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Review

Potentially Toxic Elements' Contamination of Soils Affected by Mining Activities in the Portuguese Sector of the Iberian Pyrite Belt and Optional Remediation Actions: A Review

Clarisse Mourinha [1], Patrícia Palma [1,2], Carlos Alexandre [3], Nuno Cruz [4], Sónia Morais Rodrigues [4] and Paula Alvarenga [5,*]

1 Departamento de Tecnologias e Ciências Aplicadas, Escola Superior Agrária de Beja, 7801-295 Beja, Portugal; clarissemourinha_17@hotmail.com (C.M.); ppalma@ipbeja.pt (P.P.)
2 Instituto de Ciências da Terra, Universidade de Évora, Rua Romão Ramalho 59, 7000-671 Évora, Portugal
3 Departamento de Geociências e MED-Mediterranean Institute for Agriculture, Environment and Development, Universidade de Évora, Apartado 94, 7002-554 Évora, Portugal; cal@uevora.pt
4 CESAM & Departamento de Ambiente e Ordenamento, Universidade de Aveiro, 3810-193 Aveiro, Portugal; nmcc@ua.pt (N.C.); smorais@ua.pt (S.M.R.)
5 Linking Landscape, Environment, Agriculture and Food Research Center, Associated Laboratory TERRA, Instituto Superior de Agronomia, Universidade de Lisboa, Tapada da Ajuda, 1349-017 Lisboa, Portugal
* Correspondence: palvarenga@isa.ulisboa.pt

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Abstract: Both sectors of the Iberian Pyrite Belt, Portuguese and Spanish, have been exploited since ancient times, but more intensively during and after the second half of the 19th century. Large volumes of polymetallic sulfide ore were extracted in open pits or in underground works, processed without environmental concerns, and the generated waste rocks and tailings were simply deposited in the area. Many of these mining sites were abandoned for years under the action of erosive agents, leading to the spread of trace elements and the contamination of soils, waters and sediments. Some of these mine sites have been submitted to rehabilitation actions, mostly using constructive techniques to dig and contain the contaminated tailings and other waste materials, but the remaining soil still needs to be treated with the best available techniques to recover its ecosystem functions. Besides the degraded physical structure and poor nutritional status of these soils, they have common characteristics, as a consequence of the pyrite oxidation and acid drainage produced, such as a high concentration of trace elements and low pH, which must be considered in the remediation plans. This manuscript aims to review the results from studies which have already covered these topics in the Iberian Pyrite Belt, especially in its Portuguese sector, considering: (i) soils' physicochemical characteristics; (ii) potentially toxic trace elements' concentration; and (iii) sustainable remediation technologies to cope with this type of soil contamination. Phytostabilization, after the amelioration of the soil's properties with organic and inorganic amendments, was investigated at the lab and field scale by several authors, and their results were also considered.

Keywords: Iberian Pyrite Belt; mining activities; soil contamination; trace elements; soil remediation; phytoremediation; soil amendments

1. Introduction

The Iberian Pyrite Belt (IPB) is located in the SW of the Iberian Peninsula, forming an arch about 240 km long and 35 km wide, extending from Grândola (Portugal) to Seville (Spain). It represents one of the most important volcanogenic massive sulfide districts in the world [1,2]. The IPB was formed 350 million years ago, connected to active hydrothermal volcanism that led to the formation of a volcano-sedimentary complex [2]. In the IPB, more than 80 known deposits have been referenced, containing an estimated 1700 Mt total reserves (massive sulfides and stockworks) containing 14.6 Mt of Cu, 13.0 Mt of Pb, 34.9 Mt of Zn, 46,100 t of Ag, 880 t of Au and significant amounts of other metals, in particular Sn [3]. The massive sulfide ore is composed mainly of 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 [4].

Gossans (superficial iron oxide caps) were obvious surface markers of the massive sulfide mineralization in the IPB and were responsible for the beginning of the exploitation, which occurred from the Chalcolithic until the Roman period for Cu, Au and Ag [3]. After centuries of almost complete inactivity, the mines were reactivated during the 19th and the 20th centuries, focusing on the production of Cu and sulfuric acid [2].

This intense mining activity, developed over more than 3000 years, caused a considerable impact, modifying the landscape and leading to the contamination of soils, water and sediments [2,5–7], mostly with potentially toxic trace elements (PTEs) which were associated with the polymetallic sulfides explored (Cu, Pb, Zn, Fe, As, and Sb, as well as Co and Mn [7]). Of course, in these areas, PTEs can also result from natural geochemical processes that are common in geological environments where sulfide deposits exist, for instance from the weathering of the top of the sulfide orebody forming the gossans and releasing acid rock drainage [8,9]. However, the amount released into the soil is negligible compared to that released because of the mine exploitation.

The main environmental impacts were caused in the last two centuries, when the mining activities were expanded and intensified, until a large part of the mining activities ceased, mostly due to the exhaustion of the ore, leading to the closure and abandonment of the facilities used for the mine works [2,5,6]. Considering the relevant mines of polymetallic sulfides in Portugal, which include Neves Corvo, Aljustrel, São Domingos, Lousal and Caveira [5], only Neves Corvo and Aljustrel are currently in operation [2,10].

Historically, there were no concerns with regard to the fact that mining activities could negatively affect the surrounding ecosystem [11]. On top of that, their closure was made, in most cases, without any environmental concerns or remediation actions, leaving behind huge amounts of sulfide-rich mine wastes (e.g., gossan, host volcanic and shales, modern and roman slag, metallurgic ash and pyrite ore) with high metal and metalloid contents [5,7,12,13]. Some of these deposited mine wastes have a high potential to produce acid mine drainage (AMD), which represent a serious contamination problem, especially due to the low pH and high concentrations of PTEs (metals and metalloids) that can affect soil, surface waters and their sediments [14–17], leading to complete landscape disruption. The bare and potentially contaminated soil was left exposed, without vegetation or the capacity for its development, and is prone to erosion and is continuously affected by acid drainage from the waste materials left uncovered.

The mining activity has changed the landscape and culture of the surrounding areas, leaving a rare heritage of industrial archeology that includes underground galleries, open pits, industrial ore processing systems, railway tracks, etc., which are important to preserve and, if possible, promote their musealization [12]. However, it also left a huge legacy of abandoned mines, without any type of planning or implementation of programs to minimize environmental impacts after their closure [12]. The rehabilitation of post-closure mines was not mandatory by law, or mining companies were not required to comply effectively with the existing policies and regulations for their rehabilitation of [18].

To avoid the multiple impacts created by mining in the past, in 2001, the Portuguese government, assumed by Decree-Law No. 198-A/2001, 6 July 2001 [19], attributed to EXMIN, currently EDM (Empresa de Desenvolvimento Mineiro, S.A.), the concession for the recovery of degraded mining areas in the country, financed by the central administration with public funds [20]. EDM is responsible for the hierarchy assessments, remedial works, and the monitoring plans pre- and post-remediation. So far, it has identified 199 abandoned and contaminated areas and is now working on their rehabilitation, some of them in the IPB (Lousal and Ajustrel have their rehabilitation projects finished and São Domingos is ongoing).

In Portugal, as in other countries with significant mining activity, there is an important law establishing the legal framework for the activities of prospection and exploitation of the existing geological resources, which applies to the companies which are active (Law No. 54/2015, of 22 June) [21]. This law, referring to the mining explorations in all phases, will promote the use of the best available practices concerning health and safety at the mining works, but also the compliance with appropriate environmental protection and landscape recovery measures. Nowadays, a mine's closure requires the return of the land to viable post-mining use, and obliges companies to have a project for the remediation of the affected area [22].

This review aims to discuss the soil contamination associated with the mining activities in the Portuguese sector of the IPB and the possible solutions for their remediation. This review will present: (i) soil physicochemical characteristics and PTE concentrations in the most representative abandoned mines (Aljustrel, Lousal and São Domingos); (ii) the rehabilitation measures which were already developed; (iii) other sustainable remediation options to cope with this type of soil contamination, i.e., phytotechnologies; (iv) native vegetation, already adapted to these soils; and (v) soil amendments to potentiate the success of the phytoremediation.

2. Soil Characteristics in Abandoned Mines at the Portuguese Sector of the IPB

2.1. General Considerations

2.1.1. Main Impacts in the IPB

Mining activities are one of the most important anthropic causes of soil degradation and pollution in the world [8,23–25]. Mine soils in post-mining locations have great spatial variability in their properties (e.g., pH, particle size distributions, PTEs content), largely dependent on the characteristics of the ore that was processed and on the materials which were deposited at the site [26–28]. In fact, in addition to altering soil properties affecting the vegetation cover, mining activities are an environmental concern for terrestrial and aquatic ecosystems, mostly because of the high amounts of tailings that were left deposited at the site [29–33].

In addition to high concentrations of PTEs in the tailings, they exhibit extremely low pH, high salinity, low water holding capacity, low organic matter content and, in short, low levels of soil fertility (i.e., ecological functions of soils), hindering the natural growth of plants [33]. However, the most important issue associated with sulfide-rich mine tailing deposits is the production of AMD [5,11]. The exposure of these materials to atmospheric conditions causes the oxidative dissolution of sulfide minerals, leading to the very long-lasting and polluting process of AMD [14–17,34–37]. Mining waste and the subsequent production of AMD have a profound impact on the quality of the surrounding soils, water, sediments, and biota [5,14,38]. The generation of acidic waters from the erosion of massive sulfides, the washing of mine residues and the drainage of mine waters gave rise to extremophile ecosystems [2], such as those reported by Samiento et al. [39], where negative pH values were found (−1.56) in the Tinto and Odiel Basins (Spanish sector of the IPB), never found before in AMD.

Considering the characteristics already mentioned, these areas are devoid of vegetation due to the harsh soil conditions that prevent the rooting of plant species [11,24,40,41]. This bare soil is easily exposed to water [24] and wind erosion [42], thus stimulating the widespread dispersion of pollutants and the enlargement of the affected area.

There are some studies, developed over the years in different locations of the IPB, in which soil degradation was demonstrated, namely in terms of soil fertility and high concentrations of some PTEs, mainly Cu, Zn, Pb and As [28,29,43–55].

Due to all of these constraints, and even removing the main sources of continuous contamination (i.e., tailings and dispersed wastes), soils in abandoned mines have limitations for plant colonization: physical factors (e.g., coarse texture, lack of structure, low clay content, low water holding capacity), chemical factors (e.g., low organic matter, and nutrients content, acidic pH, low cation exchange capacity), and, above all, high levels of

PTEs [29,48,49]. Moreover, these soil characteristics favor the mobility and bioavailability of PTEs [56], which can lead to the decrease in soil fertility [57,58], have a profound impact on the activity, diversity and structure of the microbial community [59], and pose a threat to human health through the food chain [55,60].

Therefore, an important impact which should be considered is the contamination of the agricultural and pastural soils in the vicinity of these mine areas, and in the quality of the food and feed produced in these soils [61]. González et al. [8] found agricultural soils to be affected by the mining activity near the Tinto and Odiel River basins (Spain), mainly with As, Cu, Pb, and Zn. The most worrying aspect was the high bioavailability of these elements, which allowed the investigators to select specific soils where agricultural activities are not recommended. A similar issue was approached by Alvarenga et al. [55], who surveyed the accumulation of PTEs in vegetables produced in small allotment gardens in the vicinity of abandoned pyrite mines in the IPB (Lousal, Aljustrel and São Domingos) and found, generally, situations of concern—the maximum total concentrations for As, Cu, Pb, and Zn were extremely high in some of the sampling sites. However, the PTEs' bioavailable concentrations were low, mostly due to the soil's neutral pH values, lowering the risk of plant uptake of those elements [55].

2.1.2. Total versus Extractable PTEs Concentrations

The upper layers of soil around the mining and extraction areas can contain high concentrations of PTEs, depending on the ore which was mined. These concentrations can be compared with soil quality guidelines values, from dose–response relationships, to assess the probability of harm: total concentrations above the recommended threshold values are considered to pose a risk [48,49,62]. However, the danger of pollutants in soils does not depend only on their total concentration, but also mainly on their availability [8,48,49,62,63]. The availability of an element can be considered as the potential of an element to pass from the soil into its solution, while the term bioavailability is the degree to which an element in a matrix is free for uptake by a specific organism [8]. Taking that into consideration, PTEs' (bio)availability is increasingly being used, alternatively to their total concentrations, as a key indicator of potential risks that contaminants pose to both environmental and human health [62,64]. However, the bioavailability of an element is a function of its specific physical and chemical form in the soils, and of the ability of the organism to absorb or ingest it [8]. Consequently, it is not easy to measure, due to its organism-dependence. Therefore, the bioavailable fractions are usually assessed by chemical methods, because the water-soluble, exchangeable and acid-soluble fractions, which constitute the extractable fractions, represent the more mobile, active and accessible pool of PTEs in the soil to the organisms [48,49,61,62,64–66].

The PTEs' mobility depends on their speciation, which is affected by several soil parameters [8]; the intrinsic characteristics of the soil can alter the chemical speciation and fractionation of metals, influencing their mobility, bioavailability, leaching and toxicity [67]. For instance, soil pH has paramount importance in the adsorption of metals by soil substances, such as organic matter and clay minerals, changing the surface charge and the ionizability of metals adsorbents [68], which then affect the bioavailability and toxicity of PTEs for the soil organisms.

2.1.3. Soil Quality Guidelines Values

Another aspect which is also very important is to have "soil quality guidelines values", in order to evaluate soil contamination. However, only recently have soil contamination issues gained recognition by different organizations: the Food and Agriculture Organization of the United Nations (FAO) organized a Global Symposium on Soil Pollution in 2018 [69], and pointed to soil pollution as a hidden reality [70]; the International Union of Soil Sciences (IUSS) [71] proclaimed 2015–2024 as the International Decade of Soils; the European Environment Agency (EEA), which devoted the Signals 2019 to the "Land and soil in Europe" [72], and finally, the European Union (EU), which selected "Soil Health and Food" as one of its Missions in the Horizon Europe framework program, beginning in 2021 [73], and is now fully committed in the launch of a framework to assess soil quality, under the motto "Healthy soil for a healthy life". This document aims to comprehensively address land and land degradation, and to help in achieving land degradation neutrality by 2030, with two important specific objectives related to the thematic of this review, which are identifying contaminated sites and restoring degraded soils [74].

The absence of specific soil policies observed during all these years at the EU level has allowed some countries, including Portugal, to lack specific legislation to assess contaminated soils [75,76]. In the absence of this legislation, the soil clean-up criteria adopted by the Portuguese Environmental Authorities was the "Interim Canadian Environmental Quality Criteria for Contaminated Sites [77] (Table 1), which can be criticized, since the pedogenetic conditions in both countries are different, giving rise to soils with very distinct background levels. In other documents, such as the study produced by Tóth et al. [78] to evaluate the contamination of European soils with PTEs, the threshold values used were from the Ministry of Environment of Finland (Table 1), which can also be inadequate to assess the PTEs' threshold values in Portugal. Despite some efforts of the Portuguese Environmental Agency (APA), which prepared a draft proposal in 2015, Portugal lacks legislation to assess soil contamination and the chain of procedures for its rehabilitation. To fulfill this void, recently, the APA prepared a Technical Guide with Reference Values for the Soil (Table 1), which aims to assist those interested in the selection of reference values applicable to the main soil contaminants, to be used in the processes of soil quality assessment and confirmation of the results achieved with remediation [79].

Table 1. Limit values to assess contaminated soils proposed for Portugal and for other countries, as examples (Canada and Finland). Arsenic, Cu, Pb and Zn were selected, the PTEs usually affecting the IPB soils.

	Canada *		Finland **		Portugal ***	
	Agricultural Use	**Industrial Use**	**Lower Guideline**	**Higher Guideline**	**Agricultural Use**	**Industrial Use**
As (mg kg^{-1})	12	12	50	100	11	18
Cu (mg kg^{-1})	63	91	150	200	140	230
Pb (mg kg^{-1})	70	600	200	750	45	120
Zn (mg kg^{-1})	200	360	250	400	340	340

* Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health, in soil with agricultural and industrial use [80]; ** lower guideline value (all land uses) and higher guideline value (industrial and transport areas) from the Ministry of Environment of Finland [78]; *** recommended limit values for the remediation of soil intended for agricultural use, with the use of groundwater, and for industrial use, from the Technical Guides of the Portuguese Environmental Agency are represented in red, Table E [79]. All values refer to the pseudo-total PTE concentrations (i.e., aqua regia extractable, or equivalent procedure).

2.2. Trace Elements Contamination in Abandoned Mines at the Portuguese Sector of the IPB

The abandoned polymetallic sulfide mines in the Portuguese sector of the IPB (Alentejo region), which needed intervention to reduce the environmental impacts, were São Domingos, Aljustrel, Lousal and Caveira [5,7]. The mine works at these mines were very important in pre-Roman and Roman times, and again, with intensive exploration, during part of the 19th and 20th centuries [5]. Afterwards, the production was discontinued in those mines, and only the production in Aljustrel, after one decade of inactivity, was reactivated in 2008 by the Almina Company, the activity of which is mainly focused on Cu concentrate production, but following the current best available practices to avoid environmental impacts [81]. The same practices, avoiding environmental disruption, are followed in the Neves-Corvo mine, presently explored by the Lundin Mining Company, which produces Cu, Zn, Pb and Ag concentrates.

2.2.1. Aljustrel Mine

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 e Gavião) which were explored from 1850 to 1991 [5,82]. The major environmental impacts at this mine were the AMD with origins in the large volume of tailings which were dispersed in Algares, São João and Feitais, which affected the hydrological system in the surroundings for a long period: Água Forte, Água Azeda, and Roxo streams, all in the Sado and Mira Hydrographic Region [14,83–87]. Aljustrel mine, as will be presented in Section 3.2, was rehabilitated by EDM, which allowed a progressive improvement in the quality of the water and sediments of those streams.

Previous studies have evidenced the contamination load of PTEs in the mine area, which are now rehabilitated by EDM, and around the Aljustrel [43,82]. The results showed severe soil contamination, mainly with As (up to 3936 mg kg^{-1}), Cu (up to 5414 mg kg^{-1}), Cd (up to 61.6 mg kg^{-1}), Pb (up to 20,000 mg kg^{-1}) and Zn (up to 20,000 mg kg^{-1}), about two orders of magnitude above the regional South Portuguese Zone background values [82,88]. The highest concentrations for the same elements found by Alvarenga et al. [43] in the Aljustrel mine area were 1800 mg kg^{-1} for Cu, 945 mg kg^{-1} for Zn, 565 mg kg^{-1} for As and 3500 for Pb mg kg^{-1}. However, it is important to note that the soils sampled in this study were colonized by *Cistus ladanifer*, an endemic shrub that can be found even in contaminated sites [43].

2.2.2. Lousal Mine

The Lousal polymetallic massive sulfide 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 [89]. The deposit was explored from 1900 to 1988, mainly for pyrite, comprising 50 Mt of ore with 1.4% Zn, 0.8% Pb and 0.7% Cu [5,22,89]. The pyrite was milled in the crushing plant and after being transported by railroad to Barreiro, was used to produce superphosphate for the fertilizer industry, by the same owner of the mine (SAPEC). The closure of the Lousal Mine in 1988 was due to the unsustainability of sulfur extraction from pyrite and the low Cu and Zn contents of the mined ores [22].

The potential environmental risk at the site originated mainly from the drainage from the tailing deposits (Figure 1a), still with high concentrations of PTEs, and from the road network of the mine, in some cases constructed with the rejected materials [90]. Silva et al. [91] reported high concentrations of several PTEs in soils collected near the tailing deposits, specifically As (0.2–16.4 mg kg^{-1}), Cu (292–7013 mg kg^{-1}), Pb (871–12,930 mg kg^{-1}), Zn (126–7481 mg kg^{-1}). The AMD formed there had a potentially negative effect in the Corona stream, documented by different authors [89–91].

Lousal mine was well preserved right from its closure, thanks to the intervention of the Fréderic Velge Foudation (belonging to SAPEC) and the Grândola Municipality, which less than 10 years after the closure of the mine began the rehabilitation of the area and its infrastructures. Part of the structures are well preserved, an important testimony of the geological and mining patrimony, comprising also a Mining Museum, a Science and Technological Centre, and an underground gallery, which are visited by students and tourists [22].

To lower the environmental impact at the Lousal mine, the EDM constructed an artificial wetland system (Figure 1b), mostly relying in a phytoremediation process, to protect the Corona River from the AMD with origins in two main sources: the milled ore deposited in the railway area and the old mine open pit. The first group of lagoons, under aerobiose, favor iron precipitation, while the second group operate in anaerobiose, to promote heavy metals' precipitation [22].

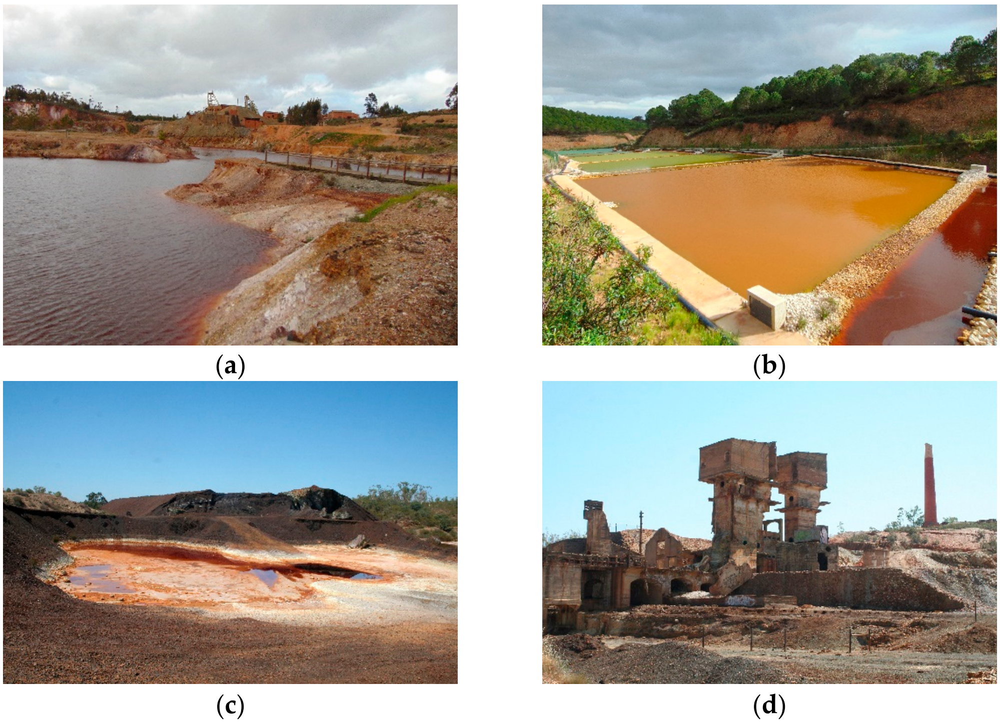

Figure 1. Some aspects of non-active mines of the Portuguese sector of the IPB: (**a**) general view of the Lousal mine, with the tailing deposits in the background of the image; (**b**) the artificial wetland system constructed by EDM to treat the AMD at the Lousal mine (with the different color of the water in the lagoons evidencing the treatment); (**c**) mining wastes deposited in São Domingos, a continuous source of AMD; (**d**) the Achada do Gamo sulfur factory, an emblematic infrastructural feature of the mining exploration at the São Domingos mine (images (**a**,**b**) courtesy of Cátia Micaelo, December 2016).

2.2.3. São Domingos Mine

The São Domingos mine is perhaps the most emblematic of the abandoned mines in the Portuguese sector of the IPB. São Domingos was intensively exploited from 1857 to 1966, causing a documented physicochemical impact in soils, water, and sediments [5,13,92–94], as well as using microbial and biochemical indicators [48,49,95]. The mine area is characterized by an enormous pit, left after the extraction works (122 m deep), which is now filled with acidic waters, with a pH of 1.7 [92]. During the exploitation, mined raw material was crushed in a mill located near the open cast pit, and transported 3 km south, to the Achada do Gamo sulfur factory, where it was smelted to obtain high-level grades of Cu ore and sulfur products [17]. The intense mining activity created a huge amount of highly heterogeneous waste (Figure 1c) (approximately 750,000 tons) [92], including Roman and modern slags, smelting ashes, and pyrite-rich waste dumps [93] (Figure 1d). The negative impact is observed along the São Domingos stream valley and in the Achada do Gamo sulfur factory, because of the intensive mine drainage from these wastes, marked by significant low pH values and high concentrations of Pb, As, Sb, Cu, Zn and Fe [17,44,93]. In a study which surveyed 85 abandoned mines in Portugal, the São Domingos mine was assigned to the highest level of environmental danger [7].

Santos et al. [96] reported high concentrations for As and Pb (2600 mg kg^{-1} and 7300 mg kg^{-1}, respectively), but with low available fractions (0.01 M diethylene triamine pentacetic acid, DTPA, extraction), representing less than 1.5%. The low availability of the PTEs at the São Domingos mine were also corroborated by Alvarenga et al. [49], which, despite the high total concentrations found for As (up to 1956 mg kg^{-1}), Cu (up to 1928 mg kg^{-1}), Pb (up to 10,795 mg kg^{-1}), and Zn (up to 2140 mg kg^{-1}), their availability (assessed by extraction with $CaCl_2$ 0.01 M) was very low, <1% for As, Cu and Pb, and <10% for Zn of the total concentrations.

In fact, the soils that were sampled in São Domingos were predominantly thin and developed on mining wastes, mainly composed by gossaneous materials and host rocks, evidencing low pH (4.53), low organic matter content (1.687%, w/w), and very low values for N and P (0.004% N (w/w) and 2.23 mg kg^{-1} for extractable P, dry weight, DW basis), which are very inadequate to establish plant cover. Potassium was the only essential element which presented a higher extractable content (105.8 mg kg^{-1}) [96].

In the São Domingos mine, Freitas et al. [92] corroborated the high concentrations for As (37.2–1291.0 mg kg^{-1} DW) and Pb (234.2–12,217.5 mg kg^{-1} DW), but also for Cu (87.3–1829.0 mg kg^{-1} DW) and Zn (103.8–713.7 mg kg^{-1} DW), as well as soils with pH values ranging from acidic to neutral values (4.01 to 6.73).

The concentrations which were reported for the soils in these three mining districts in the Portuguese sector of the IPB are not very different from those found in abandoned mines in the Spanish sector of the IPB (Table 2), and they indicate the need for the intervention to rehabilitate these areas (especially when comparing with the proposed or established limit values; Table 1), lowering their impact in the surrounding abiotic and biotic compartments.

Table 2. Indicative concentrations for As, Cu, Pb and Zn (minimum and maximum, or medium (*), when that value is reported) found in different mines of the Iberian Pyrite Belt (Portugal: PT; Spain: ES). n.a.: not available.

	As (mg kg^{-1})		**Cu (mg kg^{-1})**		**Pb (mg kg^{-1})**		**Zn (mg kg^{-1})**		**Reference**
Mine	**Min.**	**Max.**	**Min.**	**Max.**	**Min.**	**Max.**	**Min.**	**Max.**	
São Domingos (PT)	65	4366	27.4	6204.7	80.1	>10,000	16	8760	[94]
	37.2	1291	87.3	1829	234.2	12,218	103.8	713.7	[92]
	711	3030	203	342	666	9210	36	186	[97]
	2643 *		226 *		7343 *		43.83 *		[96]
	1600	3000	231	379	3100	9200	115	200	[97]
	871	3180	67	1310	425	5300	80	857	[98]
	32	5598	19	1928	19	14,041	68	2140	[49]
	711	1800	203	379	666	5008	113	186	[54]
Aljustrel (PT)	n.a.	565	226	1800	301	3500	140	945	[43]
	6	3936	10	5414	13	2000	22	20,000	[88]
	6	3936	10	5414	13	2000	22	20,000	[82]
	n.a.		362 *		1250 *		254 *		[58]
Lousal/Caveira (PT)	597	6377	292	7013	126	7481	871	12,930	[91]
	62	662	79	325	95	2280	166	878	[97]
	198	426	232	245	432	721	350	497	[54]
	133	1300	196	2800	932	48,000	193	785	[54]
	180 *		231 *		302 *		180 *		[99]
Rio Tinto (ES)	13	142	62	586	49	265	79	215	[100]
	50	77	153	495	168	598	302	795	[101]
	13	204	47	586	34	598	66	795	[102]
	106	181	62.6	72.1	104	159	79.1	104	[46]
	581	1452	226	1391	826	2093	112	1501	[103]
	89	1300	291	399	254	2722	65	265	[45]
	19	994	27	1160	41	4890	95	897	[104]
	2	15,195	20	3090	18	6350	45	870	[105]
	203	621	326	752	864	2395	314	570	[106]
Tharsis (ES)	400	658	402	977	689	2017	184	295	[107]
	3	6290	4	690	14	24,820	16	420	[105]
	569	668	957	1827	1904	2679	467	973	[45]
	569	668	957	1827	1904	2679	467	973	[45]

3. Remediation of Mine-Degraded Sites in the Portuguese Sector of the IPB

The long history of metalliferous mining in the IPB left a legacy of abandoned mines and associated spoils, including enormous sulfide-bearing waste rock piles, tailings and flooded pits [108]. These mine wastes are a continuous source of environmental contamination, mainly AMD, which arises from the oxidation of the sulfide wastes, a process which is well-known and has been thoroughly described [14,34–37]. Remediation of mine-degraded sites is imperative to reduce the potential risks to the surrounding ecosystems and, consequently, to humans, and a source of continuous AMD formation [109–111]. Consequently, these mine waste deposits should be removed and/or controlled. However, we agree with Matos and Martins [5] that rehabilitated mining areas should maintain a mining landscape as a testimony of the extractive activity.

3.1. Conventional Solutions

There are several techniques that can be used to reduce the potential risk of these sites. Their selection depends on the level and nature of the contamination, the type of soil, the characteristics of the contaminated site, the contaminant's availability, and the existence of relevant regulations [112]. The focus of the remediation may be: (i) the containment/isolation of the contaminated materials, soils and/or wastes, hereafter classified as constructive techniques, but which some authors consider in the group of the physical treatments [113]; (ii) the immobilization/stabilization of the contaminants in the contaminated material (soils or tailings); or (iii) the extraction/removal of the contaminants from the soil. The choices are always site-specific, since there is no standard procedure and, often, it is necessary to combine strategies [114–116].

Remediation techniques for contaminated sites targeting specifically the contaminants (i.e., treatments, in a strict sense) can be performed in situ or ex situ [113,115,117]. The techniques can be further classified regarding the process used in the treatment, specifically as physical (e.g., soil washing, electrokinetic), chemical (e.g., adding chemicals to soil which will react and immobilize the contaminants), or biological (e.g., using plants and/or microorganisms, to degrade, immobilize or extract the contaminant) [113,115].

Abandoned mine sites are particularly difficult to remediate due to the large extension of the contaminated areas, with a very heterogeneous distribution of multiple metal(loids), which can reach very high concentrations at some sites [118]. Consequently, conventional technologies that could be appropriated to PTE-contaminated soils, such as stabilization/solidification using cement-based binders or waste materials, including lime-slag blends [119], soil washing, or electrokinetic technologies [33,120], are unsuitable due to their high implementation costs, making them impractical and financially unviable [121,122]. In fact, physical remediation methods, such as soil washing and electrokinetic remediation, can remove some of the PTEs from contaminated soil, but they are very expensive and can only be applied to small areas of soil. On the other hand, chemical remediation methods (e.g., addition of chelates, acid/alkali or oxi-reduction agents) are not environmentally friendly because they (usually) release additional chemicals into the environment, leading to environmental problems, such as the risk of groundwater contamination with the used reactants [113].

Therefore, excavation, storage, and capping—constructive techniques—are often the chosen solution to the mine site rehabilitation, because they are easier to apply, do not depend on the characteristics and concentration of the contaminants or on soil properties, increasing the potential success of the intervention, and decreasing the time needed to complete remediation works.

3.2. The Example of the Aljustrel Mine

Because of all these reasons, constructive techniques are widely applied in the rehabilitation of soil in vast industrial areas, such as mine sites, and were the remediation strategies used by EDM in the rehabilitation of the mining areas located in the Portuguese sector of the IPBs, Lousal and Aljustrel, which has already been concluded, and in the current works that are being undertaken in São Domingos mine.

For example, in Aljustrel, the dispersed slag deposits, mining residues, and contaminated soils were removed (Figure 2a) and confined in a specific sector (Algares), the deposits were sealed with limestone and clay (Figure 2b) and some of the exposed areas were covered with clean clay soil and vegetation (Figure 2c), channels were constructed in the perimeter to collect the potentially acidic drainage waters (Figure 2d), which were forwarded to evaporation-concentration ponds (Figure 2e) and treated in an artificial wetland to protect the downstream hydrological system (Água Forte stream and Roxo stream) (Figure 2f).

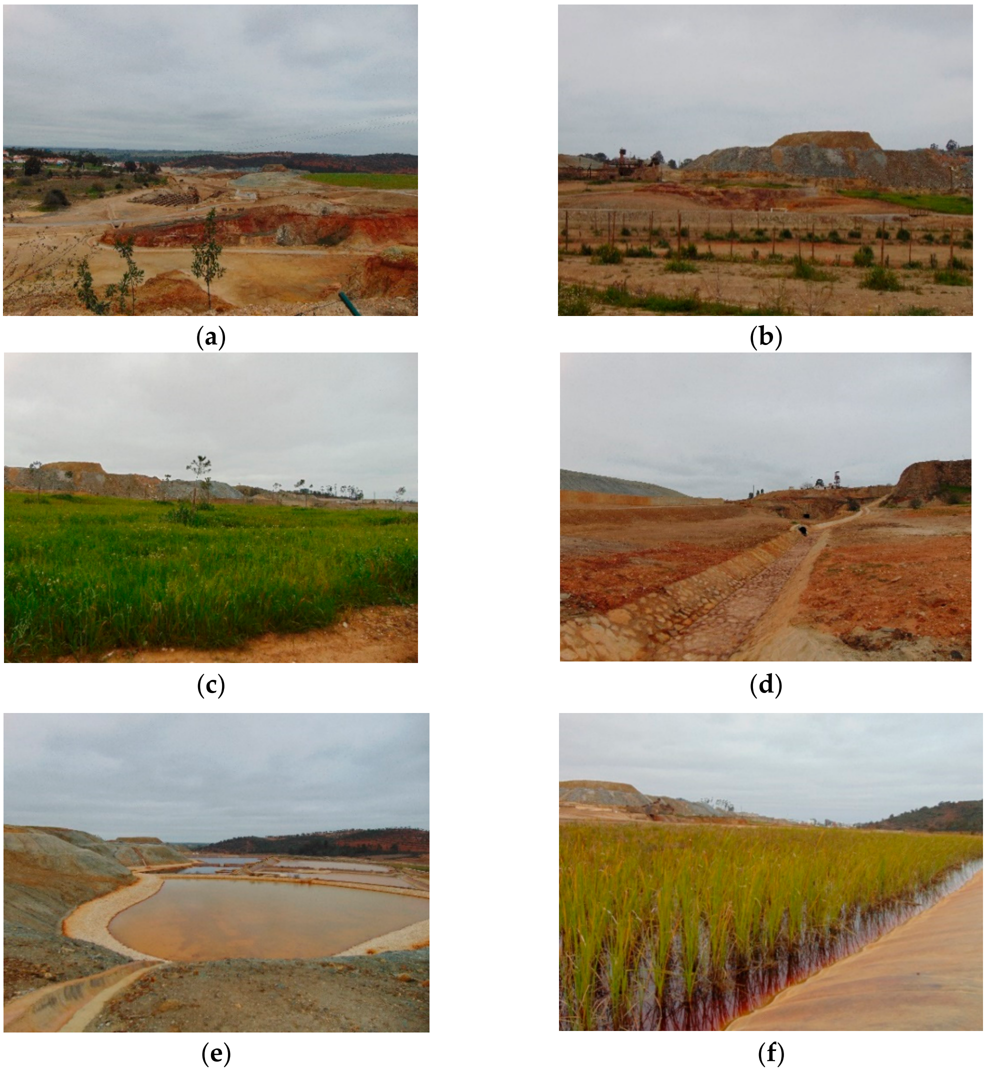

Figure 2. Remediation measures executed by EDM in the old part of the Aljustrel mine: (**a**) overall view; (**b**) confined materials deposited in Algares; (**c**) area covered with clean soil and revegetated with a mixture of herbaceous plants; (**d**) perimetral channels to collect the acid drainage waters; (**e**) evaporation-concentration ponds receiving the drained waters; (**f**) artificial wetland to treat AMD waters (images courtesy of Cátia Micaelo, December 2016).

All of the rehabilitation processes aimed to achieve the valorization of the old mine structures, such as the cementation tanks (Figure 3a), mining headgears, the Transtagana chimney (Figure 3b), and adits (Figure 3c), with secondary minerals formed through the oxidation of sulfides (Figure 3d) [123]. The recovery of the mining heritage will allow the development of a future Aljustrel Mining Park, similarly to the Lousal mine, which has a Mining Museum and an Educational and Scientific Centre, and the development of geological tourism is also envisioned for the São Domingos mine.

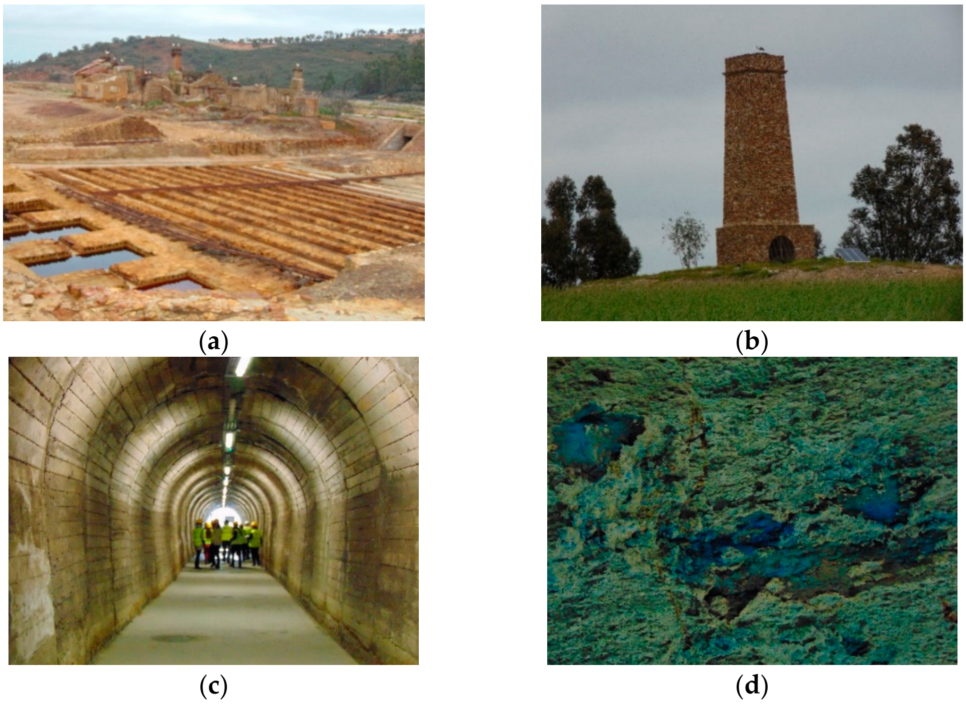

Figure 3. Valorization of the mining heritage during the remediation measures executed by EDM in the Aljustrel mine for the future Aljustrel Mining Park: (**a**) old cementation tanks; (**b**) the reconstructed Transtagana chimney; (**c**) the rehabilitation made in the Algares +30 level adit (gallery), allowing the observation of (**d**) the formation of secondary minerals through the oxidation of sulfides (Images courtesy of Cátia Micaelo, December 2016).

All these interventions are crucial and undoubtably of major importance, with social, economic, and environmental importance to the region. However, conventional constructive techniques can lead to partial or total disruption of the biota and soil structure in the site, which are often fragile, contributing to the deterioration of soil ecosystems [122,124,125]. In addition, conventional dig, dump, and capping techniques often have important disadvantages that limit their effectiveness, since they do not act on contaminants' bioavailable fractions and require infrastructure that increases the economic cost of implementation [29].

In the Spanish sector of the IPB, the situation and the adopted solutions were similar. Several initiatives were triggered by the Regional Government for the remediation of abandoned mines, aiming to achieve a reduction in the environmental impact of AMD, namely to the Odiel river basin; measures included geotechnical stabilization and revegetation of waste piles, the construction of rainwater drainage systems, the sealing of mine adits, and the treatment of the acidic drained waters [108]. However, the attempts to treat the AMD waters using anoxic limestone drainage and anaerobic wetlands were reported as being ineffective, due to several drawbacks, for example the chemistry of the water (highly acidic and with high metal contents) and climatic constraints (variability of water discharge) [108]. In fact, Quental et al. [17] concluded that, once the decomposition of pyrite begins, there is no turning back in the process without the action of neutralizing agents, because grains of pyrite existing in the mining wastes continue to stimulate the production of H+ ions.

Therefore, it is very important to develop environmentally sustainable strategies, that can treat and stabilize contaminants in the soils which are left after the excavation, or even the tailings and contaminated soils, efficiently and economically, promoting their progressive full recovery in a more long-lasting mode [126,127].

3.3. Phytotechnologies

It is essential to develop environmentally sustainable measures to be implemented after the cessation of the mining activity, restoring the physical, chemical and biological properties of the soil, such as its structure, water holding capacity, levelling the pH to circum-neutral values, increasing nutrient content, and recovering the microbial community, in order to activate the nutrient cycles essential to restoring a healthy soil [6,128,129]. It is also very important to minimize the effects of the erosive agents that are far more aggressive in bare soils, and, finally, to reduce the total PTE content or their mobility and bioavailability [110,129].

In contrast to the conventional physical and chemical techniques for soil remediation, phytoremediation has been defended as an alternative or complementary strategy to constructive techniques in order to remedy soils and tailings contaminated with PTEs, which is able to respond to the above-mentioned conditions [130,131]. However, this is a very challenging task, especially in the IPB, located in a semiarid environment, where the contamination impact is exacerbated due to the long periods of drought and the high temperatures of the dry season [118]. Consequently, it is important to understand the conditions needed to be successful using phytotechnologies in the abandoned mines of the IPB.

Phytoremediation is consensually considered an economically and ecologically sustainable strategy for the recovery of soils contaminated with PTEs, taking advantage of the plants' ability to interact with these elements, in the rhizosphere with their associated microbiota, or after their uptake and, eventually, translocation and accumulation in their aerial parts [33,56,121,132–134]. This technique can be applied in large and multi-contaminated areas and has the advantage of being carried out in situ, without excavating the contaminated soil, reducing the risk of exposure for workers or of secondary contamination in the transport of the contaminated media when ex situ technologies are considered [33,121].

Phytoremediation includes several processes often classified in accordance with the process/mechanism by which plants interact with contaminants [115]. The main phytoremediation mechanisms include: phytostabilization (immobilization of pollutants in the rhizosphere by the action of roots, bacteria and soil amendments); phytoextraction (uptake and accumulation of PTEs in the aerial part of the plant); phytostimulation or enhanced bioremediation (degradation of xenobiotics—organic compounds—in the rhizosphere by the action of microorganisms, stimulated by the plant's exudates); phytodegradation (degradation of xenobiotics within the plant tissues by specific enzymes produced by the plant); phytovolatilization (conversion of pollutants to volatile forms and subsequent release into the atmosphere), phytodesalinization (removal of salts in saline soils with halophytes), and rhizofiltration (removal of contaminants from polluted aquatic environments) [121].

The efficiency of each of the mentioned phytoremediation mechanisms regarding PTEs depends on several factors, most of which are related to the plant species and the soil characteristics. These factors include the physicochemical properties of the soil, the bioavailability of the PTEs in the soil, microbial activity, plant exudates produced, and the ability of the plants to adsorb, absorb, accumulate, sequester, translocate, and detoxify PTEs [115]. Generally, the main restrictions that limit the widespread use of phytoremediation techniques are the commitment to decontaminate pollutants in the soil up to their corresponding safety limits, which are based only on total concentrations, and/or the management of the harvested contaminated plant material [135]. Other limitations include the differential tolerance of the plants to specific contaminants, climate limitations and long-term requirements for this process [136,137].

Of all the referred phytoremediation mechanisms, phytostabilization and/or phytoextraction are the processes which have been considered to have applicability in mine contaminated soils [130,138] or tailings [33].

Phytostabilization involves the establishment of vegetation cover on the surface of contaminated sites, with the main objective being to reduce the contaminants' mobility. The process of the immobilization of contaminants within the vadose zone integrates different contributions, such as the reduction in leaching, controlling erosion, creating an aerobic environment in the root zone, and through the release of organic molecules that binds the contaminants, rendering them immobile [139–141]. The recovery of soil health, defined as the ability of the soil to perform its functions, is one of the major achievements of phytostabilization [129].

Phytostabilization is probably the most suitable technique for mine sites, considering the large areas which are affected, with moderate to high levels of metals and metalloids, allowing long-lasting stabilization effects without the need to deal with the harvested contaminated plant material [11,142]. In fact, plants adequate for phytoextration processes, i.e., with the ability to accumulate or hyperaccumulate PTEs in their harvestable parts, are often wild, with small biomass, and the PTEs in mine-contaminated soils are not always in bioavailable forms for their uptake. Harvested biomass would need to be treated as contaminated material, and the system would require a continuous landscape intervention with all the agronomical practices associated with a crop production cycle (e.g., plowing, sowing, fertilizing, irrigating, harvesting) [137]. In fact, one major shortcoming of the selection of phytoextraction is the time span needed to achieve the targeted reduction in PTEs concentration [137], which some investigators have tried to overcome by increasing PTEs availability/mobility by the use of, for instance, metal chelators (e.g., EDTA or DTPA [143]), or by coupling the phytoremediation with electrokinetic technology, which has the ability of increasing the bioavailability of metals for desorption and transportation [120].

Nevertheless, phytoextraction also has some advantages over phytostabilization, such as the possibility of gradually decreasing total PTEs concentration in the contaminated soil [130], and the fact that the collected biomass can be valorized, for instance using energy crops, such as Miscanthus [144,145] or Salix [146,147]. Phytoextraction is preferred, for instance, in agricultural soils (e.g., soils around the former Pb smelter Metaleurop Nord; Al Souki et al. [144]), because the main aim for remediating agricultural soils is to decrease the total PTE content to below a threshold value. On the other hand, phytostabilization is more adequate for the remediation of large areas, e.g., mine-contaminated soils, where the main focus is the reduction in PTEs' mobility and the restoration of soils' ecosystem functions, and where the income generated in the process is not such a strong factor [148]. However, it is important to indicate one shortcoming of phytostabilization: the environmental recovery of soils and waters is only effective in the medium to long term.

More recently, the application of phytotechnologies has evolved to a point where phytoextraction and phytostabilization are somehow combined, with or without the application of amendments, and the definition has evolved into a different concept, which is phytomanagement, considered as a gentle remediation option (GRO), i.e., in situ techniques that do not have a significant negative impact on soil function or structure, and that can create a range of additional economic, social and environmental benefits [126,137,149–151]. In fact, phytomanagement can be directed to different objectives, from PTE removal from the soil to phytoextraction, soil stabilization, phytostabilization, and includes the use of amendments to modify PTEs' mobility or the inclusion of soils microorganisms in the system [150].

However, despite the positive performance of all these techniques in laboratory and greenhouse experiments, validations and field demonstrations remain scarce [152], and the development of agronomic practices for their improvement is extremely necessary [126].

3.4. Plant Selection for the Phytoremediation

The selection of plant species is a crucial aspect for the success of phytoremediation. There are two main criteria to be considered during plant selection, unfortunately often mutually exclusive: plant resistance to high concentrations of PTEs, and high biomass production [153]. In the case of phytostabilization, the plants used are selected specifically for their ability to immobilize metallic contaminants in the root area, instead of accumulating them in the stem tissues, while if the phytoextraction is foreseen, the ability to accumulate specific PTEs is more appreciated [140].

There are some plant species that can grow spontaneously and colonize soils with unfavorable properties and high levels of PTEs, indicating different behaviors regarding the absorption and accumulation of specific elements [29,154]. These native plants are well-adapted to the various stressors associated with mining areas, including adverse climatic conditions, but they also maintain specific and functional diversity, as well as the ecological succession of the natural ecosystem [155].

Baker [156] proposed the classification of these plants into three groups: (i) excluders, when they limit the absorption and translocation of potentially toxic elements, maintaining low concentrations of these elements in their aerial tissues, at least up to a critical value above which the exclusion mechanism breaks down, resulting in unrestricted transport and toxicity (plant/soil concentration factors < 1); (ii) indicators, which accumulate PTEs in their harvestable parts in concentrations similar to those present in the polluted soil (plant/soil concentration factors near 1); and (iii) accumulators, which increase the absorption, translocation and accumulation of PTEs in their above-ground biomass, reaching levels that far exceed those present in polluted soil (the ratio of the concentration of the element in the plant to that in the soil > 1) [156–159].

Metal-tolerant plants prevent toxicity from excess PTEs through special cellular mechanisms, as long as the metal concentrations in the soil do not exceed the metal tolerance levels. Several tolerance mechanisms have been proposed to explain how some plants compete successfully in toxic environmental conditions, being able to develop tolerant ecotypes, such as the exudation of organic ligands from the root, changing the cell wall, resulting in a decreased permeability to the toxic metal ion, taking up the element but rendering it harmful by deposition in the cell wall or vacuoles, excreting it, or modifying their mechanisms (e.g., producing specific enzymes) to allow their harmless accumulation [160,161]. These characteristics allow them to thrive in soils that are very toxic to non-adapted species. Plants capable of tolerating PTEs' toxicities and growing in metalliferous soils are called metallophytes [24,162]. Some metallophytes are inclusively considered as hyperaccumulaters, because they possess specialized mechanisms to accumulate metals in their tissues up to several times higher than their concentrations in the soil [130].

Taking all these into consideration, it is very important to assess the native species and populations in soils affected by mining activities in the IPB, because, among that group, there may be interesting candidates for use in the revegetation of soils in rehabilitated areas, or in phytoremediation projects [103,118]. In fact, currently, there is a growing interest in the use of species and populations of native plants for the revegetation of sites polluted by PTEs [163–165]. This strategy avoids the introduction of non-native and potentially invasive species that can result in a decrease in the local phytodiversity and endanger the harmony of the ecosystem [165], allowing the conservation of the metallophyte biodiversity [166].

One other aspect in favor of using native plants in a phytoremediation strategy in the mines of the IPB is their adaptability to the harsh semi-arid climate of the Mediterranean area. For instance, in Aljustrel, the maximum temperature can reach 40 °C in the summer, from June to September, and a minimum of 5 °C in the winter (from December to March), while the mean annual rainfall in the area is estimated to be 550 mm, with 85% of that rainfall occurring during the wet period, from October to April [88].

In the Aljustrel mine, even in the most contaminated area (Algares), now rehabilitated by EDM, Alvarenga et al. [43] found *Cistus ladanifer* (Gum Cistus, Esteva) to be spontaneously colonizing the area (Figure 4a), and they evaluated the behavior of the plant regarding its Cu, Pb and Zn uptake and accumulation. *C. ladanifer* largely succeeded in preventing these elements from reaching toxic levels in the leaves, with low leaf/soil concentration ratios (0.05 for Cu, 0.02 for Pb and 0.69 for Zn, mean values, n = 22) [43]. Therefore, they considered *C. ladanifer* as a Cu and Pb excluder, with a restrictive mechanism to the uptake of these metals into the aerial plant parts, and as an indicator of Zn, at least to a certain level of total Zn concentration in the soil [43].

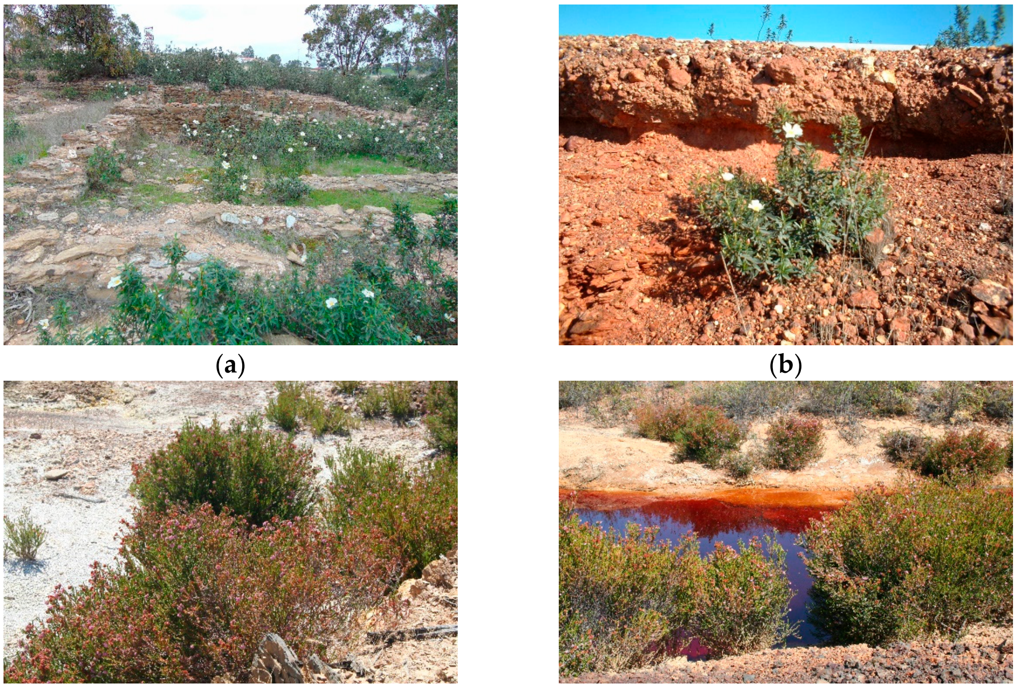

Figure 4. Native plant species found in mines in the Portuguese sector of the IPB: (**a**) *Cistus ladanifer* L. in Aljustrel mine and (**b**) in São Domingos mine; (**c**) *Erica andevalensis* in tailing deposits in the São Domingos mine and (**d**) close to AMD-affected streams in the São Domingos mine.

Natural vegetation at Aljustrel was surveyed by Candeias et al. [82], identifying the presence of *Quercus rotundifolia*, *C. ladanifer*, *Genista hirsute*, *C. salviifolius*, *C. crispus*, *C. monspeliensis* and *Lavandula luisieri*, while Eucalyptus plantations (*Eucalyptus camaldulensis*) have replaced the original oak forest [82]. *Cistus* is a typical Mediterranean shrub, adapted to drought and low nutrient availability, ubiquitous in the soils of the IPB [92]. The widespread of *C. ladanifer* and *Q. rotundifolia* (Azinheira) was also identified by Farago et al. [157] while surveying the area of Neves Corvo, an active mine in the IPB. They found that *C. ladanifer* behaved as a Cu accumulator in the mine area, on the contrary to the results found by Alvarenga et al. [43], and as an indicator of Pb and Zn [157]. In fact, the classification of a plant as an excluder/indicator/accumulator does not always agree among the studies from different authors, mostly because the classification suggested by Baker [156] relies in the ratio of the concentration of the element in the plant to its total concentration in the soil [43,156,157], and it is consensual that the plant responds to the bioavailable fraction of an element, and not to its total concentration [8].

Several authors studied the plant community at the São Domingos mine [92,96,167–170]. Freitas et al. [92] performed a wide survey, identifying 24 plant species in the mine area. The higher concentrations for Pb and As, precisely the PTEs with higher concentrations affecting this mine, were found in the semi-aquatic species: *Juncus conglomeratus* (84.8 and 23.5 mg kg^{-1} DW), *Juncus efusus* (22.4 and 8.5 mg kg^{-1} DW) and *Scirpus holoschoenus* (51.7 and 8.0 mg kg^{-1} DW), respectively [92]. Additionally, in this study, Pb above 20 mg kg^{-1} was found in the leaves of three species of *Cistus* [92]. Santos et al. [96] addressed the adaptability of *C. ladanifer* in the São Domingos mine (Figure 4b). These authors found that an effective antioxidant enzyme-based defense system endured *C. ladanifer* to cope with the co-existence of several stress factors besides high PTEs content, such as high temperature, UV radiation, drought [96].

A reduced number of trees was found in the São Domingos contaminated area, all showing accumulation of specific PTEs in their aboveground tissues: *Eucalyptus*, *Quercus* and *Pinus* species [92]. The authors suggested the use of these trees in the phytoremediation of the less-contaminated peripheral zone of areas to be remediated [92]. Andráš et al. [171]

evaluated the bioaccumulation of *Pinus* sp. and *Quercus* sp. regarding different PTEs in the São Domingos area (Pb, Zn, As and Sb), and concluded, by their low bioconcentration and translocation factors, that these trees were not adequate for phytoextration purposes, but were more adequate for phytostabilization.

The natural vegetation in the São Domingos mining area was also assessed in the scope of the MINEO project [17], and their observations were similar to those of Freitas et al. [92]. The plants were dominated by *Cistus* spp. and *Lavandula* sp. in the schists and basin margins, with *C. ladanifer* reflecting acidic soils which were non-carbonated and very degraded [17]. The dominant shrubs identified at São Domingos were *Lavandula stoechas* L. subsp. *pedunculata* (Miller) Samp. and Rozeira and *Genista hirsuta* Vahl, trees were dominated by *Quercus ilex*, while *Juncus* sp. was found near water streams [17].

Semi-aquatic species from the Juncaceae family have been identified by other authors in the IPB, such as Henriques and Fernandes [172], who evaluated the metal content in the soils and their uptake and distribution in rush (*Juncus conglomeratus* L.) plants growing in pyrite mine tailings at Lousal, while Alvarenga et al. [14] identified *S. holoschoenus* as one of the predominant macrophytes in the banks of the Água Forte stream, heavily affected by AMD from the Aljustrel mining area, prior to the EDM rehabilitation program in the area.

Other authors have indicated the presence in São Domingos of two endemic species of the genera *Erica*, which have the capacity to grow in metal-enriched and acid soils: *Erica andevalensis* Cabezudo & Rivera and *Erica australis* L. [168–170,173]. These species are as-tolerant, even in soils with high As total concentrations, such as in the São Domingos mine, and also in mines in the Spanish sector of the IPB [168]. *E. andevalensis*'s geographic distribution is limited to pyrite mine environments (soils with pH between 3 and 4), and can be found colonizing contaminated tailings (Figure 4c) and growing in the banks of streams affected by AMD, such as those in the São Domingos mine (Figure 4d), or in the Tinto and Odiel rivers [168,169]. *E. australis* is also endemic to the Iberian Peninsula, but is not site-specific, growing also in non-contaminated areas. It can be found thriving in these soils with high concentrations of PTEs, such as As, Cu and Pb, but is only found in soils with pH values above 3.5 [92,168,169]. Márquez-García et al. [169] measured different As chemical forms, organic and inorganic (arsenite and arsenate), in soils and in both *Erica* species in the São Domingos area. They found both shrubs in soils with high concentrations of As (194–7924 mg kg^{-1} DW), and also high concentrations of As in the plants: 1–24.4 mg kg^{-1} in *E. andevalensis* (mainly arsenate) and 2.7-11.6 mg kg^{-1} in *E. australis* (mainly arsenite). The As organic forms were almost absent, suggesting that these species possess different tolerance mechanisms for the different As chemical forms [169].

Therefore, before starting any phytoremediation process, it is imperative to study the natural vegetation of the polluted sites, in search of potential candidates [174,175], and this strategy was adopted by several authors who surveyed the indigenous IPB plants or evaluated their use in field experiments (Table 3).

The tailings from the mine represent a great danger to human and environmental health, and the establishment of vegetation cover in mine tailings can help to reduce the dispersion of pollutants into the surroundings [183]. The implementation of vegetation cover to stabilize mine waste has been suggested by some authors as a desirable long-term solution [33,165], considering this an environmentally friendly, sustainable, and relatively inexpensive technique [136,183]. In fact, the establishment of vegetation cover in tailings will prevent downwards leaching, the dispersion of contaminated particles by the wind, and lateral flow [184]. However, the germination and development of vegetation directly on tailings can be very difficult, sometimes impossible, especially in areas with a Mediterranean climate, even considering mine ecotypes [155]. Wang et al. [33] reviewed the possibilities of in situ phytoremediation of mine tailings, using tolerant plants, and the more efficient strategies to cope with their detrimental characteristics, e.g., low pH, high salinity, low water holding capacity, high PTEs concentrations, and deficiencies in organic matter and nutrients.

Table 3. Native plant species surveyed or used in some remediation projects in the IPB.

Plant(s)	Study Location	Main Features	References
Erica australis L. and *Nerium oleander* L.	Río Tinto (Huelva, Spain), soils with extreme acidity and elevated concentrations of PTEs (e.g., Cu, Cd, Pb)	*E. australis* was indicated to be used in early stages of phytostabilization programs, ideally to improve the soils/substrate physical and chemical properties and favor the establishment of less tolerant species, such as *N. oleander*	[53]
Erica andevalensis	Río Tinto mine tailings with very high As, Cu, Fe and Pb concentrations (up to 4114, 1050, 71,900 and 15,614 µg/g dry weight, respectively	The ability of *E. andevalensis* to grow in these contaminated substrates, makes it a good candidate to be used in the phytostabilization of Rio tinto mine tailings	[46]
Several species of the genera *Erica*, *Quercus*, *Lavandula*, *Cistus*, *Genista*, and *Cytisus*	Río Tinto (Huelva, Spain)	Río Tinto mine flora is made of Fe, Cu, Zn, Ni, As, and Pb excluders, although some analyzed species can be considered Mn accumulators	[103]
Pinus pinaster Aiton, *Quercus rotundifolia* Lam.	São Domingos mine, with high concentrations of Pb, Zn, As, and Sb	The overall low translocation factors evidence their ability to be used in phytostabilization projects	[94]
Cistus ladanifer L.	Technosols with gossan and sulfide wastes from the São Domingos mine	The application of a gossan/Technosol layer over sulfide wastes allowed *C. ladanifer* germination, but plant survival was not good after 50 days	[28]
Cistus ladanifer L.	São Domingos mine soils, with high total As and Pb concentratios, and in gossan mine wastes	Tolerance mechanisms of *C. ladanifer* to As- and Pb-contaminated soils is due to an effective antioxidant enzyme-based defense system. *C. ladanifer* is suitable for the phytostabilization of mine soils with similar characteristics	[96,176,177]
Cistus ladanifer L.	Brancanes, Caveira, Chança, Lousal, Neves Corvo and São Domingos mines	*C. ladanifer* plants are able to survive in mining areas with polymetallic contamination at different element concentrations in total and available fractions, avoiding the accumulators of the majority of the analyzed elements	[54]
Erica andevalensis Cabezudo & Rivera and *Erica australis* L.	São Domingos mine, with high As concentrations (194–7924 mg kg^{-1} soil DW)	Both plants species are well-adapted to the high As concentrations in soils, with different tolerance mechanisms	[51,169]
E. australis, *E. andevalensis*, *Lavandula luisierra*, *Daphne gnidium*, *Rumex induratus*, *Ulex eriocladus*, *Juncus*, and *Genista hirsutus*	São Domingos mine tailings, with high concentrations of As, Ag, Cr, Hg, Sn, Sb, Fe, and Zn	Considering the tolerance of the referred plants, they are recommended for the rehabilitation and recovery of this type of degraded mining areas	[47]
Erica andevalensis and *Erica australis*	São Domingos mine, acid soils highly contaminated with Pb, As and Sb (also Cu and Zn in some sites)	*E. andevalensis* grows in soil with pH 3–4, while *E. australis* is only found in soils with pH > 3.5. Their extreme tolerance suggests their use in the recovery of sulfide mine areas	[168]
Cistus ladanifer L.	Aljustrel mine soils, with low pH and elevated concentrations of Mn, Cu, Pb and Zn	*C. ladanifer* evidenced the capacity to grow in contaminated soils, being a Cu and Pb excluder and Zn indicator, making it a good candidate to be used in the phytostabilization of similar mining areas	[43]

Table 3. *Cont.*

Plant(s)	Study Location	Main Features	References
Several species of the genera *Erica*, *Quercus*, *Lavandula*, *Cistus*, *Genista*, and *Cytisus*	Río Tinto (Huelva, Spain), soils with extreme acidity and elevated concentrations of PTEs	Río Tinto mine flora is made up of Fe, Cu, Zn, Ni, As, and Pb excluders, although some analyzed species can be considered Mn accumulators	[103]
Cynodon dactylon (L.) Pers.	Field experiment installed at the Aznalcóllar soils affected by a toxic mine spill (low pH, contamination with As Zn, Cu, Pb, and Cd)	Dominant species of grass in all treatments of contaminated soils with different amendments application	[178]
Brassica juncea (L.) Czern.	Aznalcóllar soils affected by a toxic mine spill (low pH, contamination with As Zn, Cu, Pb, and Cd)	Successful installation of plant cover in a 4-year field experiment	[179,180]
Eucalyptus camaldulensis	Guadiamar valley, affected by the Aznalcóllar toxic mine spill	*E. camaldulensis* tolerated elevated PTE concentrations in soil, present low bioaccumulation coefficients for those elements, and had fast growth and a deep root system, and are therefore suitable for phytostabilization	[181]
Lamarckia aurea (L.) Moench and *Trifolium campestre* Schreb	Guadiamar Green Corridor (SW, Spain) 18 years after the Aznalcóllar toxic spill (contamination with Cu, Zn, Cd, As and Pb)	These plants were dominant in severely contaminated soil. High Cu and Cd potential toxic concentrations in aerial parts, which indicate plant adaptation mechanisms to live in severely polluted soils	[182]

Despite all these shortcomings of the phytoremediation of mine tailings, several field studies have shown that phytostabilization can effectively reduce the movement of PTEs in mine-contaminated soils, by modifying the speciation, as well as improving the physicochemical properties of the soil [129,185–187]. Some of these studies were applied to IPB contaminated sites, such as those conducted by different teams in the soils affected by the toxic spill of pyrite residue at Aznalcóllar (southwest Spain) in 1998. For instance, Clemente et al. [179,180], following a 4-year active phytoremediation program in a soil contaminated with As, Zn, Cu, Pb, and Cd in that area, using organic amendments (cow manure and compost) and lime and growing two successive crops of *Brassica juncea* (L.) Czern., followed by natural attenuation, achieved successful results without further intervention. In an experimental field at El Vicario, also in the area affected by the toxic mine spill from Aznalcollar, a team from Seville was able to establish a field experiment with soils amended with different materials (biosolid compost, sugar beet lime, and combination of leonardite plus sugar beet lime), and they were successful in the stabilization of the same PTEs [188,189], and in the regrowth of natural vegetation [44,178,190–192], allowing the improvement of some soil properties [193], such as the diversity of arbuscular mycorrhizal fungi [194] and in the soil carbon sequestration potential [195].

However, the physical and chemical properties of these soils (low nutrient and organic matter content and extreme pH), associated with high concentrations of PTEs, sometimes hinder the vegetation establishment in contaminated sites [196], and, to be successful in a phytostabilization strategy, it is very important to improve the soil's capacity to sustain vegetation cover [161], which can be achieved by adequately amending the soil, for example with organic and inorganic additives [43,57,58,81,127,197,198].

3.5. Soil Amendments in Phytotechnologies

The addition of organic and/or inorganic additives to mine soils, or even tailings, has been a widely used strategy to promote suitable conditions for plant growth, coping with their main constraints, by adding essential nutrients and organic matter, reducing the acidity, increasing the water holding capacity, and making PTEs less mobile or bioavailable, increasing their association with organic matter, carbonates or metal oxides [109,127,129,152,175,186,199–202]. The improvement in these soil properties is of major importance, not only to promote plant growth, but also to increase soil microbial activity [28,203–205].

Soil amendments can be organic or inorganic materials. While organic amendments are mainly applied to increase soil organic matter content, but also provide nutrients and may have the ability to increase soil pH, inorganic amendments are mainly applied with the purpose of alleviating soil acidity, one of the major problems of soils in pyritic environments. The addition of alkaline amendments will increase the pH of soil and, therefore, reduce the availability of metals, while the application of organic materials will improve plant nutrition and growth [58,152,196,206,207]. Nevertheless, it is not negligible the role of some organic amendments in the correction of pH and in the PTEs immobilization. That was proven by many studies developed in contaminated soils in the IPB, as specified in Table 4 [57,58,129,196,208–212].

In fact, the combination of metal-tolerant plants (phytostabilization) and organic or inorganic additives (chemical stabilization), sometimes termed “assisted phytostabilization” or “aided phytstabilization”, and considered as a sustainable in situ phytoremediation strategy [57,202,203,208,213]. Assisted phytostabilization will simultaneously reduce the mobility/bioavailability of PTEs in soil, thus reducing the leaching and transference through the trophic web, improving soil microbial properties and facilitating plant establishment (revegetation) [142]. Phytostabilization strategies have the potential to mitigate the environmental impact of soils contaminated by PTEs, improving the physical, chemical and biological properties of mining soils [23,142,214–218]. Plus, they have great potential to be applied in large areas [219].

In most of the studies aiming at the evaluation of proper materials to ameliorate mine soils, waste-derived materials were considered. This was achieved taking into account the European Waste Framework Directive (2008/98/EC) [220], which states that the disposal of waste in landfills should be the last option to be considered in its management and that the integration of certain wastes in the production system should be promoted. This approach is also aligned with the European targets considering a circular economy.

There are many examples of studies performed with the aim of improving the quality of mine-contaminated soils in the IPB, by the addition of waste-derived amendments (Table 4). While some of these studies aimed at the remediation of soils from abandoned pyrite mines, others intended to ameliorate agricultural soils which were contaminated by the Aznalcóllar spill accident [193].

It is possible to group the waste-derived amendments used in different groups, and some representative results are presented in Table 4, including:

(i) Organic amendments produced in wastewater treatment plants, such as sewage sludge (biosolids) or biosolids compost [57,58,188,192,208,221–223], or in the management of the organic fraction of municipal solid wastes, which can be composted [49,57,179,185,197,208,222,224,225];

(ii) Wastes or by-products typical of specific areas of the IPB, and that sometimes are problematic for their over-production or seasonality, such as the olive pomace, “alperujo”, the solid by-product from the extraction of olive oil [210,223], sugarbeet sludge, an alkaline residual waste from the sugar manufacturing process [58,188,192,222,223,226], paper mill sludge [81,200], or from animal production, such as slurries and manures (e.g., pig slurry [142,202,210,227], cow manure or slurry [142,200], poultry manure [200], composted horse manure [228], and green waste compost [49,57,58,206,208,209,211];

(iii) Ash-based materials, which are very alkaline (i.e., pH ranging from 9 to 13), used mainly as liming agents, increasing the pH and buffering capacity of acid soils, but that can also provide nutrients, such biomass-ash or biomass-ash-based material (e.g., granules) from the pulp and paper industry [81,229–233], or coal combustion fly ash [36].
(iv) More uncommon wastes (organic or inorganic) which are not so usually used as agricultural soil amendments, but could be used in the rehabilitation of mine soils, avoiding their landfilling, and allowing their valorization, such as drinking water treatment residuals [198], polyacrylate polymers [234], or hydroxyapatite, chegemite, and calthemite [29].
(v) Biochar, a material which results from the pyrolysis of different organic materials under limiting oxygen conditions [235], has been proposed successfully to remediate soils affected by high concentrations of PTEs [196,236–238]. In fact, biochar is a carbonaceous material which is highly porous, with a large surface area, low density, high cation exchange capacity, and alkaline pH, which makes it a very interesting material to be used in the remediation of PTE contaminated mine soils, by reducing their available concentrations in the amended soils, important in a phytostabilization strategy.

In some studies, inorganic and organic additives were used in combination, complementing each specific deficiencies [152,207,239–241], which is evidenced in the information in Table 4.

There is also another possibility to improve the process; that is the combined use of plants and their associated microorganisms, partially aided by the use of organic and inorganic additives and soil management practices (plant selection, soil management practices, crop rotation, short rotation coppice, intercropping/row cropping, planting methods and plant densities, harvest and fertilization management, pest and weed control and irrigation management) [126,150].

Table 4. Examples of combination of amendments used in the remediation of soils affected by mining activities in the IPB, or in similar edaphoclimatic conditions, application doses, soil characteristics, and important conclusions.

Type of Amendment(s)	Origin of the Soil/Main Contaminants	Lab or Field Experiment/Doses	Main Outcomes	References
Four different amendments: municipal waste compost, biosolid compost, leonardite (a low grade coal rich in humic acids) and a litter	Soil from the Aznalcóllar mine spill accident (acid, elevated concentrations of Cd, Cu and Zn)	In situ experiment (in containers), 100 Mg ha^{-1} of each material in one year (Mora et al. 2005) and 50 Mg ha^{-1} 12 months later (Pérez-de-Mora et al. 2006)	The amendments increased soil pH and carbon content and diminished soluble PTEs concentrations. The organic amendments increased soils biological indicators (enzymes activities and microbial biomass)	[221,222]
Organic amendment: biosolid compost (BC) and the inorganic amendment: sugar beet lime (SL), a residual material from sugar beet processing	Soil from the Aznalcóllar mine spill accident (acid, elevated concentrations of As, Cd, Cu and Zn)	In situ experiment (in containers), 100 Mg ha^{-1} of each material in one year (Mora et al. 2005) and 50 Mg ha^{-1} 12 months later (Pérez-de-Mora et al. 2006)	Four to six years after the initial amendment applications, the results indicate that the need for re-treatment is amendment- and element-dependent	[192]

Table 4. *Cont.*

Type of Amendment(s)	Origin of the Soil/Main Contaminants	Lab or Field Experiment/Doses	Main Outcomes	References
Biosolid compost (BC), sugar beet lime (SL), and a combination of leonardite (LE), plus sugar beet lime (LESL)	Soil from the Aznalcóllar mine spill accident (acid, elevated concentrations of Cd, Cu and Zn)	In situ experiment in soil plots, two consecutive years of application (2002 and 2003): SL 30 Mg ha^{-1} yr^{-1}, BC 30 Mg ha^{-1} yr^{-1}, and a mixture of 25 Mg ha^{-1} of LE mixed with 10 Mg ha^{-1} of SL	A 4-year study was undertaken, $CaCl_2$-extractable metal concentrations decreased and were similar in all treatments	[188,190]
Organic amendment: biosolid compost (BC) and the inorganic amendment: sugar beet lime (SL), a residual material from sugar beet processing	Study site at the Aznalcóllar mine spill accident (acid, elevated concentrations of Cd, Cu and Zn)	In situ experiment in soil plots, two consecutive years of application: SL 30 t ha^{-1} yr^{-1} and BC 30 t ha^{-1} yr^{-1} (the experiment started in 2002, continued to be monitored)	In general, the amendments increased soil pH and total organic carbon (15 years after treatment). The available PTEs concentrations ($CaCl_2$ extraction) decreased drastically with time in all cases. Seven tree species were established	[193]
Biosolid compost (BC), fresh "alperujo" (AL), the solid by-product from the extraction of olive oil), and sugarbeet lime (SL),	Two different soils from the Aznalcóllar polluted area (pH 3.32 and 7.76)	Microcosms under controlled conditions, 40-week-period (doses were calculated to be similar to those applied in the field experiments (approximately 30 t ha^{-1})	pH increased in the acidic soil, by the addition of the alkaline by-products (SL and BC), decreasing PTEs availability and slight improving the biochemical status during the first weeks of incubation. In neutral soil, the addition of by-products did not cause any change	[223]
Sewage sludge (SS), compost produced from the organic fraction of municipal solid waste (MSWC), and agricultural wastes compost (AWC)	Soils from the Aljustrel mine (acid soils, with elevated concentrations of Cu, Pb and Zn)	Greenhouse experiment with 25, 50 and 100 Mg ha^{-1} of SS, and similar application rates of the other materials to equalize the organic matter added	Better results with 50 Mg ha^{-1} of the amendments: improvement in the soils physicochemical properties, decrease in PTEs extractability, increase in plant biomass, and better responses from the ecotoxicological indicators and soil enzymatic activities	[57,58]

Table 4. *Cont.*

Type of Amendment(s)	Origin of the Soil/Main Contaminants	Lab or Field Experiment/Doses	Main Outcomes	References
Sewage sludge (SS), sugar beet sludge (SBS), or of a combination of both	Highly acidic (pH 3.6) metal-contaminated soil, from the Aljustrel mine (Cu, Pb and Zn)	Greenhouse experiment. SS was applied at 100 and 200 Mg ha^{-1} (dry weight basis), and the SBS at 7 Mg ha^{-1}. Sown with *Lolium perenne*.	SS, particularly in combination with SBS, corrected soil acidity, while improving other soil physicochemical properties, decrease CaCl2-extratable Cu, Pb and Zn, while decreasing soil ecotoxicity response and soil enzymatic activities	[242]
Mixed municipal solid waste compost (MMSWC) and green waste-derived compost (GWC) as immobilizing	Soils from the Aljustrel mine (acid soils, with elevated concentrations of Cu, Pb and Zn)	Semi-field experiment, outdoors. Application ratio was 50 Mg ha^{-1} for both composts, but GWC was additionally limed and supplemented with mineral fertilizers. Sown with *Agrostis tenuis*	Both treatments had an equivalent capacity to raise soil organic matter and pH, allowing the establishment of a plant cover, and effectively decreasing bioavailable Cu and Zn Amended soil had higher soil enzymatic activities, especially in the presence of plants	[197]
Drinking water treatment residuals (DWTR)	Soils from the Aljustrel mine (acid soils, with elevated concentrations of Cu, Pb and Zn)	Greenhouse experiment, with the equivalent to 48, 96 and 144 Mg DM ha^{-1}, with and without lime application ($CaCO_3$ 11 Mg DM ha^{-1})	The highest application doses of DWTR with lime, allowed a reduction in mine ecotoxicity indicators, beside the expectable improvement in soil physicochemical properties and PTEs extractability	[198]
Biomass-ash based material (e.g., granules) from the pulp and paper industry and biologic sludges from paper mill wastewater treatment plant	Soils from the Aljustrel mine (acid soils, with elevated concentrations of Cu, Pb and Zn)	Pot experiment. Biomass ash (A) and biological sludge (S), in different granular formulations (90% A + 10% S, and 70% A + 30% S w/w, dry weight basis: dw) were added to soil (2.5, 5.0 and 10% (w/w, dry matter), with and without the application of municipal solid waste compost (MSWC) (dose equivalent to 50 t ha^{-1})	Soil pH increased to neutral values and Cu and Zn $CaCl_2$ extractability decreased. Some soil enzymatic activities increased, and soil-water extract toxicity decreased, however phytotoxicity to *Agrostis tenuis* Sibth. was observed	[81]

Table 4. *Cont.*

Type of Amendment(s)	Origin of the Soil/Main Contaminants	Lab or Field Experiment/Doses	Main Outcomes	References
Cow manure, compost, dry matter basis, and lime	Site affected by the toxic spill of pyrite residue at Aznalcóllar, extremely acidic values (mean pH 4.1). Elevated concentrations of As, Zn, Cu, Pb, Cd)	Field experiment, 4-year, in situ phytoremediation, cow manure (36 t ha^{-1}), compost (13.6 t ha^{-1}), dry matter basis, and lime (up to 64 t ha^{-1}) growing two successive crops of *Brassica juncea* (L.) Czern.	The success of active phytoremediation followed by natural attenuation was evident, by the correction of soil pH, the lowering of extractable PTEs and plant establishment	[180]
Pig slurry (PS) and olive mil-waste compost (C); in combination with hydrated lime (HL)	Mine spoil soil from the mining area of La Unión-Cartagena (Murcia, SE Spain), acid (pH 3.5), high concentrations of As, Pb (14 532 mg kg^{-1}) and Zn	Mesocosm experiment, in columns, initial dose of 60 t ha^{-1} C and 60 m^3 ha^{-1} PS, respectively, and a second addition, 2 weeks later, of 30 t ha^{-1} and 30 m^3 ha^{-1} of de same materials with 15.5 t ha^{-1} of HL, (equal available N provided), sown wit *Lolium perenne*	The amendments (especially the compost) successfully reduced PTEs solubility modifying pH, and slightly reduced the direct and indirect soil toxicity to plants, invertebrates and microorganisms but with the risk of N leaching in some treatments	[225,227]
Olive mil-waste compost, fresh pig slurry, and hydrated lime	Mine soil highly contaminated with PTEs, from the mining area of La Unión-Cartagena	Field experiment, 2.5-year, 60 t ha^{-1} compost, 60 m^3 ha^{-1} fresh pig slurry, and hydrated lime (2.3 t ha^{-1}) plantation with *Atriplex halimus*	Globally, a successful phytostabilization experiment, with improvement in soil health considering chemical, microbial and ecotoxicity indicators	[129]
Rockwool industrial waste, agriculture wastes (plant remains + strawberry substrate) and wastes from liquor distillation of Arbutus unedo L. fruits	Sulfide mine wastes from the São Domingos mine (acidic, high electrical conductivity and total PTEs concentrations (As and Pb)	Greenhouse pot experiments (13 months) to evaluate the effect of two amendment mixture doses (30 or 75 Mg/ha) containing distinct organic and inorganic wastes from: green agriculture (plant remains + strawberry substrate at 2:3 m/m), *Arbutus unedo* L. and *Ceratonia siliqua* L. fruit spirit distillation; and rockwool used for strawberry crops. Limestone rock wastes were also used at 55 Mg/ha to raise the mine wastes pH to ≈ 4	The leachate characteristics were not influenced by amendment doses, but they all presented low concentrations of PTEs after 13 months. The same materials were used to design Technosols, to make an alkaline barrier to isolate sulfide-rich wastes, and plant *Lavandula pedunculata* and *Cistus ladanifer*	[243,244].

Table 4. *Cont.*

Type of Amendment(s)	Origin of the Soil/Main Contaminants	Lab or Field Experiment/Doses	Main Outcomes	References
Three different nanoparticles (NPs) were applied: hydroxyapatite (HANPs), (ii) hematite (HMNPs) and (iii) maghemite (MNPs)	Soil from São Domingos mine, developed over spoils and mining sulfide-rich wastes, mainly composed of gossaneous materials and host rocks (Spolic Technosols)	Incubation experiment. Stock suspensions were prepared of each NPs, 5 g NPs/L (100 mL stock suspensions were added per 10 g of soil)	Phosphate and iron oxide NPs were efficiency to reduce PTEs mobility in mine soils, some more efficient to As and others to Pb	[29]

More ways to improve large-scale applications are being studied, including the application of genetic engineering approaches, such as transgenic transformation, the addition of nanoparticles and phytohormone-assisted phytoremediation, plant growth-promoting bacteria, arbuscular mycorrhizal fungi inoculation [138,161], the use of chelating agents, planting transgenic plants, using bacteria and applying plant growth regulators [245].

However, the rehabilitation of mining areas is a long process in which the dynamics of the PTEs are uncertain, and therefore periodic monitoring and adaptive management are necessary [113,139,213,246,247]. Moreover, soil ameliorants used to increase PTEs immobilization may need to be reapplied periodically to maintain their effectiveness [139,192].

4. Conclusions

Mining is an activity that has significantly contributed to socio-economic development but also to environmental degradation, both in the area explored and in the surrounding region. One of the most worrying environmental risks is related to the waste deposits, whose weathering contributes to acid drainage and the spread of PTEs. The drainage of these acidic waters causes the dispersion of metals and the contamination and acidification of waters and soils.

For this reason, it is important to proceed with the environmental recovery of these sites, it being necessary to plan and carry out the remediation of the soils. The removal and confinement of these waste materials is very important, as well as the rehabilitation of the damaged structures which were left abandoned.

However, the amelioration of the soil's properties in large areas surrounding the mining sites after these interventions is of paramount importance to enable the recovery of essential soil functions and soil health. This can be completed via the correction of soil acidic pH and OM and nutrients limitations, which can be performed by means of the application of low-cost waste-derived organic and inorganic amendments, followed by phytostabilization, selecting the adequate plants. This strategy will allow the improvement of the overall soil health and the replenish of its ecosystem functions.

This recovery depends on creating and maintaining the ideal conditions for plant growth. Additionally, it is important to use native plants because they are better in terms of survival, growth, and reproduction under environmental stress than plants introduced from other environments. The rehabilitation of mining areas is a long, expensive, and complex process, and it should encompass monitoring as an essential component of its management strategy.

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