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RESEARCH ARTICLE

Vegetation establishment in soils polluted by heavy metal(loid)s after assisted natural remediation

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Abstract
Background and aims This field-base study evaluates the long-term effectiveness of in-situ remediation measures applied to soils residually polluted by potentially toxic elements (PTEs) in an area affected by a mining spill in SW Spain.
Methods To evaluate the remediation treatments success, their influence on key soil properties and on the development of spontaneous vegetation in the treated soils was investigated. The treatments were based on human derived by-products valorization, and consisted of: biopiles, marble sludge and gypsum mining spoil addition, and their combination with an organic amendment (vermicompost).
Results Amendments application improved the soil properties and reduced PTEs availability. As a result, an enhancement in spontaneous development of vegetation cover and diversity of plant species in the treated soils was followed. *Spergularia rubra* and *Lamarckia aurea*, two primary plant species growing in the studied area and that exhibit strong association to soils with the highest levels of pollution, showed high Pb and As accumulation in shoots ande in roots. Exceptionally, accumulation of these pollutants occurred in *L. aurea* roots, which can explain its high presence in soils with more limited vegetation development and in which no additional plant species can thrive.
Conclusions The occurrence of *S. rubra* and *L. aurea* in the amended soils may be indicative of improved soil conditions and reduced toxicity induced by the remediation measures implemented. They may also be considered key species in the area since their presence can promote the recolonization

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of the degraded soils by species less tolerant to their residual pollution.

Keywords Soil pollution · Soil remediation · Amendment · Assisted natural remediation · *Lamarckia aurea* · Bioaccumulation factor

Introduction

Soil, as a fundamental element of ecosystems, plays a crucial role in providing essential environmental functions and ecosystem services. Among these, soil productivity is one of the most essential services for the human well-being and its development (Kabata-Pendias 2010; Adhikari and Hartemink 2016). Nevertheless, soil faces several soil degradation processes that may threaten its quality, both natural and human-induced. Of the anthropogenic causes, soil pollution by potentially toxic elements (PTEs) represent one of the major threats and concerns worldwide (FAO and ITPS 2015), since it poses a risk to ecological systems, human health, and food production. Among all chemical pollutants, PTEs, including heavy metals and metalloids, can persist tightly bound in soil (Pilon-Smits 2005; Igalavithana et al. 2022). This can lead to cumulative impacts in organisms, ultimately making them a significant contributor to environmental pollution with implicit adverse effects to human health (Muyessar and Linsheng 2016). Although certain PTEs can act as essential elements and are involved in biological functions, such as Cu and Zn, they can turn potentially toxic when specific thresholds are exceeded (Gall et al. 2015). Other elements such as As and Pb are among the most hazardous PTEs, as very low concentrations of them can cause toxicity (Rahman and Singh 2019), causing serious problems of contamination in the food chain, with the consequent health risk (Simon 2014). Therefore, in order to preserve soil functions, degraded soil ecosystems polluted by PTEs would require assisted natural remediation, ANR (Adriano et al. 2004; Raklami et al. 2021).

With the aim of reducing the PTEs harmful effects in polluted soils, a wide range of techniques for soil remediation, either in-situ or ex-situ, and involving the use of both organic and inorganic amendments, have been developed and tested to assist natural remediation processes (Adriano et al. 2004; Park et al. 2011; Liu et al. 2018). The addition of amendments to the soil is considered as an economical and environmentally efficient solution that addresses pollutant toxicity and enhances critical biogeochemical mechanisms (Rodríguez-Jordá et al. 2012; Nirola et al. 2016). Moreover, the revalorization of mining and agro-food industry wastes through their application as amendments in degraded soils aligns with zero-waste strategies (Greyson 2007; Pietzsch et al. 2017). Numerous case studies corroborate the viability of organic and/or inorganic soil amendments under field conditions (Fernández-Caliani and Barba-Brioso 2010; González et al. 2012). More precisely, liming or calcium and organic matter-rich amendments are among the most effective ones, through the correction of soil acidic pH, the enhancement of soil physicochemical properties, the increase of nutrient availability and the immobilization of certain PTEs (Bernal et al. 2007; Pérez-de-Mora et al. 2007), which prevent from the potential spread of pollutants into the ecosystem. Consequently, a promotion in re-colonization and re-establishment in barren polluted soils by the vegetation from surrounding areas in the remediated soils may be achieved in turn (Fernández-Caliani and Barba-Brioso 2010; Xiong et al. 2015) through the enhancement of plant germination and growth (Clemente et al. 2015; Madejón et al. 2018; Sierra-Aragón et al. 2019).

Industrial activities, such as mining, represent one of the most significant potential sources of soil pollution by PTEs (Dermont et al. 2008; Liu et al. 2018), and several remediation treatments have been implemented in mining polluted areas. One of the greatest metal mining accidents worldwide took place in 1998 in Spain, after the collapse of the tailings dam of the Aznalcóllar pyrite mine, which resulted in the spill of acidic waters and tailings containing high concentrations of PTEs (Grimalt et al. 1999; Simón et al. 1999; Sanz-Ramos et al. 2022). Following, extensive cleanup and rehabilitation measures were implemented in the affected area to guarantee the safety of the local inhabitants and promote the full recovery of the area in the long term. However, several decades after the accident, numerous patches of residual polluted soils where vegetation cannot even germinate still remain in the area, and represent an environmental risk for their high PTEs concentrations (García-Carmona et al. 2017). Since the residual polluted patches are deeply integrated into a large recovered area (the Protected Landscape of Guadiamar Green Corridor), the mixture of adjacent recovered soil with the remaining polluted soil represents a plausible, economic, and minimally invasive technique. This treatment has been tested in previous experiments in the area with successful results directly tied to the improvement of soil properties and reduced PTEs solubility (García-Carmona et al 2017; Lorente-Casalini et al. 2021).

When evaluating the restoration processes of degraded or polluted areas, the presence of key components of ecosystems such as vegetation plays a crucial role as indicators of the extent of soil pollution. Trace elements, and particularly heavy metals, can be accumulated by plants, which are able to adapt to varying levels of environmental pollution (Kabata-Pendias 2010). Furthermore, passive restoration, which involves the natural recolonization of a polluted area by native vegetation and that ocurres in parallel to the conditions improvement, is crucial when assessing the effectiveness of remediation measures (Álvarez-Rogel et al. 2021), as these native plants may act as "nurse plants", promoting the growth of species with lower tolerance to stress conditions (Navarro-Cano et al. 2018). Additionally, the development of vegetation cover is relevant when considering the effectiveness of a specific treatment applied to a polluted soil, since it provides an extra physical protection and may reduce possible re-movement of pollutant particles and migration to groundwater (Pérez-de-Mora et al. 2006). However PTEs toxicity in plants can limit processes such as seed germination, root development, and growth, or disrupt the uptake of essential nutrients leading to plant death (Kabata-Pendias 2010). Nonetheless, a wide variety of strategies, both physiological and behavioral, allow numerous plant species to tolerate remarkably high PTEs concentrations (Baker et al. 2010; Viehweger 2014), such as metallophytes species inhabiting metalliferous deposits (Baker et al. 2010). Also, certain plant species not exclusive to metal-rich environments, known as pseudometallophytes (Baker et al. 2010), also exibit exceptional capacity to adapt to unfavourable soil conditions caused by pollution. Under moderate levels of soil metal toxicity, they can show higher biomass production and have competitive advantages over other species (Poschenrieder et al. 2001). Consequently, these species may contribute to improve the physicochemical and biological conditions of the polluted soils by handling the PTEs concentrations, enhancing nutrient availability, and increasing soil organic carbon (Arienzo et al. 2004; Bolan et al. 2011).

The aim of this study is to evaluate the long-term effects of in-situ remediation measures, based on the addition of inorganic and organic amendments (six different treatments), which were applied to soils residually polluted by PTEs. The influence of the treatments will be determined by analyzing: i) the changes induced in the main soil properties; ii) the mobility and bioavailability of PTEs after remediation and ageing; iii) the natural settling of PTEs tolerant plants, as an indicator of the success of the remediation actions used; and iv) the bioaccumulation and translocation factors of PTEs in these tolerant plant species, for a better understanding of the mechanisms that allow them to survive to the great concentrations present in the studied soils.

Material and methods

Study site and experimental design

The study site was located in the area nearby the tailings dam of the Aznalcóllar mine (Seville, SW Spain), which was most severely affected by the Aznalcóllar mining spill. This area is characterized by the presence of heterogeneously distributed bare soil patches of varying sizes, where high levels of pollution are still detected (Fig. 1a and b). For this study, three of these unvegetated residually polluted soil patches were selected (Fig. 1c). Within each of these patches, an experimental plot of 24 m^2 was set up, and divided into six subplots of 4 m^2 with a different treatment applied in each of them (Fig. 1d). The six treatments selected were the following: 1. BS: Biopile (50% w/w mixture of polluted soil -PS- with adjacent recovered soil -RS-); 2. BVS: Biopile + vermicompost; 3. GS: Gypsum mining spoil (5 kg m^{-2}); 4. GVS: Gypsum mining spoil + vermicompost; 5. MS: Marble sludge (5 kg m^{-2}); 6. MVS: Marble sludge + vermicompost. The doses applied of every

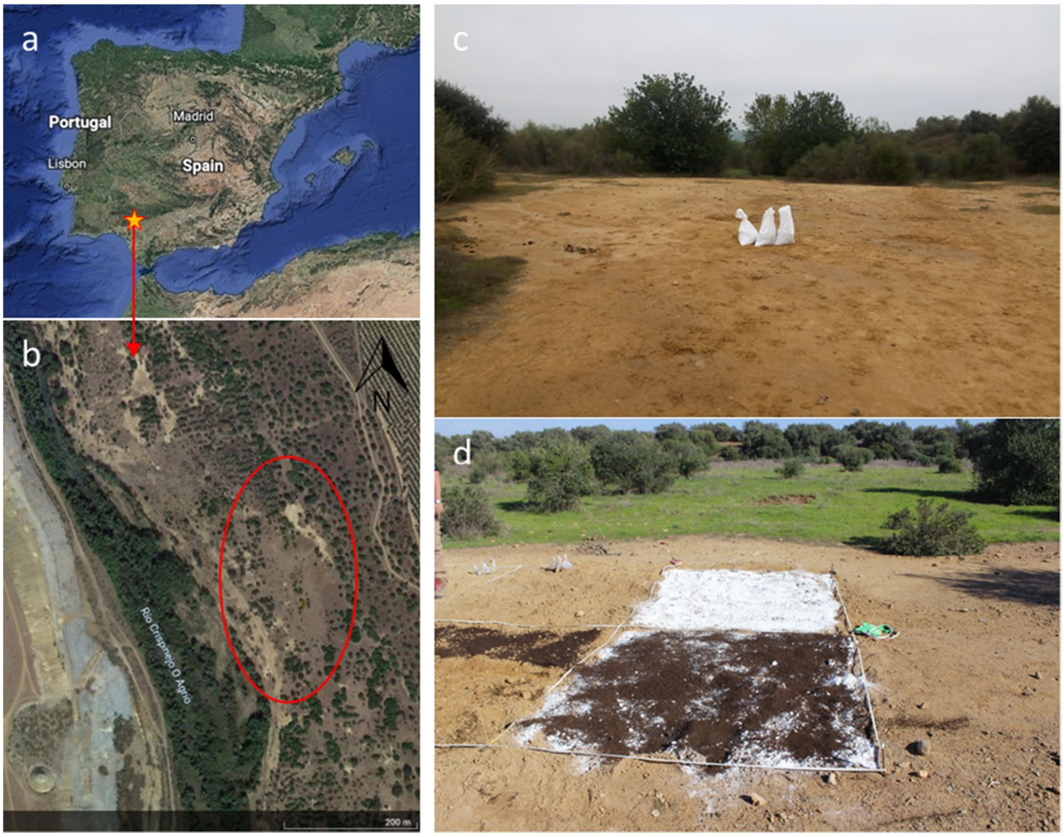

Fig. 1 Left: Study area location (**a**) and aerial image of selected unvegetated patches (**b**). Right: Detailed image of bare soils (**c**) and treatments application (**d**)

amendment was 5 kg m^{-2} for each subplot. The selected amendments were chosen for being calcium and organic matter-rich amendments, and in the case of the inorganic amendments, for representing low-cost waste materials generated in very large amounts that need to be sustainably managed (Rayed et al. 2019; García-Robles et al. 2022). The doses of gypsum mining spoil and marble sludge were selected according to the doses previously applied in the area for calcium-rich amendments (Madejón et al. 2018), and the ratio for the BS treatment was successfully tested in a previous ex-situ experiment (García-Carmona et al. 2017). In all cases, the dose of vermicompost was 5 kg m^{-2} (equivalent to 50 t ha^{-1}) because the organic amendments had been previously applied in the area at a rate of 15–25 t ha^{-1} (Cabrera et al. 2005, 2008) and resulted insufficient to promote vegetation growth. The characterization of the amendments (biopile, vermicompost, marble sludge and gypsum mining spoil) is shown in Table S1.

Soil and vegetation sampling

After a period of eighteen months following the implementation of the treatments, coinciding with the second spring, surface soil composite samples (0 – 10 cm) for each treatment were collected, and the key soil properties of them were determined. In addition, composite samples were also taken from untreated polluted soil (PS) within the unvegetated soil patches, from reclaimed soil adjacent to them (RS), and from soils unaffected by the spill near the studied area (US), which were considered reference soils for the different degrees of pollution. Moreover, vegetation cover and plant species richness present in every reference soil (in a representative 4 m^2 surface) and treatment applied were measured to monitor the vegetation development in the plots. This was done using a 0.25 m^2 quadrat divided into 100 cells, which was placed on the surface of each of the studied soil, and all the cells with presence of a herbaceous species were counted, both for total vegetation cover and for the specific cover of each species individually. Also, richness, considered as the mean total number of different species encountered on the quadrat, was determined for each treatment. This procedure was performed in triplicate for each experimental plot and treatment. Moreover, to analyze the potentially toxic elements (PTEs) uptake by the main colonizing species in the plots, samples of *Spergularia rubra* (L.) J. Presl & C. Presl and *Lamarckia aurea* (L.) Moench were collected.

Analytical methods

Soil properties

Soil samples were air dried at room temperature and sieved (< 2 mm). The main soil properties and constituents including pH, electrical conductivity, calcium carbonate content, and organic carbon content were analyzed following standard methods (MAPA 1994). Soil pH was determined in a soil/water ratio 1:2.5 with a 914 pH/Conductometer Metrohm (Herisau, Switzerland); electrical conductivity (EC, dS/m) in a soil/water extract (1:5) using a Eutech CON700 conductivity-meter (Oakton Instruments, Vernon-Hills, IL, USA); calcium carbonate content (%$CaCO_3$) was measured by manometric method according to Barahona (1984); and organic carbon (%OC) was quantified by acid-oxidation method according to Tyurin (1951).

Total concentration and selective extractions of PTEs in soils

Total concentration of the main PTEs (xx_T) present in the studied soils (Pb, As, Zn, Cu) were determined by X-ray fluorescence (XRF) with a NITON XL3t-980 GOLDD + instrument (Thermo Fisher Scientific, Tewksbury, MA, USA) ($n = 3$). The accuracy of the method was confirmed by analyzing a certified reference material (CRM052-050 RT-Corporation Limited, Salisbury, UK; $n = 6$). The average recoveries for the studied elements were 108.0 ± 9% of the CRM. Also, selective extractions of PTEs were performed in all treatments to assess the risk of mobility and the bioavailability of these elements in soils. In this sense, a soil:water extract of 1:5 was prepared to obtain the PTEs water-soluble fraction (xx_W) (Gomez-Eyles et al. 2011), since this extraction simulates the proportion of the elements that can lixiviate with rain water (Romero-Baena et al. 2021). Meanwhile, a extraction with 0.05 M EDTA (pH = 7) was followed to obtain the bioavailable fraction (xx_EDTA) for living organisms (Quevauviller et al. 1998). The PTEs concentrations for both extracted forms were measured by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) in a PerkinElmer NexION® 300D spectrometer (Waltham, MA, USA). The accuracy of the method for extracted forms was also confirmed by analyzing certified reference material SPS-SW1 Batch 133 (Spectrapure Standards, Manglerud, Norway; $n = 6$). The recovery of the reference material for the studied elements by ICP-MS determination was 99.2 ± 0.8%.

PTEs concentration in plants

Collected plant samples were divided into shoots and roots to analyze them separately, washed with distilled water, and dried (70 °C for 48 h). Afterwards, all plant material was finely ground and digested in a microwave XP1500Plus (Mars®) in HNO_3:H_2O_2 (1:1) (Sah and Miller 1992), and the concentration of the main PTEs in each part of the plant was measured by ICP-MS (PerkinElmer NexION® 300D spectrometer). The bioavailable (EDTA-extractable) PTEs fraction in soil samples was selected to calculate the bioaccumulation factor (BAF) for both parts, to assess the capacity of plants to uptake PTEs from the soil and either transport them to the shoots or accumulate them in roots. BAF, therefore, was calculated as the ratio between the PTEs concentration measured in plant (mg kg^{-1} dry weight) and the EDTA-extractable PTEs concentration in soils (mg kg^{-1} dry soil) (Anning and Akoto 2018; García-Carmona et al. 2019), since this fraction represents PTEs bioavailable forms for plants (Kidd et al. 2007). Finally, the extent of elements migration from roots to shoots was estimated through the translocation factor (TF), calculated as the ratio between PTEs concentration in shoots to that in the roots of the plants (Zacchini et al. 2009; Boi et al. 2021). Plants with both factors > 1 for a given element are considered as accumulators and suitable for phytoextraction, while plants with both factors < 1 are considered as non-accumulators or pollutant-stabilizing, thus being suitable for phytostabilization (Buscaroli 2017).

Statistical analyses

Descriptive statistics of PTEs content in soils and plant material were calculated to check their normality, while homogeneity of variance was explored using Levene's test. The analysis of mean comparisons was performed by non-parametric Kruskal–Wallis test, in accordance to sample size (Theodorsson-Norheim 1986). Kruskal–Wallis post hoc test ($p<0.05$) was used to determine significant differences. Principal component analysis (PCA) was carried out to identify the relations between soil properties, PTEs fractions, and treatments. Also, to analyze the relation between PTEs concentrations in plants and their total and bioavailable concentrations in soils, Spearman's correlations were performed. All the statistical analyses were carried out with a confidence level of 95% using SPSS v.28.0 (SPSS Inc., Chicago, USA).

Results and discussion

Main soil properties related to pollution

The key soil properties of the different reference soils and under each of the treatments applied are shown in Table 1. Soils with high levels of pollution remaining (PS) were mainly characterized by a strongly acidic pH (3.5), high EC (> 3 dS/m), and low organic carbon content (< 1%) due mainly to the lack of vegetation cover. In contrast, both the recovered soil (RS) and the unpolluted soil (US) were characterized by a less acidic pH, especially in US (> 6), significantly lower EC (< 1 dS/m), and significantly higher organic carbon content than PS (> 2%). These results are consistent with the ones reported by Sierra-Aragón et al. (2019) in polluted soils within the same area. Regarding the treated soils, the pH in them was higher compared to PS and to RS in all cases, and even reached higher values under marble (MS, MVS) and gypsum (GS, GVS) treatments than those of US. However, EC did not experience a strong decline in the amended soils, and values remained significantly higher than those of RS and US. The organic carbon content in amended soils did not reach that of the RS and US either, although among treatments it was higher in soils where vermicompost was added, for the direct effect of this organic amendment (Adak et al. 2014; Shen et al. 2022). Overall, US and RS were more strongly associated to a higher content of OC while PS was inversely correlated to OC content and pH, and, as for treatments, the strongest correlation was that of MS and MVS with a more neutral pH, as well as with the highest content in calcium carbonate (Fig. S1).

Table 1 Main soil properties (EC: Electrical conductivity; $CaCO_3$: Calcium carbonate equivalent content; OC: Organic carbon content) ($n=6$) related to the Aznalcóllar mining accident in the reference and treated soils

	pH		EC (dS/m)		$CaCO_3$ (%)		OC (%)	
	Mean	*sd*	Mean	*sd*	Mean	*sd*	Mean	*sd*
US	6.06 de	*0.28*	0.08 a	*0.06*	0.33 a	*0.14*	2.32 bc	*1.60*
RS	4.28 ab	*0.48*	0.98 b	*0.61*	0.52 a	*0.25*	3.68 c	*1.46*
PS	3.49 a	*0.23*	3.12 d	*0.63*	0.87 a	*0.06*	0.61 a	*0.09*
BS	5.37 cd	*0.87*	2.35 cd	*0.30*	0.84 a	*0.32*	1.14 ab	*0.16*
BVS	4.96 bc	*0.41*	2.15 c	*0.51*	0.70 a	*0.33*	1.62 ab	*0.38*
GS	6.22 def	*0.29*	2.38 cd	*0.06*	1.11 ab	*0.39*	0.89 a	*0.11*
GVS	6.41 ef	*0.19*	2.36 cd	*0.04*	0.78 a	*0.37*	1.67 ab	*0.26*
MS	6.78 ef	*0.19*	2.29 c	*0.07*	2.76 bc	*2.34*	1.20 ab	*0.24*
MVS	7.07 f	*0.07*	2.14 c	*0.26*	2.89 c	*1.23*	1.41 ab	*0.24*

US Unpolluted soil, *RS* Recovered soil, *PS* Polluted soil, *BS* Biopile, *BVS* Biopile + vermicompost, *GS* Gypsum, *GSV* Gypsum + vermicompost, *MS* Marble, *MVS* Marble + vermicompost. *Sd* standard deviation ($n=6$). Values followed by different letters are significantly different according to Kruskal–Wallis test ($P<0.05$)

Total, water-soluble and EDTA-extractable PTEs concentrations

When assessing the effectiveness of remediation measures and the risk to the ecosystem of the polluted soils treated, determining PTEs fractions is critical. Even after soil remediation and recolonization by vegetation, acid releases may occur, so that enough liming or other amendment material should be applied to buffer against these situations, which can represent a threat to future scenarios in the remediated soils (Wong et al. 1998). The total concentrations measured in the unpolluted soils (US) can be considered as the background levels for the potentially toxic elements (PTEs) present in the soils of the study area (Table 2). The mean total concentrations for Pb, As, Zn and Cu in US were similar to the background levels recorded in the same area both shortly after the accident (Simón et al. 1999) and by more recent studies (García-Robles et al. 2022), although Pb showed slightly higher values in this occasion, which may be explained by the natural variability of this element found in the natural soil. Recovered soils (RS) showed total PTEs concentrations approximately fivefold higher than those of US for Pb, Zn and Cu, and almost 15-fold higher for As. In addition, RS showed the highest concentrations for Zn and Cu, while for As and Pb the highest concentrations were reached in PS, 10- and 23-times above background levels, respectively. When comparing the levels measured for these elements with the regulatory thresholds established by the Regional Government of Andalusia (BOJA 2015) [10,000 mg kg^{-1} for Zn, 595 mg kg^{-1} for Cu 36 mg kg^{-1} for As, and 275 mg kg^{-1} for Pb] the concentrations of As and Pb both in PS and RS widely exceeded these regulatory limits.

In relation to treatments, the dilution effect of the amendments over total PTEs concentrations was relevant for some elements, especially in biopile soils (BS and BVS). In this sense, total Pb and As concentrations were strongly reduced in BS and BVS compared to PS, showing concentrations similar to those in RS. Meanwhile, Zn levels in these treatments were intermediate compared to PS, while for Cu no changes were observed after the application of the treatments, indicating that the dilution effect for this element was not a determining factor. The rest of the amended soil treatments showed higher As and Pb total concentrations compared to RS, although still significantly lower than those in PS. Thus, PS was strongly related to high total concentrations of As and Pb, while RS did so for Zn and Cu total concentrations. This may be related to the association of Cu and Zn with the OC content, related to a specific binding by adsorption and complexation to soil organic matter (McLaren et al. 1981; Balasoiu et al. 2001; Yin et al. 2002), which led the RS, where the highest OC was found, to retain higher total concentrations of these elements. Moreover, the low total concentrations of Cu and Zn found in PS may be related to the increase in mobility of these elements with decreased soil pH (Wang et al. 2006; Zeng et al. 2011). Therefore,

Table 2 Total (T) PTEs concentrations (mg kg^{-1} dry soil) ($n=6$) in the reference and treated soils

	Pb_T		As_T		Zn_T		Cu_T	
	Mean	*sd*	Mean	*sd*	Mean	*sd*	Mean	*sd*
US	100.6 a	*78.4*	19.5 a	*4.0*	74.2 a	*11.7*	44.2 a	*18.3*
RS	501.3 b	*142.3*	279.7 bc	*44.7*	416.7 c	*229.6*	216.8 b	*127.2*
PS	1003.4 c	*219.7*	451.8 f	*41.4*	215.9 ab	*82.5*	121.6ab	*29.2*
BS	505.7 b	*134.9*	252.2 b	*84.4*	335.2 bc	*71.1*	103.7 ab	*35.3*
BVS	536.4 b	*43.3*	286.1 bcd	*53.3*	372.0 bc	*77.1*	134.6 ab	*55.2*
GS	560.1 b	*57.3*	374.1 cdef	*61.9*	263.6 bc	*87.5*	124.5 ab	*19.0*
GVS	684.1 bc	*91.8*	407.4 ef	*53.4*	270.5 bc	*57.9*	132.5 ab	*32.1*
MS	668.1 b	*238.2*	383.6 cdef	*58.9*	273.3 bc	*58.4*	126.7 ab	*21.7*
MVS	680.1 b	*195.3*	392.8 def	*68.0*	283.6 bc	*60.2*	122.4 ab	*20.2*

US Unpolluted soil, *RS* Recovered soil, *PS* Polluted soil, *BS* Biopile, *BVS* Biopile + vermicompost, *GS* Gypsum, *GSV* Gypsum + vermicompost, *MS* Marble, *MVS* Marble + vermicompost. *Sd* standard deviation ($n=6$). Values followed by different letters are significantly different according to Kruskal–Wallis test ($P<0.05$)

the acidic pH in PS could have led to a strong leaching of these elements at depths below the top 10 cm sampled.

With the aim to accurately evaluate PTEs toxicity in the soil, particular emphasis should be given to their solubility and bioavailability, which represent the fractions that are available for uptake by living organisms and that can spread within the soil and through the landscape, thus posing a potential toxicity risk to terrestrial ecosystems (Alibrahim and Williams 2016; Bagherifam et al. 2019). In this regard, water-soluble fraction of pollutants can be readily absorbed by plants and incorporated into the food chain by bioaccumulation, representing actual bioavailability and short-term metal dynamics. Moreover, Ghosh et al. (2004) found that water-soluble form of As was more toxic compared to total As and inflicted greater inhibitory effect on various microbiological parameters in polluted soils compared to other bioavailable forms. Consequently, water-soluble As may be indicative of As availability to microbial populations (Fernández et al. 2005). Concerning this fraction, the highest water-soluble concentrations of As and Pb were recorded in RS, while for Zn and Cu they were recorded in PS (Table 3), in contrast to what was observed for total concentrations of these PTEs. The high solubility of Zn and Cu under acidic conditions led to the high water-soluble concentrations found in PS. Meanwhile, higher As and Pb solubility in RS can be related to the high organic matter content in this soil, as well as to its specific composition, since these elements are usually related to the labile dissolved organic carbon (DOC) pool (Egli et al. 2010; Gangloff et al. 2014; Li et al. 2018). Thus, by different competing effects with these elements, organic matter in soil can lead to an increase in their availability by maintaining them in more soluble and labile forms (Sauvé et al. 2000; Sierra-Aragón et al. 2019).

Regarding treatments, Pb solubility strongly decreased in all treated soils, especially in limed soils, since the application of Ca-rich compounds has been found to be generally efficient for Pb immobilization (Kumpiene et al. 2008; Romero-Freire et al. 2015). However, As solubility increased in carbonate soils and with higher organic carbon content, so that the highest As soluble concentrations between treatments were found under GVS and MVS. The increase in As mobility after the application of liming treatments and the increase of soil pH has been reported by previous studies (Simón et al. 2010; Romero-Freire et al. 2014). Also, an increase in As solubility induced by organic amendment, as in vermicompost treatments in our case, has also been pointed out (Karczewska et al. 2017; Aftabtalab et al. 2022). This could be associated with As competition with organic matter for sorption sites and metal oxide surfaces, which may represent a primary mechanism for As release and thus increasing its mobility (Redman et al. 2002; Bauer and Blodau 2006). On the other hand, the behavior of Zn and Cu solubility under treatments was very similar in both, and directly related to their strong negative correlation with pH (Wang

Table 3 Water soluble (W) PTEs concentrations (mg kg^{-1} dry soil) ($n=6$) in the reference and treated soils

	Pb_W		As_W		Zn_W		Cu_W	
	Mean	*sd*	Mean	*sd*	Mean	*sd*	Mean	*sd*
US	0.0067 c	*0.0015*	0.032 b	*0.009*	0.243 a	*0.043*	0.169 b	*0.026*
RS	0.0401 d	*0.0521*	0.096 c	*0.021*	18.193 bc	*8.790*	0.628 c	*0.256*
PS	0.0102 c	*0.0053*	0.051 bc	*0.035*	44.860 c	*17.813*	3.235 d	*1.414*
BS	0.0041 ab	*0.0008*	0.019 a	*0.006*	22.774 c	*7.821*	0.161 b	*0.066*
BVS	0.0044 b	*0.0016*	0.020 a	*0.005*	5.517 ab	*2.554*	0.165 b	*0.033*
GS	0.0029 a	*0.0014*	0.020 a	*0.002*	0.294 a	*0.220*	0.093 a	*0.259*
GVS	0.0058 bc	*0.0029*	0.042 bc	*0.008*	0.214 a	*0.118*	0.136 ab	*0.020*
MS	0.0033 ab	*0.0016*	0.033 b	*0.017*	0.054 a	*0.033*	0.108 ab	*0.173*
MVS	0.0028 a	*0.0016*	0.091 c	*0.052*	0.050 a	*0.029*	0.130 ab	*0.192*

US Unpolluted soil, *RS* Recovered soil, *PS* Polluted soil, *BS* Biopile, *BVS* Biopile + vermicompost, *GS* Gypsum, *GSV* Gypsum + vermicompost, *MS* Marble, *MVS* Marble + vermicompost. *Sd* standard deviation ($n=6$). Values followed by different letters are significantly different according to Kruskal–Wallis test ($P<0.05$)

et al. 2013; Laurent et al. 2020), showing Spearman's correlation coefficients with pH of -0.933 and -0.833 respectively ($n=9$). Thus, soils rich in $CaCO_3$ content were the most effective in decreasing their soluble concentrations, which were those amended with marble (MS, MVS) and gypsum (GS, GVS), the treatments with a higher pH. This is in accordance with previous studies that highlighted the effectiveness of soils rich in $CaCO_3$ in retaining these elements (Aguilar et al. 2004). On the contrary, the highest water-soluble concentrations for Cu and Zn were found under BS and BVS treatments, where the pH was neutralized in a lesser extent, and especially in the case of Zn (Fig. S2), which reaches the highest mobility under acidic conditions and it is considered to present a higher mobility in soil with respect to Cu (Rocco et al. 2018; García-Carmona et al. 2019).

EDTA-extractable fraction of PTEs is also used to assess their bioavailability in soils (Kidd et al. 2007; García-Carmona et al. 2019). Unlike water-soluble fraction, EDTA-extractable fraction is regarded by different authors as a more reliable predictor of long-term availability of these elements in soils (Hurdebise et al. 2015). Moreover, among the different extraction methods frequently used for evaluating the bioavailable fraction of PTEs in soil (e.g. DTPA, EDTA, $CaCl_2$, and $NaNO_3$), EDTA was selected since it is considered more suitable for acidic soils (Hammer and Keller 2002; Feng et al. 2005), and it has a stronger extraction capacity than other extraction methods (Quevauviller et al. 1998; Han et al. 2020) This can be related to the EDTA high extraction potential, which may provide the maximum element extractability and, thus, indicate the higher levels of metal mobility (Labanowski et al. 2008). Furthermore, chelating agents such as EDTA are considered a more accurate indicator of metal availability to plants, as they can more effectively remove soluble metal–organic complexes that are potentially bioavailable (Bolan et al. 2008).

EDTA-extractable fraction in US showed the lowest concentrations for all PTEs except for Pb, where the highest concentration was found followed by RS (Table 4). These values may be the result of an overestimation caused by the EDTA's significant binding capacity for Pb and its great efficiency in mobilizing this element from the soil (Shen et al. 2002; Santos et al. 2010). In addition, high Pb EDTA-extractable concentrations found in US and RS may be enhanced by the high organic carbon content in these soils coupled with EDTA capacity to effectively displace organically-bound fractions of metals present in soil through formation of strong chelates (Elliott and Shastri 1999; Nakamaru and Martín-Peinado 2017). The specific increase in Pb availability in soil due to the application of organic compounds has been previously proven (Angin et al. 2008). On the other hand, in PS the EDTA-extractable fraction was significantly the lowest for Pb, and for As and Cu were lower than in the amended soil treatments. Regarding the treatments

Table 4 EDTA extractable PTEs concentrations (mg kg^{-1} dry soil) ($n=6$) in the reference and treated soils

	Pb_EDTA		As_EDTA		Zn_EDTA		Cu_EDTA	
	Mean	*sd*	Mean	*sd*	Mean	*sd*	Mean	*sd*
US	8.12 d	*1.51*	0.08 a	*0.02*	7.66 a	*1.48*	5.89 a	*1.18*
RS	4.22 c	*1.04*	0.63 ab	*0.27*	50.52 bc	*7.66*	46.71 d	*5.89*
PS	0.38 a	*0.16*	0.48 ab	*0.11*	51.90 bc	*2.16*	20.99 b	*4.68*
BS	2.29 b	*0.74*	0.52 ab	*0.26*	58.43 c	*13.77*	25.97 bc	*5.75*
BVS	1.39 ab	*0.37*	0.70 ab	*0.19*	45.90 bc	*10.17*	32.47 bc	*9.22*
GS	0.37 a	*0.13*	0.95 b	*0.27*	42.73 bc	*12.40*	29.30 bc	*4.03*
GVS	1.19 ab	*0.35*	2.92 d	*0.69*	50.54 bc	*14.84*	35.59 cd	*8.19*
MS	0.60 a	*0.32*	1.06 b	*0.34*	36.88 b	*11.48*	30.38 bc	*6.47*
MVS	0.78 a	*0.22*	1.99 c	*0.31*	59.98 c	*14.70*	33.87 c	*9.79*

US Unpolluted soil, *RS* Recovered soil, *PS* Polluted soil, *BS* Biopile, *BVS* Biopile + vermicompost, *GS* Gypsum, *GSV* Gypsum + vermicompost, *MS* Marble, *MVS* Marble + vermicompost. *Sd* standard deviation ($n=6$). Values followed by different letters are significantly different according to Kruskal–Wallis test ($P<0.05$)

applied to the amended soils, BS and BVS showed higher concentrations of Pb extractable with EDTA, driven by the higher organic carbon content in these treatments, while marble and gypsum treatments did so for As. Overall, vermicompost treatments showed higher concentrations of EDTA-extractable pollutants, which can be attributed to a positive correlation between organic matter content in soil and EDTA-extractable contents of PTEs, as previously reported by Zeng et al. 2011.

Species richness and vegetation cover after remediation measures

The presence of vegetation in the studied soils eighteen months after the application of the treatments was evaluated compared to that present in the US. In this soil, a mean of about 12 different plant species was found growing on it (Fig. 2a). Compared to US, species richness was slightly lower in RS, which could be related to the higher soluble concentrations found for

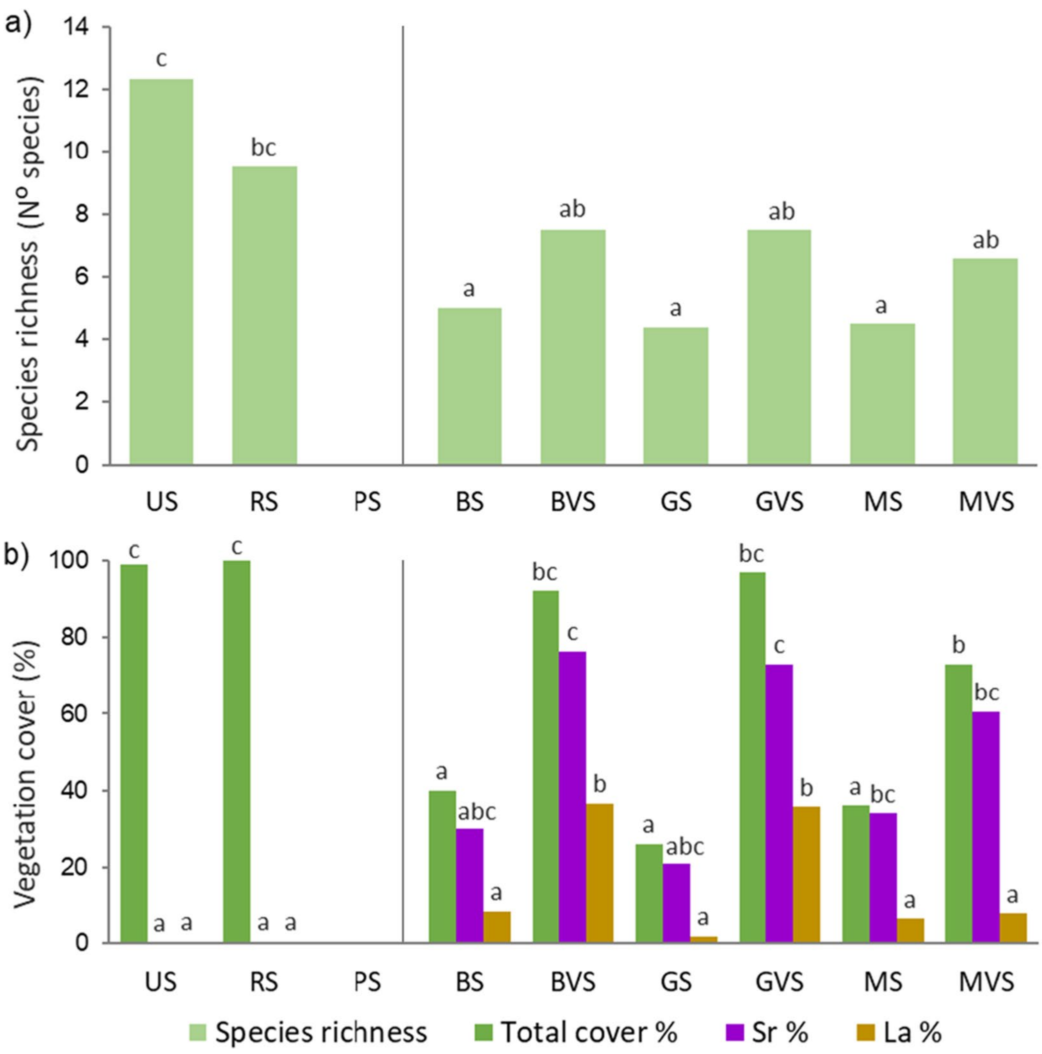

Fig. 2 **a** Mean plant species richness present in each of the soils and treatments studied. **b** Total vegetation cover (%), and *Spergularia rubra (Sr)* and *Lamarckia aurea* (La) specific cover in each of the soils and treatments studied. US: Unpolluted soil; RS: Recovered soil; PS: Polluted soil; BS: Biopile; BVS: Biopile + vermicompost; GS: Gypsum; GSV: Gypsum + vermicompost; MS: Marble; MVS: Marble + vermicompost. Bars with different letters are significantly different according to Kruskal–Wallis test ($P < 0.05$)

the elements with highest mobility such as Zn and Cu, which in concentrations that exceed those required as nutrients may cause phytotoxicity to specific plant species (Nagajyoti et al. 2010). The high mobility of these elements could be, therefore, the main factor influencing the decrease in vegetation diversity and even, as in the case of PS, the responsible for the complete lack of vegetation on this soil, where the highest mobility for these elements was reached. In this regard, García-Carmona et al. (2019) reported that the absence of vegetation in the soils that remain polluted in the studied area is mainly due to the high water-soluble concentration of Cu and Zn, rather than the high total concentration of As and Pb. Regarding the treated soils, species richness was half in the treatments with vermicompost addition compared to US, while for those without vermicompost it represented about just one-third. Meanwhile, both US and RS were totally covered by vegetation unlike PS, where vegetation growth was completely inhibited (Fig. 2b). Under vermicompost treatments, vegetation cover was slightly lower if compared to US and RS, while for the treatments without vermicompost addition the vegetation cover represented less than half of that appearing when vermicompost was added, driven by the lower organic carbon content on these treatments. However, in general, all the treatments applied on PS resulted in enhanced soil properties and decreased soil toxicity, enabling the growth of vegetation to different extents, with the vermicompost treatments showing the greatest vegetation cover and species richness. Thus, vermicompost treatments were the most effective ones in terms of plant recolonization and development on the polluted soils, emphasizing that the addition of organic amendments in bare polluted soils is essential to facilitate the reestablishment and recolonization by the pioneer vegetation (Wong 2003). This vegetation development found on treated soils represents the spontaneous and natural response of the local vegetation to the changes produced in the soil by the amendments after eighteen months, so that the vegetation development in the treated soils could be expected to be similar to that found in the RS in the medium term. This could be assisted not only by the changes in soil properties induced by the treatments, but also by vegetation recolonization itself, since its presence produces many beneficial effects at the rhizosphere level and on the surrounding polluted soil. These can range from stimulation of microbial activity, improved aeration and stabilization of the soil to the reduction of PTEs concentrations and their stabilization (Erickson 1997; Davis et al. 2002). Moreover, the very presence of vegetation may also facilitate other plant species to subsequently colonize the area through various mechanisms that reduce the potential transfer of elements from the soil to the plants, as the modification of rhizosphere pH or the exudation into the soil of organic acids that bind pollutants (Rutkowska et al. 2020).

Frequently, in soils polluted by PTEs, their toxicity restricts the growth of all but the most tolerant plant species (Wong 2003). In our case, polluted soils did not show vegetation cover at all. However, eighteen months after the application of the amendments, mainly two species highly tolerant to the present PTEs concentrations appeared in all the treated soils: the herbaceous plants *Spergularia rubra* (L.) J. Presl & C. Presl and *Lamarckia aurea* (L.) Moench, being *S. rubra* the one with higher colonization percentage in all treatments (Fig. 2b), present in about one third of the surface in treatments without vermicompost and in more than two thirds in those with vermicompost. Both species are frequently found in the soils polluted after the Aznalcóllar spill, particularly in those areas where PTEs concentrations remain higher, with acidic pH and high EC, and their presence being restricted mostly to them (Madejón et al. 2006; Montiel-Rozas et al. 2016; García-Carmona et al. 2019). In this study, both species were dominant in the treated polluted soils where conditions (i.e., PTEs concentrations) remain more restrictive for vegetation growth. On the contrary, their presence was barely detected in US and RS, where a higher number of less pollution-tolerant species are present.

PTEs concentration and accumulation in plants

To fully evaluate the success of remediation strategies implemented on polluted soils, the determination of PTEs fractions in soil may not be sufficient to accurately predict the PTEs transfer risk to plants, since plant uptake not always correlates with them (Proto et al. 2023). Therefore, for a more accurate assessment of revegetation success, plant-based approaches should be used, either by carrying out plant bioassays or measuring PTEs concentrations in spontaneously growing vegetation in remediated soils, as this is a

Table 5 PTEs concentrations (mg kg^{-1} dry weight) ($n=3$) in aboveground part and in roots for the two main herbaceous species present in the different treatments applied after eighteen months

	Pb_Shoot	Pb_Root	As_Shoot	As_Root	Zn_Shoot	Zn_Root	Cu_Shoot	Cu_Root
	Spergularia rubra							
US	3.5 a	16.0 a	0.6 a	0.9 a	104.4 a	72.1 a	6.8 a	8.0 a
RS	20.8 ab	24.7 ab	9.4 abc	17.3 bc	316.1 c	340.7 c	23.9 ab	30.1 b
PS	-	-	-	-	-	-	-	-
BS	18.4 ab	24.0 ab	9.1 ab	10.2 ab	265.6 abc	411.3 c	27.1 b	18.8 ab
BVS	35.1 bc	72.0 c	14.6 abc	24.4 c	302.8 bc	248.7 bc	28.1 b	33.0 b
GS	37.0 bc	32.5 ab	23.2 c	19.3 bc	214.0 abc	158.0 ab	28.3 b	29.4 b
GVS	42.6 c	63.6 c	17.5 bc	25.6 c	151.8 ab	127.3 ab	21.7 ab	30.1 b
MS	21.3 abc	43.1 abc	8.2 ab	16.9 bc	171.5 abc	154.9 ab	19.8 ab	21.2 ab
MVS	30.3 bc	50.4 bc	10.9 abc	14.4 bc	144.6 ab	150.8 ab	17.0 ab	20.2 ab
	Lamarckia aurea							
US	2.5 a	18.7 a	0.5 a	1.8 a	28.2 a	50.0 a	5.9 a	14.6 a
RS	37.8 b	65.1 abc	11.3 ab	27.3 abc	235.2 c	259.8 bc	20.7 ab	50.0 b
PS	-	-	-	-	-	-	-	-
BS	29.6 ab	50.1 ab	13.5 ab	16.7 ab	159.4 abc	317.4 bc	26.4 ab	44.1 ab
BVS	37.7 b	131.1 cde	16.4 ab	50.7 bcd	212.8 bc	235.4 bc	27.3 ab	52.1 b
GS	43.2 b	99.2 bcd	25.1 b	49.8 bcd	146.7 abc	132.1 ab	26.5 ab	53.3 b
GVS	36.7 b	231.0 f	17.0 ab	60.0 cd	78.7 ab	163.6 ab	24.4 ab	70.9 b
MS	55.4 b	149.4 de	28.0 b	67.7 cd	139.7 abc	238.3 bc	42.5 b	67.7 b
MVS	32.8 ab	168.9 ef	21.4 ab	87.9 d	81.3 ab	163.4 ab	26.3 ab	53.5 b

US Unpolluted soil, *RS* Recovered soil, *PS* Polluted soil, *BS* Biopile, *BVS* Biopile + vermicompost, *GS* Gypsum, *GSV* Gypsum + vermicompost, *MS* Marble, *MVS* Marble + vermicompost. *Sd* standard deviation ($n=6$). Values followed by different letters are significantly different according to Kruskal–Wallis test ($P<0.05$)

more reliable indicator of PTEs transfer potential in soils (Milton et al. 2002; Proto et al. 2023).

According to the predominant presence of *S. rubra* and *L. aurea* in the treated soils, their PTEs accumulation capacity was assessed (Table 5). Both species were able to accumulate high concentrations of PTEs both in their shoots and roots, which in most cases correlated significantly with the total and bioavailable concentration of the PTEs in the soil. In contrast, no direct correlation was observed with the soluble fraction of PTEs in soil, except for Zn concentrations (Table S2). In general, the concentrations measured in *L. aurea* were higher than in *S. rubra* for all elements except for Zn, which accumulated at a higher rate in *S. rubra*, and especially in the shoots of this species. The high Zn accumulation in *S. rubra*, and especially in its shoots, was previously reported by other authors (El Berkaoui et al. 2021). Meanwhile, *L. aurea* showed elevated PTEs accumulation for the other studied elements, highlighting the concentrations of Pb and As measured particularly in its roots. This confirms the high ability of this species to accumulate multiple PTEs, both in its shoots and roots, and an exceptional high capacity to accumulate specific elements in roots such as Pb (Condori 2004; Midhat et al. 2017).

In relation to plant indexes, the bioaccumulation factor (BAF) was calculated considering the PTEs bioavailable (EDTA-extractable) fraction in soil, since this fraction is considered more precise for this end (Losfeld et al. 2015). This is based in the fact that the danger of PTEs lies in their solubility and bioavailability rather than in their total concentrations, since they better represent the fractions that are available for uptake by living organisms and that can spread within the soil (Marguí et al. 2007; García-Carmona et al. 2019). Moreover, total metal concentrations in soil are considered to correlate poorly with metal concentrations in plant tissues, since the amount of an element that is actually available to plants is different from that assessed by strong acid digestions (Buscaroli 2017). In this sense, BAF pointed out that *S. rubra* and *L. aurea* have a significant capability for accumulating Pb and As, both in their shoots and in their roots (Fig. 3). According to the values obtained for these elements in both parts (BAF > 10), we could consider that these two species act as hyperaccumulators of Pb and As (Rutkowska et al. 2020). Comparing these species to each other in terms of Pb and As accumulation, *L.*

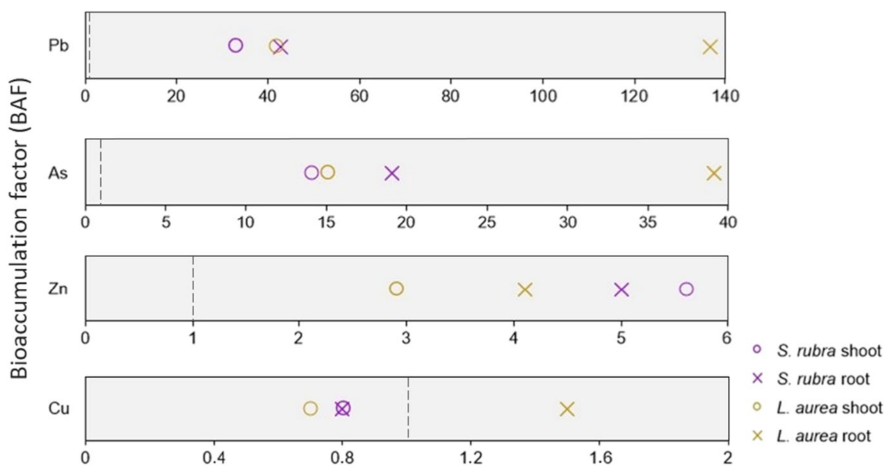

Fig. 3 PTEs bioaccumulation factor (BAF) in aboveground part and in roots for the two main herbaceous species present in the different treatments applied after eighteen months. Dashed lines represent the threshold value 1 (BAF = 1)

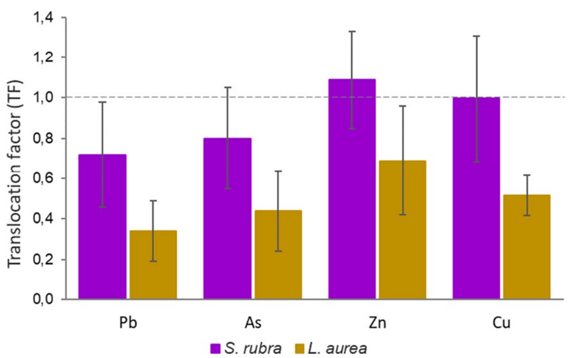

Fig. 4 PTEs translocation factor (TF) for the two main herbaceous species (*Spergularia rubra* and *Lamarkia aurea*) present in the different treatments applied after eighteen months. Dashed line represents the threshold value 1 (TF = 1)

aurea had greater BAF than *S. rubra*, especially in the roots, highlighting that *L. aurea* is particularly tolerant to high levels of these elements, showing a higher ability to accumulate them in both the shoots and roots without sustaining toxicity, as remarked by previous studies (Midhat et al. 2017). Besides, the high values observed for Pb and As BAF in roots of *L. aurea* suggest that the translocation of these elements from soil to root was considerably high, so that *L. aurea* roots act as sink for Pb and As accumulation (Ng et al. 2016).

According to Zn, BAF measured for this element in both species was greater than one (Fig. 3), although in a significantly lower degree than for Pb and As. Zn low accumulation (BAF < 1) in different grass plants was observed even at increasing concentrations (Andrejić et at. 2018; Grassi et al. 2020), and even plants restricting Zn uptake at higher concentrations in the soil (Andrejić et al. 2018). Therefore, we could consider that although not at the same scale than Pb and As, the BAF > 1 obtained for the studied species for Zn indicates that there is a considerable transfer of this element into the plant. Comparing both species, the higher accumulation of Zn showed by *S. rubra* (Figs. 3 and 4) indicates that it is highly tolerant to this element (Gutiérrez Ginés 2013), which could be one of the reasons of the higher abundance of this species compared to *L. aurea* (Fig. 2b). In terms of Cu, neither *S. rubra* nor *L. aurea* showed a significant accumulation capacity for this element (BAF < 1), which only slightly accumulated on *L. aurea* roots, and which is in accordance with the observed by García-Carmona et al. (2019) in plants growing in residual polluted soils in the same area. The low Cu accumulation capacity in grass plants (BAF < 1) was also reported in other studies (Bhatti et al. 2016; Satpathy et al. 2014).

The translocation factor (TF) calculated for the two selected species was lower than one in all cases, except very slightly for Zn in *S. rubra*, so that elements migration from the roots to the shoots of these species is not substantial (Fig. 4). Nevertheless, TF in *S. rubra* for all elements was approximately two times higher than in *L. aurea*, showing that PTEs migration to *S. rubra* shoots is higher than that in *L. aurea*. Thus, the high capacity for pollutants concentration shown by *L. aurea* in its roots could reveal the mechanism that allows this species to thrive in the most heavily polluted soils and, consequently, be used as an accurate bioindicator of trace element availability in soils in this area, which is in accordance with Burgos et al. (2008).

The natural settling of these two species, growing in the remediated soils after eighteen months, are good indicators of the success of the remediation treatments used (Álvarez-Rogel et al. 2021). In addition, although they were tolerant to the PTEs present in the soil and can accumulate some of them (BAF > 1 for As, Pb and Zn), the absence of elements translocation from roots to shoots in the studied plants indicate that the selected cost-effective remediation techniques used, over time, may follow with passive enhancement, by modification of soil conditions by colonizing plants and being the first step in facilitating the growth of other species less tolerant to the stress (Navarro-Cano et al. 2018).

Conclusions

The use of this novel cost-effective soil remediation strategy, implemented under field conditions for long-term soil remediation approach, has demonstrated significant improvements in key soil properties following treatments application, including elevated pH levels, augmented organic carbon content, and decreased salinity levels. Consequently, these treatments proved highly effective in fostering spontaneous vegetation colonization within severely degraded soil patches. Among the various remediation approaches, vermicompost amendment proved to be the most effective in promoting the vegetation recovery in the treated soils, leading to a greater diversity of plant species and increased vegetation cover in them.

The long-term field-based approach is crucial when evaluating the spontaneous recolonization of remediated soils by native vegetation, and the role of the actions implemented in achieving this. In this regard, two plant species relevant in the studied area and predominant in the treated soils after settling of treatments over time, *Spergularia rubra* and *Lamarkia aurea*, exhibited remarkable capacity in accumulating Pb and As, particularly in their root systems, indicating their high tolerance to the elevated pollutant concentrations prevalent in the study area. This points their role as key species, as they not only serve as pioneers in recolonizing the degraded soils but also facilitate the subsequent recolonization by other species less tolerant to the high pollution levels present in the studied area. Therefore, the success of the remediation strategy assessed may be promoted by the early recolonization of the soil by the high pollution-tolerant species, since their presence enhance further evolution in the soil physical, biological, and chemical conditions.

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Data availability The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

Declarations

Competing interests The authors have no relevant financial or non-financial interests to disclose.

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