pedogenesis		Affected by Self-Burning		
	A Horizon	C Horizon	C1 Horizon	C2 Horizon	C3 Horizon
Quartz	36.0	38.0	45.0	45.0	38.0
K Feldspar	7.0	8.0	9.0	6.0	6.5
Plagioclase	6.0	8.5	8.0		4.0
Muscovite	21.0	19.0	22.0	22.0	20.0
Pyrophyllite	7.0	4.0	2.5		
Kaolinite	7.5	6.5	5.0		
Hematite				7.5	8.5
Anatase	7.0	7.5	7.0	5.0	7.0
Sulphur			traces	traces	traces
Pyrite			3.5		
Jarosites	7.5	3.5		15.0	10.0
Alunites					5.0
Opal A	1.5	5.0			1.0

Samples from the waste pile with normal pedogenesis show a mineralogical composition typical of a fine-grained siliciclastic material, dominated by Quartz, Muscovite, and Feldspars, with Pyrophyllite, Kaolinite, Anatase, Jarosites, and Opal A as accessory minerals, all of them usually present in these types of materials [37–40].

Samples from the waste pile affected by self-burning showed substantial changes on accessory minerals, with a relevant presence of Fe oxides (Hematite) and sulphates (Jarosites, accompanied by its Al isomorph Alunites), as well as traces of sulphur, more evident in the C2 horizon, together with a decrease in Kaolinite and Pyrophyllite, as well as a decrease in Opal A and a slight decrease in Feldspars (namely on Plagioclases), pointing to leaching of AlSi minerals, followed by the precipitation of Hematite and Jarosites (and Alunites). In the C1 horizon, this process was clearly more incipient, since Pyrophyllite and Kaolinite still remained, Feldspars showed values similar to the A and C horizons (that is, the unburnt materials), and Pyrite was present instead of Fe oxides and sulphates.

Concerning the clay fractions (<2 µm particle size), their mineralogical composition is shown in Table 5. Samples with normal pedogenesis show again a mineralogical composition typical of this fine-grained siliciclastic material [37–39], dominated by Illite, followed by Pyrophyllite, Kaolinite, and Chlorite. Additionally, A horizon showed a much lower Illite content and the presence of Halloysite. Samples affected by self-burning showed substantial changes on accessory minerals: Kaolinite and Chlorite disappeared, Pyrophyllite vanished, Illite became absolutely predominant, and Smectite appeared (in small amounts), pointing again to leaching of more Al rich minerals. Once again, the surficial sample (C1 horizon) showed some minor differences in comparison to the C2 and C3 horizons (on Kaolinite and Pyrophyllite amounts), pointing to a more incipient stage of the process.

Table 5. Mineralogical composition (%) of clay fractions of soil horizons from São Pedro da Cova mine waste pile.

Minerals	Normal Pedogenesis		Affected by Self-Burning		
	A Horizon	C Horizon	C1 Horizon	C2 Horizon	C3 Horizon
Smectite	tr	tr	3	2	2
Chlorite	9	7			
Illite	36	73	80	96	95
Pyrophyllite	17	10	5	2	3
Halloysite	18	tr	tr	tr	tr
Kaolinite	20	10	12		

3.4. Soil Unsaturated Hydraulic Conductivity

Soil unsaturated hydraulic conductivity measurements were carried out in May and September 2020 in the A and C horizons (mine waste with normal pedogenesis) and in the C1, C2, and C3 horizons (mine waste affected by self-burning), using a mini disk infiltrometer, with a suction rate of -0.5 cm. For this purpose, 5 Ki tests were conducted on each soil horizon. At the same time, at the spot of each Ki test, hydrophobicity was evaluated through the WDPT and volumetric water content measurements using a capacitance probe (Figure 4).

Table 6 presents the results of the measurements of Ki and volumetric water content. In all tests, the WDPT was under 5 s and, therefore, the studied soil was, consistently, very hydrophilic, according to the [24] classification.

According to the mini disk test results, the values of Ki in the mine waste with regular pedogenesis were around 10^{-3} cm/s, and the volumetric water content did not seem to have an important effect on the results. In this case, the soil profile showed an insignificant Ki variation with depth.



Figure 4. Field measurements of soil unsaturated hydraulic conductivity (a) and volumetric water content (b).

Table 6. Soil unsaturated hydraulic conductivity and volumetric water content of soil horizons from São Pedro da Cova mine waste pile.

Test Location	Horizon	May 2020				September 2020			
		Ki	σ	VWC	σ	Ki	σ	VWC	σ
Mine waste with normal pedogenesis	A horizon	2.43×10^{-3}	1.58×10^{-3}	17.6	0.6	2.00×10^{-3}	1.59×10^{-3}	12.3	2.6
	C horizon	4.35×10^{-3}	1.29×10^{-4}	17.2	1.4	4.68×10^{-3}	1.14×10^{-3}	17.6	0.7
Mine waste affected by self-burning	C1 horizon	1.15×10^{-3}	1.34×10^{-3}	20.9	4.6	1.45×10^{-3}	4.18×10^{-4}	8.6	3.4
	C2 horizon	7.84×10^{-4}	4.12×10^{-4}	13.0	1.6	9.36×10^{-4}	4.05×10^{-4}	8.5	1.1
	C3 horizon	2.00×10^{-2}	5.10×10^{-3}	9.6	2.8	2.20×10^{-2}	1.56×10^{-2}	2.2	1.7

Mini disk suction rate: -0.5 cm; Ki in cm/s; σ —standard deviation; VWC—volumetric water content (%); $n = 5$ for Ki and $n = 15$ for VWC.

In contrast, the values of Ki in the mine waste affected by self-burning ranged from 10^{-4} cm/s to 10^{-2} cm/s, that is, they varied along two orders of magnitude. In this case, the soil profile showed great contrast with depth, with the intermediate Ki value (10^{-3} cm/s) in the upper layer (C1 horizon), the lowest Ki value (10^{-4} cm/s) in the intermediate layer (C2 horizon), and the highest Ki value (10^{-2} cm/s) in the lower layer (C3 horizon). Again, soil water did not seem to have influence on Ki, even in the C1 horizon, where the volumetric water content decreased from 20.9% (in May 2020) to 8.6% (in September 2020). However, the lowest Ki value in C2 horizon corresponded to the finer clay loam texture.

3.5. Leaching of PTEs and PAHs

The application of the USGS FLT in this study aimed at simulating the leaching effect of the percolation of rainwater in the upper part of a Technosol from a coal waste pile, bearing in mind the transport of PTEs and PAHs.

The leaching tests results have shown that, in the studied coal waste pile, the leachates generated from different horizons had considerably different concentrations of major (Al, Fe, K, Na, Ca, Mg, Cl, SO_4 , F, NO_3 , NO_2 , NH_4) and trace elements (As, Cd, Cr, Cu, Mn, Ni, Pb, Zn).

The pH values of the aqueous leachates from the A and C horizons, as well as from the C1, C2, and C3 horizons, were determined immediately after the agitation period and were similar and acidic, with a mean value of 4.2 ± 0.1 . The electrical conductivity (EC) values were also similar, with a mean value of 28.8 ± 6.3 $\mu\text{S}/\text{cm}$.

Regarding the total concentration of major ions in the leachates, the IC and CSF analyses showed that they tended to be low and similar in all samples (Figure 5). However, it is important to point out the concentration of ammonium in the mine waste affected by self-burning, which was higher in the C1 horizon leachate and decreased in depth (C2 and

C3 horizons). On the other hand, sulphate was the main ion component in all samples, reflecting the mineralogy of the coal waste.

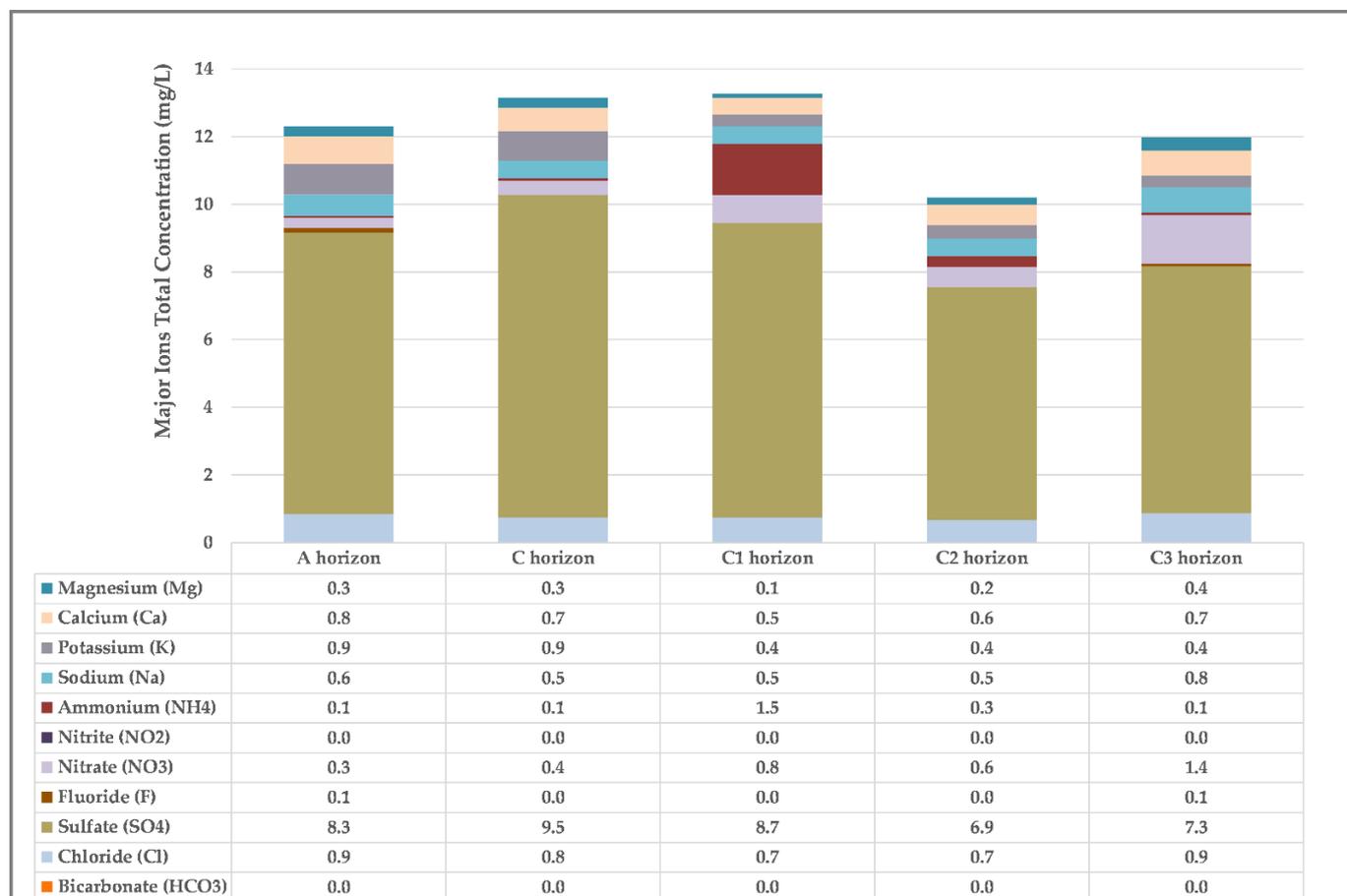


Figure 5. Concentration of major ions in soil leachates from São Pedro da Cova mine waste pile.

The AAS analysis revealed different concentration patterns of PTEs and Fe in the studied leachates.

The total concentrations of these elements found in leachates from the A and C Horizons were similar. However, some dissimilarities were found, concerning specific elements (Zn, Ni, Mn, Al, and Fe—see Figure 6). Since the corresponding leachates were generated with mine wastes under normal pedological evolution, these variations may have resulted from geochemical and mineralogical heterogeneities in the waste pile.

On the other hand, the total concentrations found in leachates from the C1, C2, and C3 horizons reflected the influence of self-burning (Figure 6). In fact, the leaching of some elements seemed to be temperature dependent, which was also observed by other authors. Higher concentrations in leachable elements were found in self-burning coal waste samples when compared with the unburned material, and these dissimilarities were ascribed to the burning process [10,14,41]. More specifically, the leachate concentration in Zn increased with depth (from 10.0 µg/L to 19.0 µg/L), as well as the concentration in Mn and Al (from 4.1 µg/L to 43.5 µg/L and from 1.0 µg/L to 314.9 µg/L, respectively). On the contrary, the concentration in Fe from these leachates decreased with depth (from 21.5 µg/L to 7.4 µg/L).

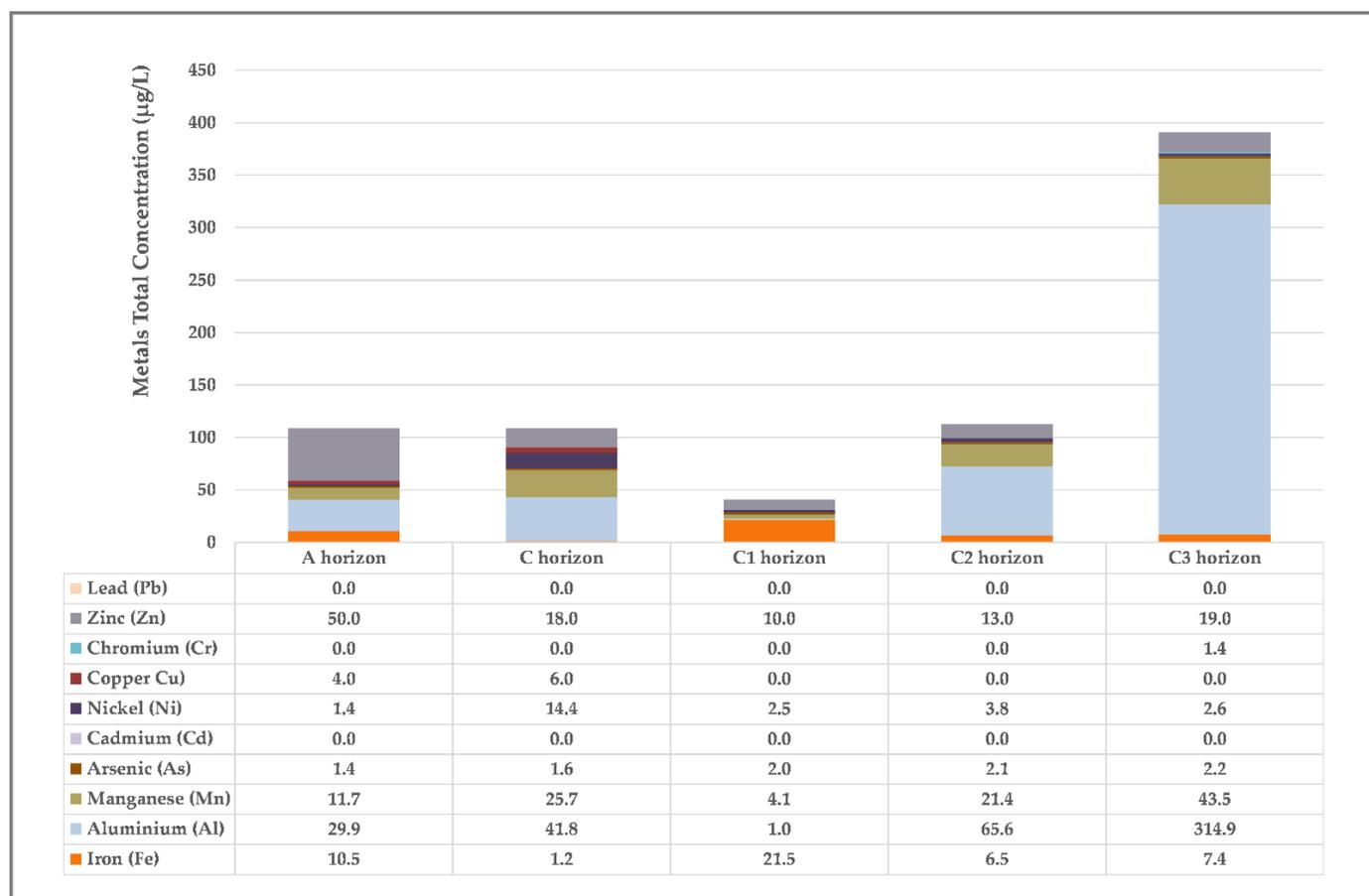


Figure 6. Concentration of PTES and Fe in soil leachates from São Pedro da Cova mine waste pile.

Previous works on the study of the chemical composition of leachates, originating from São Pedro da Cova waste pile, using different leaching test procedures [10,11], revealed that the most easily leached and accessible elements for percolation and mobilization into the environment (leaching percentage >1%) were Ca, Cd, Co, Mg, Mn, Na, Ni, S, and Zn, corroborating the PTES concentration of some elements found in leachates in the present study.

As for PAHs, the analytical results revealed significant differences in the concentration of these pollutants in leachates from different soil horizons (Figure 7). In fact, clear contrasts were found when comparing the soil with normal pedogenesis with the soil affected by self-burning. The PAHs distribution varied significantly with depth, especially in the waste pile affected by self-burning, which can also be explained by the fact that the PAHs production was temperature-dependent. Similar results were observed by [42].

Several PAHs were identified in the leachates, specifically 2–3-rings PAHs (Nap, Acy, Ace, Flu, and Phe) and 4-ring PAHs (Flt, BaA, and Chr). The PAHs in A, C, and C1 horizons showed a similar occurrence pattern, with the 3-ring Phe occupying 35%, 56%, and 24% of the total PAHs and the 4-ring Flt, BaA, and Chr being responsible for 65%, 44%, and 76% of the total PAHs, respectively. On the other hand, in the C2 and C3 horizons (where self-burning took place at higher temperatures), lower molecular weight PAHs of 2–3 rings leached at greater concentrations, corresponding to 58% and 61% of total PAHs, respectively.

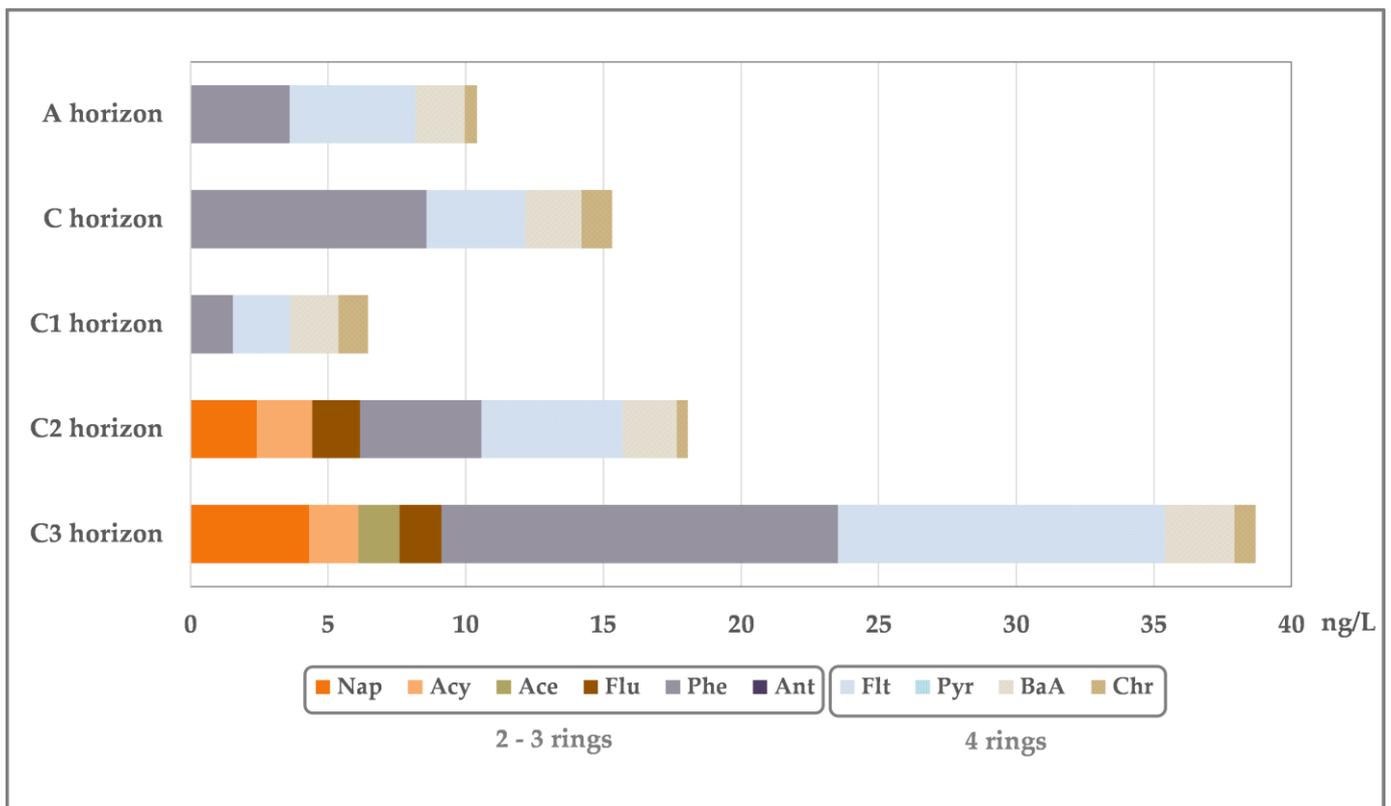


Figure 7. Concentration of PAHs in soil leachates from São Pedro da Cova mine waste pile.

4. Discussion

The research results brought out important contrasts in the studied Technosols, more precisely between the part of the coal waste pile with normal pedogenesis and the part affected by self-burning. These differences refer to the morphological features of the soil profile, as well as soil geochemistry, mineralogy, and unsaturated hydraulic conductivity. The observed contrasts have great hydrogeological relevance, bearing in mind the leaching potential of PTEs and PAHs in the coal waste pile. The pollutants susceptibility to leaching depends on several factors, such as specific element solubility and availability or release potential. Another factor that enhances leaching is the drainage conditions, which may increase the solubility and flow rates through materials containing pollutant bearing minerals [43]. Therefore, the environmental impact of coal waste containing pollutants, such as PTEs and PAHs, depends not only on the type and concentrations of these elements, but also on their mobility, which is expressed as their potential to leach in water [44].

Over the course of 5 decades after the waste deposition, the coal waste pile became gradually covered with vegetation, which, under normal pedogenetic conditions, originated a superficial layer enriched in humified organic matter (A horizon). The accumulation of this type of organic matter is the main morphological difference between the A horizon and C horizon, since there were no significant changes concerning soil texture, structure, porosity, or weathering of rock fragments. Indeed, soil organic matter plays a major role in pollutant transport, since the PTEs sorption on soil organic matter is much greater than sorption on the mineral matrix, namely, on clay minerals, iron oxides, and hydroxides [45]. Similarly, the concentration and transport of PAHs in soils is, to a great extent, controlled by sorption-desorption processes involving soil organic matter [46]. However, it should be noted that the accumulation of humified organic matter in this soil is an incipient process and, therefore, its influence on the leaching of PTEs is probably moderate.

The results also highlight a great similarity between the A horizon and C horizon, concerning soil geochemistry (especially of major elements), mineralogy, and hydraulic conductivity. Under such conditions, the overall hydrogeochemistry of leachates should

be similar in both soil horizons, and the analytical results confirm this assumption. As a matter of fact, the hydro-pedological behavior of this type of Technosol did not seem to vary in the soil profile, namely, in what concerns the leaching of PTEs and PAHs. However, some results showed minor geochemical and hydrogeochemical dissimilarities, which were probably due to the normal spatial variability in the material from the waste pile.

On the other hand, self-burning induced important changes in the Technosol from the coal waste pile. As a consequence of the extreme temperature, the normal pedological evolution was interrupted and the humified organic matter was destroyed, along with most of the organic fraction present in coal bearing rock fragments. In this part of the waste pile, significant geochemical and mineralogical transformations took place, and, as a result of the combined influence of self-burning and rainwater infiltration, three new layers (corresponding to C1, C2, and C3 horizons) were generated, with specific hydro-pedological behavior.

Therefore, the waste pile affected by self-burning developed an environment in which pollutants were more likely leached (especially in the C3 horizon) and transported to greater depths, as acidic water ($\text{pH} \approx 4$) percolates the unsaturated zone and, eventually, reaches the water table aquifer. This environment is characterized by higher infiltration (because rainfall interception by vegetation does not take place), by the absence of humified organic matter, higher K_i (in C1 and C3 horizons), the presence of minerals that are more susceptible to the leaching of some PTEs, and a greater abundance and variety of PAHs.

In both Technosols, unlike water-rock interaction in aquifers, the water-waste interaction takes place with unsaturated flow, as well as short residence times and flow paths, and, therefore, only the readily soluble components are leached.

The most relevant mineralogical transformations induced by self-burning are those concerning clay minerals (Table 5). In the Technosol with normal pedological evolution, Illite, Kaolinite, Pyrophyllite, and Chlorite are the dominant clay minerals, while, in the Technosol affected by self-burning, Illite and Smectite are dominant, especially in the C2 and C3 horizons, where higher temperatures were reached. That is, self-burning seems to favor the development of a clay fraction dominated by minerals with higher ion exchange capacity and higher specific surface, such as Smectite and Halloysite, but these minerals have very low structural order, being stable just within a narrow chemical and thermal interval; therefore, they are initially favored and quickly affected by the leaching process. Additionally, self-burning induced the formation of sulphates (Jarosites, accompanied by its Al isomorph Alunites), as well as hematite (Table 4), which are also minerals of lower structural order. Therefore, the mineralogy identified in the soil affected by self-burning is, in general terms, more susceptible to leaching. However, the influence of self-burning on the susceptibility to leaching is more evident in specific PTEs, namely, Zn, Mn, and, particularly, Al, which is more available for leaching in C2 and C3 horizons due to the destruction of Kaolinite and Pyrophyllite and the subsequent formation of Illite and Smectite.

Another important issue is that the relative abundance of the studied PTEs and Fe in the geochemical composition of the coal waste does not match their relative abundance in the aqueous leachates, suggesting particular mobilization abilities under the conditions of the leaching tests. In fact, Fe and Al are the two most abundant major elements in all the coal waste samples. Yet, in the leachates, the concentration of these elements falls into the same order of magnitude of the remaining PTEs (Table 3 and Figure 6).

As for the PTEs that are minor elements (Pb, Zn, Cr, Cu, Ni, Cd, As, and Mn), the results from Table 3 and Figure 3 show that the overall relative abundance observed in the geochemistry of the studied Technosols was similar (Cr, As, and Pb being the most abundant PTEs) but differs from the abundance observed in the leachates chemical composition (in which Zn and Mn are the most abundant PTEs). In some cases, a PTE that is relatively abundant in the soil samples, such as Pb or Cr, may be below the detection limit in the leachates.

Most of the published studies on water quality of leachates from coal mine waste piles focus on their inorganic composition, including salinity, major ions, and PTE occurrence, and the literature regarding their organic composition is scarce. Coal is a complex, organic sedimentary rock, which contains many compounds that are known to be, or have the potential to be, hazardous to humans, namely, PAHs, heterocyclic compounds, phenolics, biphenyls, and aromatic amines [47].

PAHs hydrophobicity increases with the number of aromatic rings, making them easily adsorbed onto soil organic matter and thus less available for biological uptake. Acid waters have more potential to leach PAHs than normal rainwater, due to their ability to break bonds of coal macromolecules. Rainwater is acidified when it infiltrates and percolates through the coal waste pile. This effect is very important since percolating acid water not only dissolves more PAHs but can also break bonds in high molecular weight PAHs to form low molecular weight PAHs, increasing their mobility and bioavailability [48].

The analytical results also demonstrated the clear influence of self-burning on the concentration, distribution, and leaching of PAHs in the soil profile. While higher molecular weight PAHs (Phe, BaA, and Chr) are dominant in the leachates from the Technosol, with normal pedogenesis and from the upper layer of the Technosol affected by self-burning (C1 horizon), lower molecular weight PAHs (Nap, Acy, Ace, and Flu, along with Phe) appear and become an important fraction of the hydrocarbons content in leachates from the deeper and more intensely burnt layers (C2 and C3 horizons). The leachate from the C3 horizon presents the greatest variety and highest concentration of PAHs, as a result of the higher self-burning temperature, as well as the leaching effect of the percolating water in the overlying horizons.

The distribution modes of PAHs in the soil samples suggest that the precipitation can cause downward movement of PAHs, with higher mobility of light-PAHs, as well as a higher production related to the self-burning temperatures. Some of the identified organic compounds have a health risk potential, but they are unlikely to be acutely toxic at the observed concentrations. However, water and soil pollution around the coal waste pile could lead to chronic environmental and human health effects, the extent of which is currently poorly unknown.

Previous studies have shown that the leaching of PTEs and PAHs in coal mine wastes is a complex process, which may be driven by numerous factors, e.g., [10,49,50]. The study results from the São Pedro da Cova coal waste pile were obtained by means of a hydrogeological approach, focusing on the influence of several factors that characterize the coal waste pile environment (geochemistry, mineralogy, and pedological evolution vs. occurrence of self-burning and porous medium permeability) and are in agreement with this framework.

5. Concluding Remarks

Coal mining usually generates waste piles containing inorganic and organic pollutants, including Potentially Toxic Elements (such as Al, Mn, As, Cd, Ni, Cu, Cr, Zn, Fe, and Pb) and Polycyclic Aromatic Hydrocarbons. Through leaching, these pollutants may disperse in the environment (especially in soils and water bodies) and disturb the normal functioning of ecosystems and may also cause severe damages to the health of living organisms, including humans.

The leaching of PTEs and PAHs in coal waste piles is a complex process controlled by a variety of factors, such as the granulometry and weathering of the waste material, the geochemical and mineralogical composition, climatic conditions, pedological evolution, porous medium permeability, and the occurrence of self-burning. Therefore, the study of leaching of PTEs and PAHs in coal waste pile environments should encompass the hydrogeological conditions that determine the water-waste interaction in this type of unsaturated circulation medium. Self-burning may cause severe changes in the hydrogeological setting, originating great contrasts in the leaching susceptibility of PTEs and PAHs in different zones of a given coal mine waste pile.

A hydropedological assessment of the changes induced by self-burning was carried out in two contiguous Technosols found in a coal waste pile from the mine of São Pedro da Cova, located in de Douro Coalfield, North Portugal: one was located in the waste pile with normal pedological evolution and the other was located in the waste pile affected by self-burning. The study aimed at identifying contrasting conditions in several factors controlling the leaching of PTEs and PAHs: pedological evolution (development of soil horizons), geochemical and mineralogical composition, and unsaturated hydraulic conductivity. Subsequently, the leaching of these pollutants was assessed by means of the USGS Field Leach Test.

In the Technosol with normal pedological evolution, the vegetation cover generated an O horizon (superficial layer of weakly decomposed litter) and two mineral horizons: the A horizon (with incipient accumulation of humified organic matter) and a the C horizon. On the other hand, self-burning interrupted the pedological evolution and obliterated the previous horizon differentiation, especially the accumulation of humified organic matter. After the beginning of self-burning, the soil profile developed three layers (C1, C2, and C3 horizons), mainly driven by the near surface temperature gradient.

As for the geochemistry of the coal waste, the composition of A, C, and C1 horizons was similar. Regarding C2 and C3 horizons, some contrasts were identified concerning both major and trace elements (including PTEs). The geochemical composition of the 3 horizons affected by self-burning also revealed a temperature-dependent distribution of elements, such as an increase with depth of Al and As.

Again, important contrasts induced by self-burning were found in mineralogy. The observed mineralogical changes point to a greater susceptibility to leaching, since the Technosol affected by self-burning became characterized by clay minerals with higher ion exchange capacity and higher specific surface (Illite and Smectite) and by sulphates of lower structural order (Jarosites and Alunites).

The measured unsaturated hydraulic conductivity in the Technosol with normal pedogenesis was around 10^{-3} cm/s throughout the entire soil profile. On the contrary, the influence of self-burning resulted in diverse K_i values in the intermediate and lower part of the soil profile, where temperature was higher: 10^{-3} cm/s in the C1 horizon (upper layer), 10^{-4} cm/s in the C2 horizon (middle layer), and 10^{-2} cm/s in the C3 horizon (lower layer). The lower K_i in the C2 horizon corresponds to a finer soil texture.

Considerable changes were also observed as a consequence of self-burning in the leaching of PTEs and PAHs. In all soil horizons, the concentration of major ions in the leachates is low and the dominant cations are Na, Ca, and K, while the dominant anion is SO_4 . As for PTEs, their concentration in the A horizon and C horizon is, in broad terms, similar. Yet, in the Technosol affected by self-burning, the hydrogeochemistry of PTEs is quite different from the Technosol with normal pedogenesis, but also varies among the horizons in the soil profile. In this case, the leaching of Al, Mn, and Zn increased with depth and seemed to be temperature-dependent. The study results also highlight that the relative abundance of the studied PTEs in the coal waste did not correspond to their relative abundance in the leachates. For example, Cr, As, and Pb are the most abundant PTEs in the coal waste, while in the leachates, Zn and Mn prevail.

The influence of self-burning on the type and concentration of PAHs in leachates from both studied Technosols was crucial. In fact, the leachates from the Technosol affected by self-burning showed greater concentration and variety of PAHs in the lower part of the soil profile (C3 horizon) due to the higher self-burning temperature, as well as the effect of leaching from the overlying material (C1 and C2 horizons). The analytical results also revealed that, in the C3 horizon, higher molecular weight PAHs were dominant.

The research outcomes confirmed the occurrence of important changes in the hydropedological features of a Technosol from a coal mine waste pile affected by self-burning. The hydropedological approach adopted in this study was able to encompass a broad set of features comprising pedological evolution, geochemistry, mineralogy, soil permeability,

and, finally, susceptibility of pollutant leaching as a result of the circulation of meteoric water in a coal waste pile.

Additionally, given the high wildfire risk in Mediterranean areas, it is clear that the possibility of ignition of other coal waste piles by wildfires is unquestionable, especially in a context of climate change. Therefore, the inventory, mapping, and comprehensive characterization of coal mining waste piles, principally those integrated in forested areas, provide essential information for wildfire risk assessment and management, more precisely: the evaluation of the waste piles' vulnerability to ignite and burn; the promotion of the best management practices in these forested areas; the prevention and minimization of the risk of ignition and burning of these materials.

The results are relevant for the knowledge of the environmental impact of coal mine waste piles and allow the determination of the type and concentration of chemical components (e.g., PTEs, PAHs) that may pollute soil and water. This information is crucial to define rehabilitation, protection, and management actions by decision makers.

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