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Assessment of Soil Physicochemical Characteristics and As, Cu, Pb and Zn Contamination in Non-Active Mines at the Portuguese Sector of the Iberian Pyrite Belt

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Abstract: This study aimed to evaluate soil physicochemical characteristics (pH, electrical conductivity, organic matter, total N, and extractable P and K), and potentially toxic elements (As, Cu, Pb, and Zn), in non-active mines located in the Portuguese sector of the Iberian Pyrite Belt (IPB). A total of 70 sampling sites were surveyed at Aljustrel and Lousal, in areas already rehabilitated, and at São Domingos, where rehabilitation was only beginning. The soils at São Domingos were very heterogeneous, with extreme values for some properties (e.g., minimum soil pH 2.0 and maximum As concentration, 4382.8 mg kg^{-1} dry weight basis (DW)). Aljustrel was the site that presented soils with a higher total As, Cu, Pb, and Zn concentration (median values: 441.5, 545.9, 1396.8, and 316.5 mg kg^{-1} DW, respectively), above the soil quality guidelines values proposed by the Portuguese Environmental Agency (18, 230, 120, and 340 mg kg^{-1} DW, respectively). A principal component analysis identified the most relevant soil properties to explain the data variance, which were the soil pH and Pb total concentration, followed by Cu and Zn total concentrations, allowing a separation of Aljustrel from the other mines. Pearson correlation coefficients revealed very strong associations between Pb and As, markedly found at higher concentrations in São Domingos, whereas Aljustrel had an elevated concentration of As and Pb, but also of Cu and Zn. It is evident the risk that persists in the Aljustrel mine area, which was not alleviated by the "dig, dump, and cover" techniques that were implemented to rehabilitate the area.

Keywords: mining activities; soil pollution; potentially toxic elements; soil quality guidelines values; principal component analysis

1. Introduction

In the recently launched European Union (EU) Soil Strategy for 2030 [1], medium- and long-term objectives are assumed (to 2030 and 2050, respectively), aiming to achieve good soil health. In the view of this strategy, protection, sustainable use, and restoration of soil will became the norm by 2050 [1], which will require all Member States to take decisive action during this decade. This type of strategic document was expected for a long time, and it is essential to leverage specific actions in some Member States where the legal void concerning soil contamination and remediation persists. In fact, the lack of dedicated soil policies at the EU level has allowed some countries to delay the publication of legislation with contaminant thresholds and procedures for the rehabilitation of contaminated sites [1]. That is the case of Portugal, which has prepared a draft proposal in 2015, with the support of the Portuguese Environmental Agency (APA), but that was not officially published to the present date. Therefore, APA produced a Technical Guide with Reference Values for the Soil [2], based on the Ontario Soil Quality Guidelines, that, despite not having a legally compulsory value, are being used to assist processes of soil quality assessment, remediation, and confirmation of the results achieved with remediation measures.

The EU Soil Strategy for 2030 will undoubtably determine that all Member States independently develop methodologies for assessing the risks of soil contamination, identify contaminated sites, and create conditions to the remediation of sites that pose a risk to human health or the environment [1]. Mining areas are an example of historical or orphan contaminated sites, where the polluter(s) can no longer be held responsible for the costs of remediation. To tackle this problem, and to deal with multiple situations of pos-closure abandonment of mine sites, in some cases intensively exploited for hundreds of years, the Portuguese government attributed to EXMIN, presently EDM (Empresa de Desenvolvimento Mineiro, S.A.), the responsibility for the rehabilitation of these historically degraded mining areas [3]. Since 2001, EDM has developed efforts to assess soil contamination at these mine areas, prioritized interventions, established pre-remediation plans, took actions to remediate some of the sites, and implemented monitoring plans for the post-remediation [4]. So far, EDM has identified 199 abandoned and contaminated areas and is now working on their rehabilitation [4]. Nevertheless, interventions mainly consisted of the application of constructive techniques, which, although essential to manage the risk at the contaminated sites, may not be sufficient to restore the soil's healthy status. Mourinha et al. [5] have recently published a review about the trace elements' pollution in the Portuguese sector of the Iberian Pyrite Belt (IPB) and reported some of the remediation options adopted for these IPB mines. It is important to evaluate if, in the rehabilitated areas, the soil that was left behind may still need to have its characteristics improved to be considered a healthy soil, i.e., present good chemical, biological, and physical conditions, and, therefore, be able to provide a minimum number of ecosystem services [1,6].

The mine exploitation in the Portuguese sector of the IPB was very important in pre-Roman and Roman times, and again, with intensive mine works, during part of the 19th and 20th centuries, especially in Neves-Corvo, São Domingos, Aljustrel, Lousal, and Caveira (Alentejo region) [7–9]. Nowadays, the exploitation in Neves-Corvo (Cu, Zn, Pb, and Ag concentrates, Lundin Mining Company) and Aljustrel (Cu concentrates, Almina Company, which reactivated this mine) is on-going, but they are following the current best available practices to avoid environmental impacts [10]. This means that they are going to be made accountable for the soil remediation after their activity has ceased. The same was not true for some representative polymetallic sulfide mines in the Portuguese sector of the IPB, which have been abandoned for decades, i.e., São Domingos, Aljustrel, Lousal, and Caveira, and were a source of continuous environmental impact to soils, water, sediments, and biota [11–15]. The impacts in these mine areas have been extensively assessed and documented by different authors ([5,11–26] refer to some in the Portuguese sector of the IPB).

Lousal and Ajustrel mines have their rehabilitation projects finished by EDM, and São Domingos is still ongoing [5]. However, in the surroundings of these mines, there are extensive areas exhibiting degraded and potentially contaminated soils, which are important to rehabilitate, preferably improving soil health and their ecosystem functions [1,6]. It is important to consider their constraints, namely the properties that hinder soil fertility and the concentrations of the potentially toxic elements (PTEs) in those soils [27]. As a matter of fact, the great majority of the studies which assessed the abandoned mines in the Portuguese sector of the IPB, were mainly focused on their geological and geochemical aspects, and in the environmental impacts regarding PTEs concentrations [13,14,16,19–24] and less focused in the soils characteristics, which condition their recovery, namely using phytotechnologies. Nevertheless, this type of assessment has been done in some studies, with a full characterization of the soils to be used in lab-scale or pot experiments [28–34], but only with soil from a specific site, or considering composite samples.

This study aimed to evaluate soil physicochemical characteristics (pH, electrical conductivity (EC), organic matter (OM) content, and macronutrients content, nitrogen (N), phosphorous (P), and potassium (K)), and PTEs contamination associated with the mining activities in the Portuguese sector of the IPB (As, Cu, Pb, and Zn, which are those commonly found in excessive concentrations). The study will assess the most representative non-active mines (Lousal and São Domingos), or areas outside the concession of active mines (Aljustrel). The total As, Cu, Pb, and Zn concentrations will be further compared with the soil quality guidelines values proposed by APA [2], that, in the absence of a specific national regulatory framework, may be used to assess the likelihood of risk of soil contamination, and the need for further actions to confine and manage the risk of the contaminated site, or to take active remediation measures [1]. Using multivariate exploratory techniques, the data will be statistically analyzed to evidence the soil properties that are more relevant to explain the data variance, and to potentially discriminate between mining areas and their "signature" properties.

This field survey was performed in the scope of the project Life No_Waste (Management of biomass ash and organic waste in the recovery of degraded soils: a pilot project set in Portugal—LIFE14 ENV/PT/000369), surveying a total of 70 sites in three mining areas: Aljustrel, Lousal, and São Domingos. To our best knowledge, this is the most complete soil survey in mines of the Portuguese sector of the IPB, gathering not only contaminants concentration, but also soil properties important to achieve soil health, namely, soil pH, organic matter, and nutrients content.

2. Materials and Methods

2.1. Site Description

The IPB, located in the SW of the Iberian Peninsula, forms an arch extending from Grândola (Portugal) to Seville (Spain), which is approximately 240 km long and 35 km wide [7] (Figure 1).

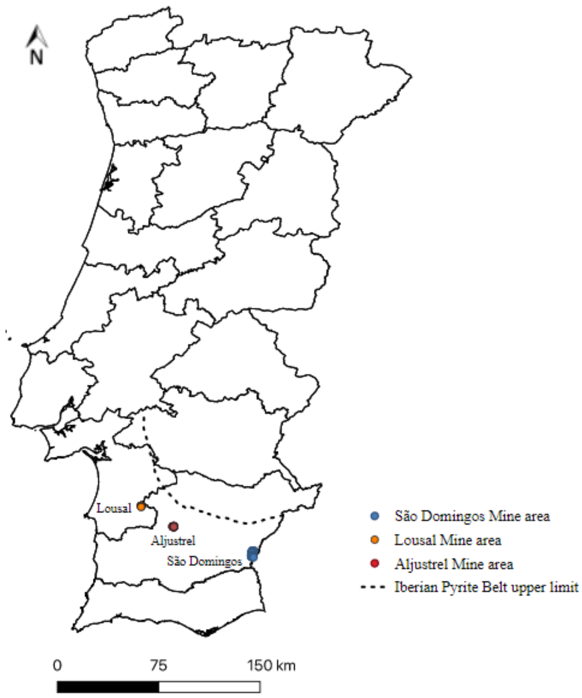

Figure 1. Map evidencing the upper limit of the Iberian Pyrite Belt, with the most important mining districts that were responsible for extensive environmental impacts: Lousal (and Caveira), Aljustrel, and São Domingos.

It was formed 350 million years ago, connected to active hydrothermal volcanism that led to the formation of a Volcano–Sedimentary Complex [7], and represents one of the most important volcanogenic massive sulfide districts in the world [7–9,35]. The massive sulfide ore is composed mainly by pyrite (FeS_2), approximately 95%, with variable amounts of chalcopyrite ($CuFeS_2$), sphalerite (ZnS), galena (PbS), and arsenopyrite (FeAsS), while a Cu-rich stock zone holds most of the remaining mineralization [35].

The Aljustrel mine is one of the greatest sulfide deposits of the IPB, containing six mineral masses rich in Cu and Zn (Feitais, Estação, Algares, Moinho, S. João, and Gavião) [6,20,21]. The major environmental impacts at this mine were caused by the large volume of tailings dispersed in the area, which affected, for a long period, the soils and the hydrological system in the surrounding area [15,36–40]. The Aljustrel mine's historically contaminated area was rehabilitated by EDM, as reported by Mourinha et al. [5] (Figure 2).

Figure 2. Google Earth image (24 May 2022) evidencing the sampling sites at the Aljustrel mine area, covering an area already rehabilitated by EDM [5]. A1 and A4: sites near the confined waste materials, Algares area; A2 and A3: sites near the perimetral channels that collect drainage waters; A5–A8: area near recent tailing deposits; A9–A10: soils with scarce vegetation, but eventually representative of natural soils; and A11–A14: soils near old tailing deposits.

The Lousal mine is located in the NW part of the Portuguese sector of the IPB, in a lineament of the volcano–sedimentary complex which also includes the old Caveira pyrite mine [22]. The deposit was explored, mainly for pyrite, until 1988, when it was closed due to the low grades of Cu and Zn in the mined ores [41]. The rehabilitation of the mine area begun less than 10 years after the closure of the mine, by the Fréderic Velge Foudation and the Grândola Municipality, which made efforts to preserve the mine structures to be used for science and touristic purposes [5]. Later, the EDM also rehabilitated a part of the mine area, mainly to treat the acid waters that formed in the milled ore deposited and in the open pit, avoiding their impact in the surrounding hydrological system [5,22–24] (Figure 3).

Figure 3. Google Earth image (24 May 2022) evidencing the sampling sites at the Lousal mine area. L1–L5: area potentially affected by acid mine drainage from old tailing deposits; L6–L10; area potentially affected from the pyrite road and railway transport network; and L11–L12: sampling points near the exit of an old mine gallery, with tailing deposits.

São Domingos is, perhaps, the most representative mine district in the Portuguese sector of the IPB, with a big pit (122 m deep), left open after the extraction works, which is now filled with acid waters [18]. São Domingos was extensively exploited from 1857 to 1966, causing considerable impacts in soils, water, and sediments, which have been assessed by different authors [12,13,18,19,25,26,42,43]. The mined raw material was crushed in a mill, located near the open cast pit, and transported to the sulfur factory at Achada do Gamo (~3 km south), where it was smelted to obtain high-level grades of Cu ore and sulfur products [16]. These works generated approximately 750,000 tons of highly heterogeneous wastes, including Roman and modern slags, smelting ashes, and pyrite-rich waste dumps [18,19], which had a considerably negative impact observed along the São Domingos stream valley and in the sulfur factory at Achada do Gamo, the major area of the waste deposits [11] (Figure 4).

2.2. Soil Sampling

Soils from the Aljustrel, Lousal, and São Domingos mines' affected areas were surveyed in July 2016, choosing areas with greater and lesser impact on the mining activity, in a total of 70 sampling sites (14 at Aljustrel, 12 at Lousal, and 44 at São Domingos). The selection of the sampling sites had the collaboration of EDM and took into consideration the fact that Aljustrel and Lousal were already rehabilitated. Therefore, the sites that were chosen covered areas which were still potentially affected by AMD, or may need further intervention, to complement the rehabilitation already performed [5].

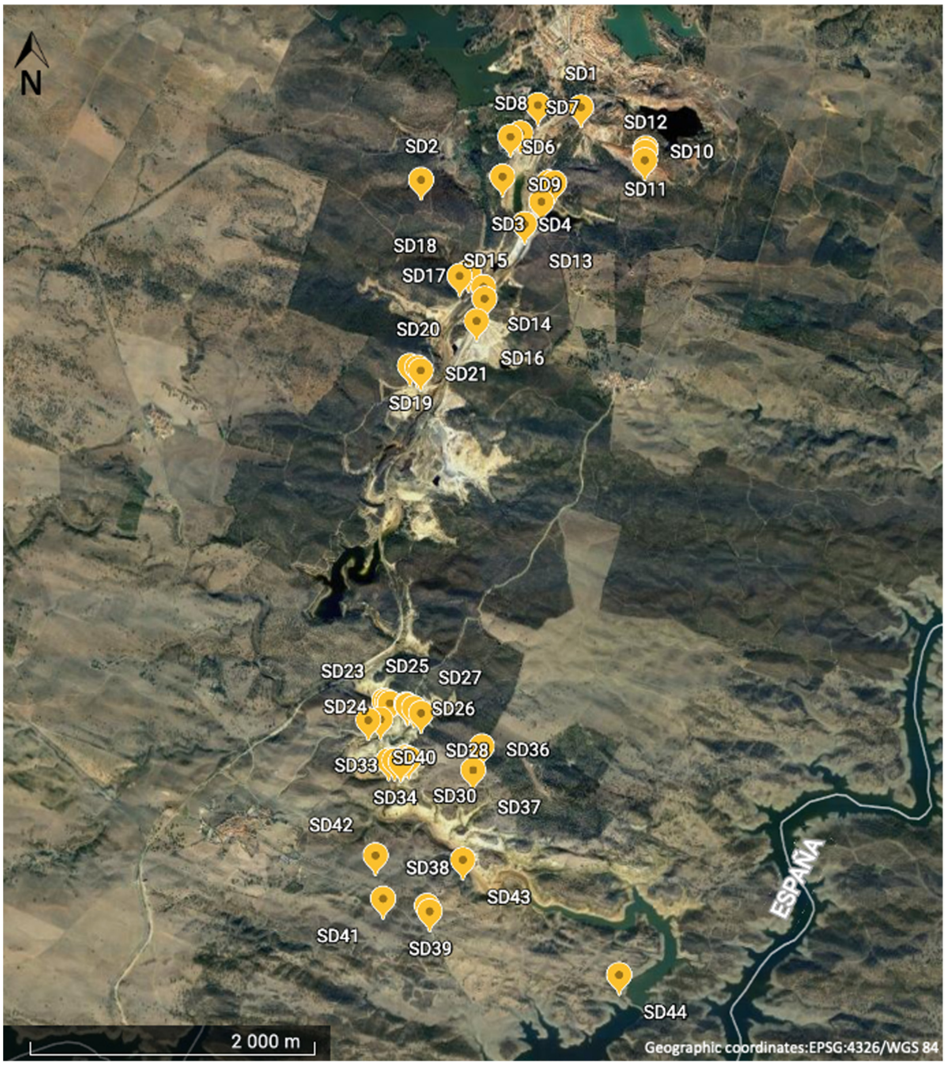

Figure 4. Google Earth image (24 May 2022) evidencing the sampling sites at the São Domingos mine area, before the beginning of the EDM rehabilitation project. SD1–SD22: area affected by the original mining works and by the acid mine drainage with origin in the different wastes which were deposited along the São Domingos stream valley; SD23–SD30: soils potentially affected by acid mine drainage, located downstream from Achada do Gama sulfur factory; and SD31–SD44: soils with diverse characteristics, scarce vegetation, but eventually representative of soils less affected by the mine works.

2.3. Soil Physicochemical Characterization

Soil samples were air-dried and sieved using a 2 mm non-metallic sieve, to collect the <2 mm fraction to further analysis. Soils' particle-size distribution were determined using the pipet method [44] and their texture class classification was performed according to the United States Department of Agriculture (USDA) classification [45]. Physicochemical characterization of the samples was performed with parameters typically used to ascertain general soil fertility characteristics: pH (H_2O), electrical conductivity (EC), total nitrogen (N), and the extractable fraction of phosphorous (P) and potassium (P). Analyses were performed according to methodologies described by Alvarenga et al. [31]: soil pH (H_2O), was determined in a soil to deionized water suspension of 1:2.5 (w/v); EC was determined in a soil to deionized water suspension of 1:5 (w/v); total N was analyzed by the Kjeldahl method ($N_{Kjeldahl}$); total oxidizable organic carbon was determined according to the Walkley and Black wet-oxidation method [46], and converted to organic matter content (OM) by multiplying by a factor of 1.72; extractable P and K were determined using the Egner–Riehm extraction procedure, with an ammonium lactate (0.1 M) in acetic acid (0.4 M) solution, with a pH in the range 3.65–3.75, sufficient to be used in acid soils [47].

2.4. Pseudo-Total As, Cu, Pb and Z Concentrations

Pseudo-total metal concentrations (As, Cu, Pb, and Zn) were determined by inductively coupled plasma-mass spectrometry (ICP-MS), using a Thermo X Series spectrophotometer. Samples were digested with aqua regia, according to ISO 11,466 [48]. Three independent replicates were performed for each sample and blank, and control standards were measured in parallel. ICP-MS element analysis was performed following rigorous quality control proceedings, and the detection limits were: 8 μg kg^{-1} for As, and 1 μg kg^{-1} for Cu, Pb, and Zn.

2.5. Statistical Treatment of the Data

The *Spearman* rank correlation coefficients (R) were calculated to evaluate the associations between the soil physicochemical properties with their pseudo-total element concentrations (n = 65). Three levels of significance were used: $p < 0.001$, $p < 0.01$, and $p < 0.05$.

A Principal Component Analysis (PCA) was performed to identify the most meaningful parameters which describe the whole data set. This multivariate exploratory technique allows the association between variables, reducing the dimension of the data matrix, transforming the original variables into the same number of uncorrelated variables, called principal components (PCs). The eigenvalues of the PCs are a measure of their variance, the participation of the original variables in the PCs is given by the loadings, and the individual transformed observations are called scores [33].

All statistical analyses were performed with the STATISTICA 7.0 (Software™ Inc., Tulsa, OK, USA, 2004).

3. Results and Discussion

3.1. Soil Physicochemical Characteristics

The soils presented a high variability in their texture classification, given that they cover different areas, but they were mainly characterized by a coarse granulometry (e.g., sand, loamy sand, sandy loam, 64% of the samples), with a lower number of samples with medium to fine granulometry (e.g., sandy clay loam, loam, clay loam, and clay, USDA texture classes) [45], with a median fraction of clay, silt, and sand, in the different sampling areas, of 15, 27, and 55%, respectively.

Considering the soils' physicochemical properties that may hinder their fertility (Figure 5), it is possible to have an idea about their range of variation. In the São Domingos mine, the area covered was larger and, as the rehabilitation was in its initial phase, the sampled soils evidenced extreme characteristics, a higher number of outliers, and, for some properties, higher or lower extreme values than in the other mines. That was the case of the soil pH (Figure 5a), with soils' pH values < 2 in some locations of São Domingos, despite its median value being higher that that found for Lousal and Aljustrel soils, and with pH < 4 in both mines, considered as very acid soils [49]. However, that higher dispersion of values in the soils sampled at São Domingos were also felt for the soil EC, soil OM content, total N, and extractable P (Figure 5b–e), being a consequence not only of the heterogeneity of the area, but also of the fact that the rehabilitation program was only beginning. The rehabilitation operations that were performed by EDM at Lousal and Aljustrel [5], which have removed and confined the most contaminated soils/wastes, had the benefit of making the whole area more homogeneous, which would facilitate further interventions (e.g., the implementation of phytotechnologies). In addition, some of the soils samples at São Domingos could be considered "natural soils", not submitted to the effect of AMD, which could have influenced this higher dispersion of values.

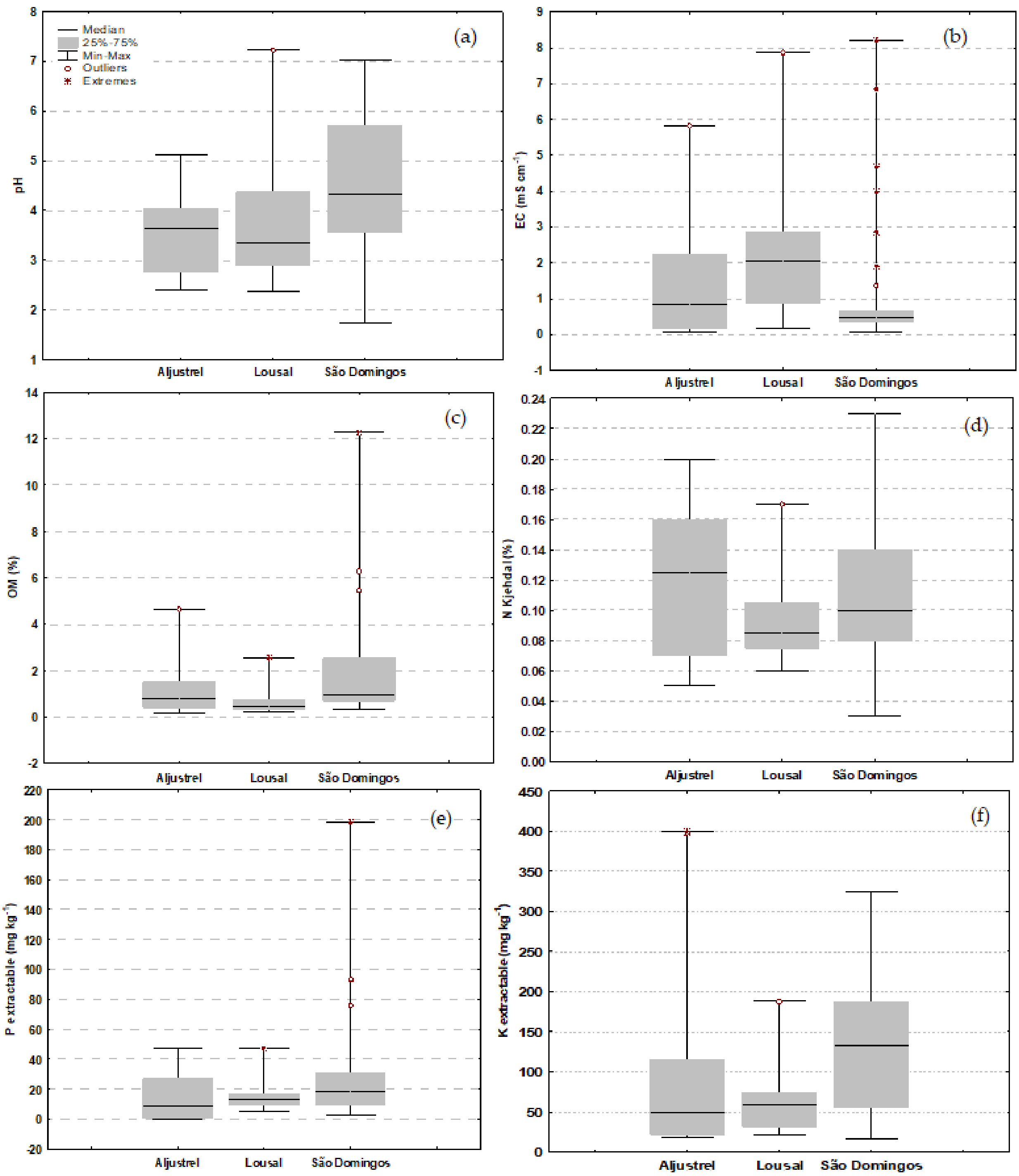

Figure 5. Boxplot representation of the most representative physicochemical properties to evaluate the fertility status of the soils in the different mining areas (sampling campaign July 2016): Aljustrel (n = 14), Lousal (n = 12), São Domingos (n = 44). (**a**) pH (H_2O, 1:5 *v*/*v*); (**b**) Electrical conductivity (EC, mS/cm, 1:5 *v*/*v*); (**c**) Organic matter content (OM, % *w*/*w*); (**d**) Kjeldahl N (%, *w*/*w*); (**e**) extractable P (mg kg^{-1}); and (**f**) extractable K (mg kg^{-1}). The mark across the box represents the median and the bottom, and the top of the box represents the 25–75% interval. All results report to a dry matter basis.

The soils were also characterized by very low OM content, with median values < 1% OM (g/100 g DW) for the three mines (Figure 5c) [49], and low macronutrients content, especially with total N and extractable P (Figure 5d,e). These values of extractable P in soils were considered as very low for this macronutrient in the three mines [49]. For extractable K, the values were different, depending on the mine, with concentrations typical of soils with low extractable K concentrations, at Aljustrel and Lousal, and with higher concentrations at São Domingos (Figure 5f).

Previous studies have alerted to the low quality of soils in some of these sites. Santos et al. [29] evaluated some of these properties in the São Domingos mine area and referred that, in some cases, the soils were developed on mining wastes composed by gossanous materials and host rocks, with very low pH values (4.53), low OM content (1.687%, w/w), as well as residual concentration for some macronutrients, especially N and P plant (0.004% N (w/w) and 2.23 mg kg^{-1} for extractable P, dry weight, DW) [29].

Considering the abovementioned soil characteristics, and if the chemical stabilization of the soils is intended, the main characteristic to be corrected would be the soil pH. The use of lime-based amendments (e.g., calcium carbonate, calcium oxide, calcium hydroxide) [31,50], or waste-derived materials with alkaline pH (e.g., biomass ashes), would, therefore, be crucial to increase the soils' pH and, potentially, reduce the PTEs extractability [5,51]. Taking this into consideration, the agronomical recommendations to increase the soil pH(H_2O) to 6.5, for soils with low OM content (between 0.5–1%), and soil pH(H_2O) < 4.5, the lime application ratio should be 4–5 t $CaCO_3$ ha^{-1}, depending on the soil texture. That target pH can be considered ideal to have lower PTEs solubility and mobility and, very important, to allow seed germination and plant survival [49,52].

However, the lime-based amendments are, usually, poor in OM and nutrients [51]. Therefore, for a successful natural attenuation, or eventually, if a phytomanagement strategy is intended, organic amendments, rich in OM, N, and P, should also be considered [27,31,32,53,54].

3.2. Potentially Toxic Elements Concentrations

The upper layers of soil affected by mining activities can contain elevated concentrations of PTEs, which depend on the ore that was mined. In the case of the mines located at the Portuguese sector of the IPB, the PTEs that are often found in elevated concentrations are As, Cu, Pb, and Zn, and these were the ones which were assessed in this study.

As for the pseudo-total concentrations for As (Figure 6a), and Pb (Figure 6c) (aqua-regia extractable), their values surpass the recommended limit values for soils intended for industrial use, considering the APA's Technical Guide [2]. Median concentration for As in the three mines were, in fact, several times higher than that limit value (18 mg As kg^{-1} DM), with a higher dispersion of values for the São Domingos mine, higher upper limit concentrations, and a higher median (Figure 6a). High concentration for total As in the São Domingos mine were also reported by Freitas et al. [18], 1291.0 mg kg^{-1} DW; Santos et al. [29], 2600 mg kg^{-1}, and Alvarenga et al. [26], 1956 mg kg^{-1}. However, some of these authors have alerted to the fact that, despite the high total concentrations for As, the extractable fractions (e.g., with $CaCl_2$ 0.01 M, which can be considered surrogate measures of their bioavailable fraction), are, usually, very low, <1% [26].

As for Pb, the limit value proposed in the Technical Guide of APA [2] (120 mg Pb kg^{-1} DM) was surpassed by more samples in Aljustrel, followed by São Domingos, than in the Lousal mine. In fact, the samples at Lousal presented low median Pb content, lower than the proposed limit value. The samples from Aljustrel can be considered the most problematic regarding Pb contamination (Figure 6c). Other authors have also reported high concentration for total Pb in Aljustrel, such as Alvarenga et al. [28], 3500 for Pb mg kg^{-1}, and Candeias et al. [20,21], which reported values as high as 20,000 mg Pb kg^{-1} of soil. Extremely high Pb concentrations were also reported by other authors in the São Domingos mine area, such as Freitas et al. [18] 12,217.5 mg Pb kg^{-1} DW, Santos et al. [29], 7300 mg kg^{-1}, and Alvarenga et al. [25,26], up to 10,795 mg kg^{-1}.

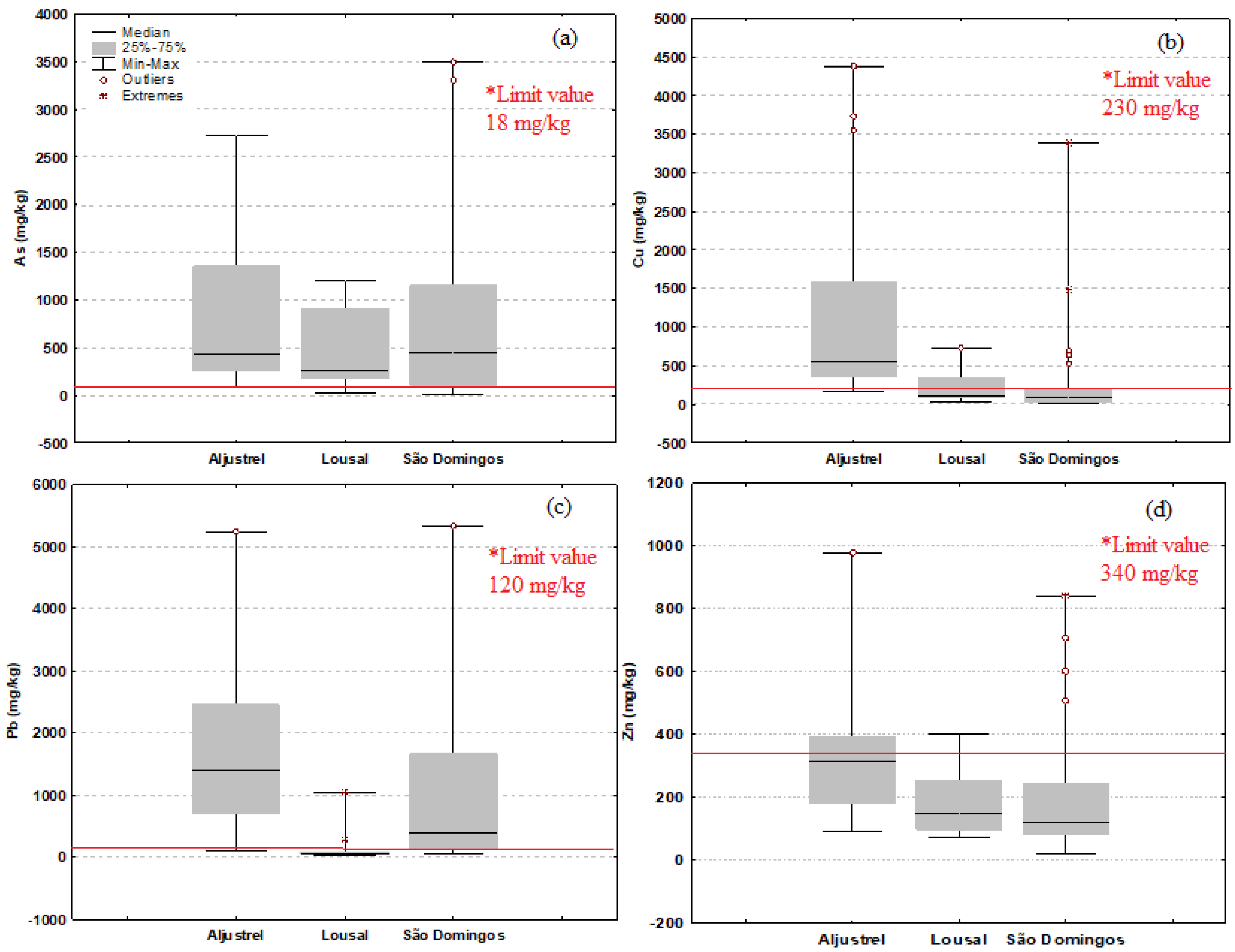

Figure 6. Boxplot representation of the pseudo-total concentrations (Aqua Regia extraction) of the most representative potentially toxic elements which affect pyrite mines in the Portuguese sector of the IPB (sampling campaign July 2016): Aljustrel (n = 14), Lousal (n = 12), São Domingos (n = 39). (**a**) As (mg/kg); (**b**) Cu (mg/kg); (**c**) Pb (mg/kg); and (**d**) Zn (mg/kg), all concentrations in a dry weight (DW) basis. The mark across the box represents the median and the bottom, and the top of the box represents the 25–75% interval. All results report to a dry matter basis. (*) Recommended limit values for the remediation of soil intended for industrial use from the APA Technical Guide are presented in red and also as a horizontal line [2].

Copper is also more problematic in the Aljustrel's soil samples (Figure 6b), with a median concentration (546 mg Cu kg^{-1} DW) above the threshold value recommended (230 mg Cu kg^{-1} DW), more than doubling its value, and with samples that can go as high as 4383 mg Cu kg^{-1} DW (Figure 6b). These values were in accordance with others reported in previous studies by Candeias et al. [20,21], that reported concentrations for Cu up to 5414 mg kg^{-1}, or by Alvarenga et al. [28], reporting 1800 mg Cu kg^{-1} of soil. The same was not true for the samples collected at Lousal and São Domingos, which were characterized by, generally, lower Cu pseudo-total concentrations (Figure 6b), below the threshold of the recommended value in most of the samples. That general high concentration for Cu can, therefore, be considered a distinctive characteristic of the soils at Aljustrel. This is a fact that is important to be taken into consideration, since, in Aljustrel, most of the samples were collected in soils which were already submitted to a rehabilitation project [5], which means that the soils that were considered rehabilitated still have a high Cu total concentration, which means that the mobility/bioavailability should be thoroughly monitored and controlled.

That same pattern was followed for Zn (Figure 6d): higher concentration in Aljustrel than in Lousal and São Domingos. However, in this case, 75% of the samples at Lousal and São Domingos had pseudo-total Zn concentration below the recommended limit value (340 mg Zn kg^{-1} DW) [2], and even the median value for Zn in Aljustrel (316 mg Zn kg^{-1} DW) was below that threshold limit value. Therefore, it is fair to say that, even though some samples that were found had an elevated concentration of Zn (979 and 840 mg Zn kg^{-1} DW as upper limits at Aljustrel and São Domingos, respectively), Zn was not the most problematic PTE found in these mine areas.

The concentration of PTEs at these abandoned mines in the IPB have been thoroughly studied by different authors, and Mourinha et al. [5] have recently published a review with indicative ranges for the concentrations of As, Cu, Pb, and Zn found in different mines in the IPB, both in Portugal and in Spain.

3.3. Evaluation of the Association between the Variables—Pearson Correlations

To have an idea about the associations between the soil physicochemical characteristics which were analyzed and the As, Cu, Pb, and Zn total concentration, Pearson correlation coefficients (r) were calculated (Table 1). Three levels of significance were used to classify the correlation as: moderate ($p < 0.05$), high ($p < 0.01$), or very high ($p < 0.001$), evidencing the strength of the associations.

Table 1. Pearson's correlation coefficients between soil physicochemical properties and potentially toxic elements pseudo-total concentrations (n = 65). Marked correlations are significant at (*) $p < 0.05$; (**) $p < 0.01$; and (***) $p < 0.001$, evidencing the strength of the associations: moderate, high, and very high, respectively.

	pH	EC	OM	$N_{Kjeldalh}$	$P_{extractable}$	$K_{extractable}$	As_{total}	Cu_{total}	Pb_{total}
EC	−0.54 ***	-	-	-	-	-	-	-	-
OM	0.33 **	−0.15	-	-	-	-	-	-	-
$N_{Kjeldalh}$	−0.03	−0.05	−0.05	-	-	-	-	-	-
$P_{extractable}$	0.31 *	−0.03	0.68 ***	0.02	-	-	-	-	-
$K_{extractable}$	0.28 *	−0.22	0.51 ***	0.06	0.09	-	-	-	-
As_{total}	−0.36 **	0.19	−0.05	0.39 **	0.04	−0.20	-	-	-
Cu_{total}	0.06	−0.07	0.11	−0.06	−0.08	0.27 *	−0.04	-	-
Pb_{total}	−0.23	0.20	0.12	−0.04	0.13	−0.16	0.42 ***	0.30 *	-
Zn_{total}	0.24	−0.03	−0.01	−0.04	0.05	−0.13	−0.12	0.43 ***	0.15

The organic matter content was highly positively correlated with the extractable P and K concentrations ($p < 0.001$), which was not surprising, given the importance of soil OM as an indicator of soil quality and it was used to assess its fertility. Soil OM also had a high positive correlation with soil pH ($p < 0.01$), meaning that less acidic soils, with higher pH values, were also those with the higher OM content.

Another interesting correlation which was found, between general physicochemical properties, was the very high negative correlation found between soil pH and its EC ($p < 0.001$) (Table 1); it is a fact, for a considerable number of metal salts, their solubility increases as the soil pH decreases [55]. This case was not an exception: considering all the results (n = 65), higher soluble salt concentrations (higher EC values) were found in the most acidic soils.

As for the PTEs correlations, very strong associations were found between total Pb and total As, and between total Cu and total Zn ($p < 0.001$), meaning that they happen to appear together as soils' contaminants in these mines. These associations corroborate the results discussed in Section 3.2: As and Pb were markedly found at higher concentrations in São Domingos, which, on the other hand, had soils not so markedly contaminated by Cu and Zn. Regarding Aljustrel, not only As and Pb were found in elevated concentrations, but also Cu and Zn, strengthening these associations regarding PTEs affecting soils in the Portuguese sector of the IPB.

3.4. Principal Component Analysis

PCA was carried out on 10 variables (pH, EC, OM content, $N_{Kjeldahl}$, extractable P, extractable K, and As, Cu, Pb, and Zn pseudo-total concentrations in the soils), with the results obtained for the 65 soil samples collected in the three mines, to identify those which can be considered key parameters to explain data variability.

The original 10 variables could be reduced to four principal components, explaining about 70% of the total variance (Table 2). The first component (PC1) explained 24.6% of the variance of the original variables, and pH was the only variable with a high positive factor loading on PC1 (>0.7), which means that, by itself, pH was mainly responsible for the samples' variability. The second component (PC2) explained 17.6% of the variance, whereas the third component explained 15.6%. Lead, Cu, and Zn pseudo-total concentrations had significant factor loadings on these principal components, Pb with PC2, with a negative correlation coefficient, and Cu and Zn on PC3, both with positive correlations. A fourth component (PC4) was necessary to explain a minor part of the variance (12.0%), and only one soil property correlated significantly with this component, with a negative value, which was soil $N_{Kjeldahl}$ content, the only characteristic related with soil fertility which was ascribed to one PC. Some of the properties were not significantly correlated to the principal components, meaning that they are not responsible for the variability observed in the data set: EC, OM, extractable P and K, and As pseudo-total concentration.

Table 2. Factor loadings of each soil parameter along the first four principal components, PC1, PC2, PC3, and PC4, which resulted from the PCA. Marked correlations, in red, are significant (correlation coefficient > 0.7).

Soil Parameter	PC1	PC2	PC3	PC4
pH	0.790	0.155	0.065	−0.150
EC	−0.573	−0.261	−0.015	0.442
OM	0.697	−0.501	−0.303	0.218
$N_{Kjeldalh}$	−0.127	−0.193	−0.364	−0.781
$P_{extractable}$	0.501	−0.515	−0.373	0.311
$K_{extractable}$	0.620	−0.059	−0.129	−0.188
As_{total}	−0.486	−0.587	−0.292	−0.351
Cu_{total}	0.220	−0.378	0.702	−0.224
Pb_{total}	−0.240	−0.764	0.240	0.088
Zn_{total}	0.182	−0.215	0.734	−0.105
Explained variance (%)	24.6	17.6	15.6	12.0

Figure 7 shows the combined plot of scores and loadings on the first three main principal components: PC1 versus PC2 (Figure 7a), PC1 versus PC3 (Figure 7b), and PC2 versus PC3 (Figure 8). The most important parameters for the definition of each component are shown at the edge of each axis, indicating the direction in which the value of the parameter increases.

Results from the PCA emphasizes the importance of soil pH, and, to a lesser extent, Cu, Pb, and Zn pseudo-total concentration, to explain the variability of the soil properties in these mine areas. These properties were just associated between themselves, and not with the other characterized soil properties, except for pH, since highly acidic soils, subject to AMD, are also those with the highest contamination level. The PCA did not allow a clear clustering of samples from the three mines, which was somehow expectable, given the similarity of these mining areas, all located in the IPB. In fact, it was possible to confirm some of the specificities of each mine site.

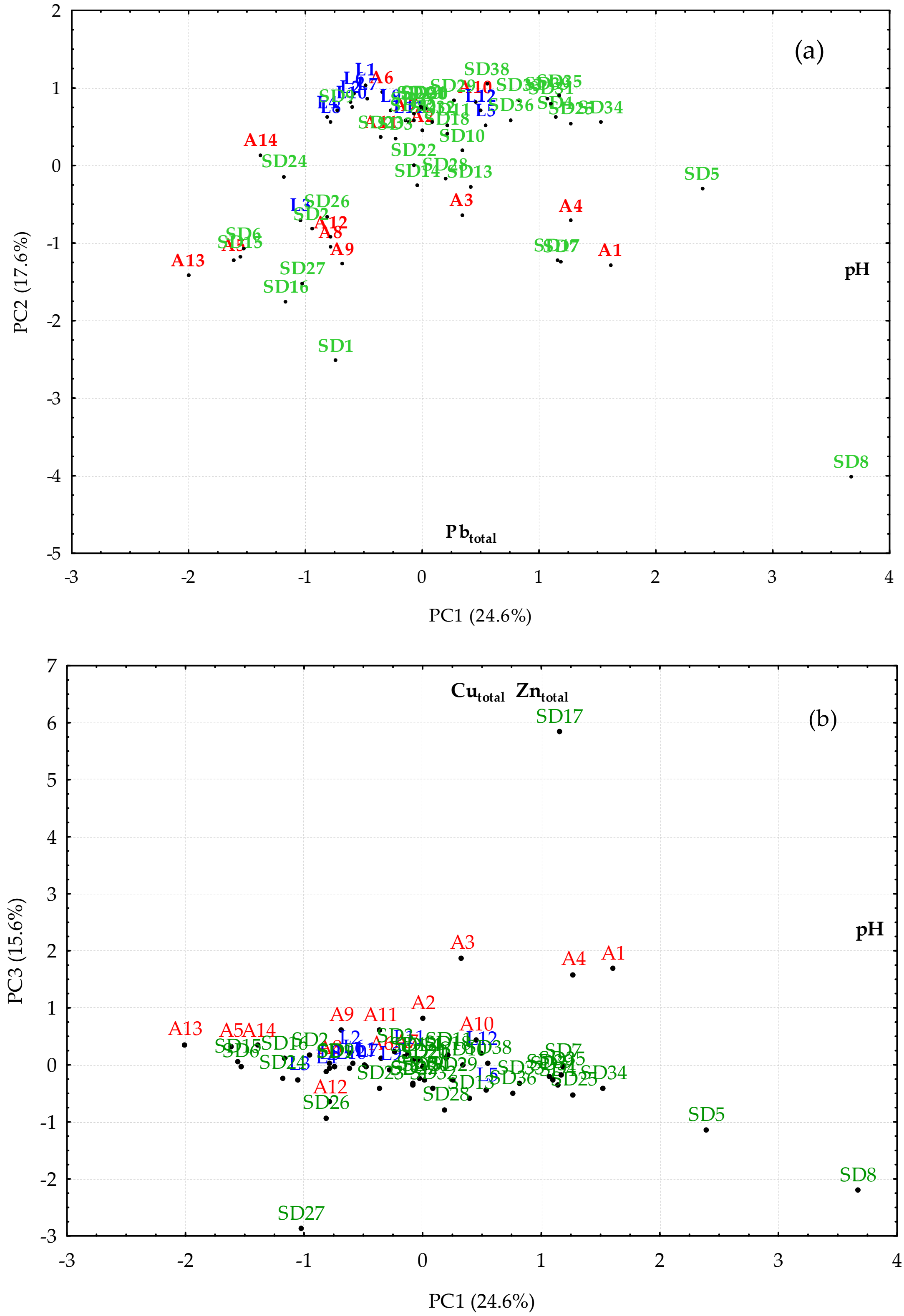

Figure 7. Scores of each sample on the three main principal components: (**a**): PC1 versus PC2; (**b**) PC1 versus PC3. The most important parameters for the definition of the two components are shown on the edge of each axis, indicating the direction in which the value of the parameter increases (pH: soil pH(H_2O); and Cu_{total}, Pb_{total} and Zn_{total}: pseudo-total elements concentration aqua-regia digestion). The color of the label indicates the mine: red for Aljustrel; blue for Lousal; and green for São Domingos.

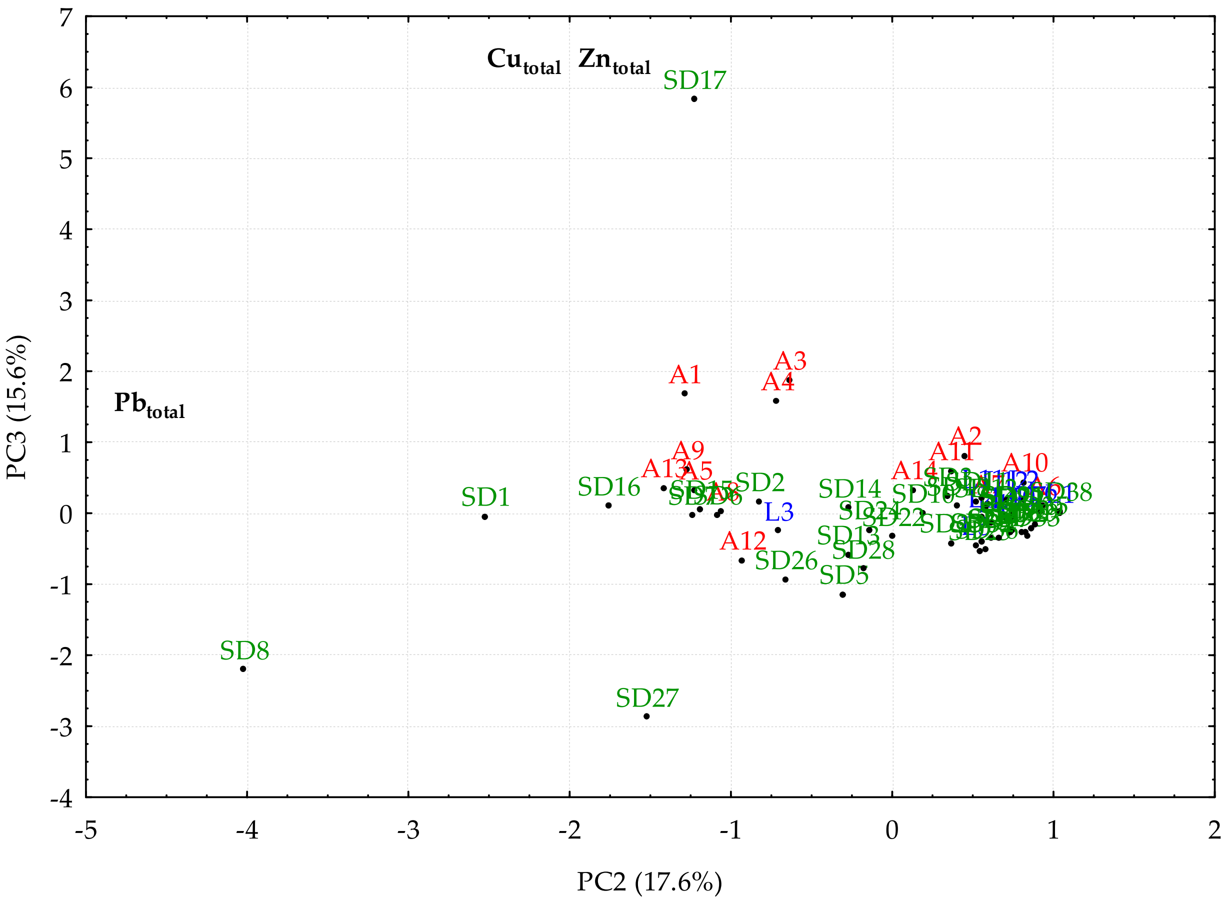

Figure 8. Scores of each sample on the principal components, PC2 versus PC3. The most important parameters for the definition of the two components are shown on the edge of each axis, indicating the direction in which the value of the parameter increases (Cu_{total}, Pb_{total}, and Zn_{total}: pseudo-total element concentrations aqua-regia digestion). The color of the label indicates the mine: red for Aljustrel; blue for Lousal; and green for São Domingos.

Considering the PC1 versus PC2 plan (Figure 7a), the samples located in the left quadrants were those with lower pH values, evidencing the more acidic soils (64% of Aljustrel's samples). Distant from these samples, in the positive part of PC1, it is possible to find two samples from São Domingos with unusually high pH values: SD8 and SD5, with a soil pH of 7.02 and 6.22, respectively, but also, a great part of the São Domingos samples (59%), corresponding to acid soils, but not as acidic as in Aljustrel (see also Figure 5a). On the other hand, the samples located downward from the origin axis of PC2, on its negative part, were those which presented higher Pb pseudo-total concentrations. There, it is possible to find the majority of the Aljustrel's samples (57%), and a smaller number of samples from São Domingos (38%) and Lousal (17%).

The PC1 vs. PC3 map (Figure 7b) evidenced that the majority of the Aljustrel's samples, located in the positive part of PC3 with a positive correlation with Cu and Zn pseudo-total concentrations, corresponded to the locations with higher concentration on those PTEs. PC3 was not able to discriminate the samples from São Domingos, which were almost all concentrated near the origin of that axis, except for SD17, in the positive part of that chart, with an exceptionally high total concentration for both elements (3383.1 mg Cu kg^{-1} and 8045 mg Zn kg^{-1}).

The plan of PC2 versus PC3 plan (Figure 8) emphasized the samples with, simultaneously, the highest Pb, Cu, and Zn pseudo-total concentration, which were those located in the upper-left quadrant, where, again, it is possible to find some samples from Aljustrel (A1, A3, A4, A5, A8, A9, and A13). Since some of these samples were collected in an area that was already rehabilitated by EDM using constructive techniques [5], it is fair to say that further intervention actions should be considered, to control not only the low pH values found, but also the high pseudo-total PTEs concentrations at the site.

4. Conclusions

The PCA identified the most relevant soil properties in order to explain data variance in the mine areas located in the Portuguese sector of the IPB, which were soil pH (24.6% of the variance, with a high positive factor loading on PC1), Pb total concentration (17.6% of the variance, with a high negative factor loading with PC2), followed by Cu and Zn total concentrations (15.6% of the variance, high positive factor loadings on PC3), allowing a separation of the Aljustrel's samples from those collected in the other mines. The Pearson correlation coefficients revealed very strong associations between Pb and As, a consequence of the co-existence of galena and arsenopyrite, and between Cu and Zn ($p < 0.001$), meaning that they happen to appear together as soils' contaminants in these mines. In fact, As and Pb were markedly found at a higher concentration in São Domingos, whereas Aljustrel had an elevated concentration for As and Pb, and for Cu and Zn. Therefore, it is evident the risk that persists in the Aljustrel mine area, with high concentration of As, Cu, and Pb, low pH, and degraded nutritional status, which was not alleviated by the techniques that were implemented to rehabilitate the area, which consisted mainly in "digging, dumping, and covering".

Further remediation measures in these mining areas are, therefore, recommended. That is true even for the mines which were already rehabilitated, especially Aljustrel. Nevertheless, it is important to emphasize that these values should also be compared with background concentrations, because these soils are naturally enriched in some of these PTEs. Comparison with the APA standards can provide some reference but should not be the only criterion to assess the need to decontaminate, nor the level of concentration that should be targeted, and the risk should also consider PTEs availability to plants and soil organisms.

One possibility to control the risk, once the complete and rapid removal of the contaminated soils is expensive, disruptive, and with high environmental and social impacts, is by rendering the PTEs less mobile and bioavailable, by the application of assisted phytoremediation, selecting proper soil amendments and native plant species, strategies that are being recommended to these types of derelict environments.

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