Soil quality changes in an Iberian pyrite mine site 15 years after land reclamation

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ABSTRACT

Reclamation of highly degraded mine lands to a sustainable environmental quality has become a major policy concern in many countries with a long mining tradition. This paper reports the soil quality status of a historical mine site fifteen years after its reclamation, using indicators of chemical reactivity, soil fertility and health, and discusses the progress and effectiveness of the implemented measures by a comparative analysis between pre- and post-reclamation conditions. Twenty composite surface samples (0–20 cm depth) were obtained for physical and chemical characterization from the open pit mine and waste disposal area, using a stratified random sampling approach. Additionally seven sites were selected to collect topsoil samples for microbiological testing. Results showed that soil quality changed noticeably over the study period (2003–2018), with overall improvements in key properties, such as structural stability, cation exchange capacity, degree of base saturation, soil organic carbon, and available phosphorus. Prior to reclamation, the mine soil was unable to support vegetation due to hyperacidity coupled with elevated levels of toxic metals and nutrient deficiencies. The combined use of sugar beet lime and composted biosolids as a low-cost, locally available, soil amendment was effective in neutralizing both active and exchangeable acidity, and reducing the mobility, plant uptake and human bioaccessibility of trace elements. The amendment addition also enhanced soil fertility, carbon storage, nutrient availability and microbial biomass (bacteria and fungi). Revegetation with *Pinus pinea* and *Nerium oleander* has proven to be a successful strategy to create a vegetative cover aesthetically pleasant and environmentally compatible with the surrounding undisturbed landscape, although further efforts should be made to monitor over time the phytotoxic and bioaccessible levels of residual metals, notably Cd, Cu and Zn. The insights gained from this land reclamation experience provide success criteria for assisting natural attenuation in other abandoned mining sites worldwide.

1. Introduction

Currently, growing concerns for the environmental impacts of mining have highlighted the importance of reclamation in mine soil studies (Feng et al. 2019). Heavy metal pollution arising from mining and smelting activities is a major environmental issue (Beane et al. 2016), unless proper reclamation measures are implemented to reduce acidity, decrease metal mobility and improve soil quality. This is particularly true in regions with a long history of mining and mineral processing like the Iberian Pyrite Belt (IPB) of Spain and Portugal, where many of the old mines were left without any environmental controls. Several studies have revealed that high levels of potentially toxic trace elements (PTE)

in soils (e.g. Fernández-Caliani et al. 2009; González et al. 2011), plants (e.g. Chopin and Alloway, 2007, Madejón et al., 2011; Alvarenga et al. 2014), river waters (e.g. Galán et al. 2003; Sánchez-España et al. 2005) and ambient air (e.g. Sánchez de la Campa et al. 2011; Fernández-Caliani et al. 2013), may pose health and ecological hazards in the mine-impacted areas of the IPB (Candeias et al. 2011; Gabari and Fernández-Caliani, 2017; Santos et al. 2017; Fernández-Caliani et al. 2019). Therefore, there is a strong need to restore sustainable use of the post-mining landscape and ensure public safety at these sites, which represent a great challenge for environmental and land-use management.

Only a few of more than 80 potentially harmful mine sites encompassing over 4800 ha of lands across the IPB (Grande et al. 2014) have

been reclaimed and revegetated in an attempt to stabilize the spoil, or material that remains after mining (Bolan and Kirkham, 2018), and support a land use similar to that before mining. To date, however, no or little monitoring has been conducted to evaluate the performance of the remedial measures put in place to prevent or mitigate the effects of land degradation (Ruiz-Cánovas et al., 2019; Madejón et al., 2021), and there have been no studies focusing on metal leaching and bioaccessibility after soil reclamation. Potential high costs of rehabilitation, the absence of clearly assigned responsibility, and the lack of clear goals for mine closure and post-mining reclamation are some factors that have contributed to inaction or have delayed the development of monitoring plans.

Even though the majority of the *in situ* remediation methods that are currently available for metal-contaminated mine soils has been extensively investigated (e.g. Bech et al. 2017; Bolan and Kirkham, 2018), the adsorption, ion-exchange and precipitation reactions accelerated by adding soil amendments have not been sufficiently addressed in the long-term. Moreover, some adsorption processes are reversible and any change in soil conditions and properties may cause re-mobilization of trace elements from the treated soils (Dybowska et al. 2006), hence the

effectiveness and suitability of these adsorption-based immobilization strategies are still under discussion.

The reclaimed mine soils (RMS) studied in this paper provide an excellent opportunity to assess, on a field scale, the immobilization efficiency of PTE once the reclamation plan was completed, and to monitor long-term changes in soil quality after application of cost-effective amendments and tree planting operations. Assessing changes in composition and properties of the RMS through a battery of tests is essential to ascertain whether the reclamation processes remain functional over long periods of time. Thus, this study was carried out on the RMS of the Poderosa mine site (Spain) with the aims of: 1) to assess the quality of the mine soils 15 years after its reclamation, by using indicators of chemical reactivity, soil fertility and health; 2) to evaluate the effectiveness of the land reclamation measures; and 3) to determine whether the reclaimed soil releases significant amounts of PTE to the environment posing threats to ecological and human receptors. The findings may be of significance for our better understanding of the process of transforming spoil to soil, and can help inform decisions on soil management of reclaimed mine sites based on a set of success criteria that includes the risks arising from the mobility and

Fig. 1. Location map of the Poderosa mining area and aerial photograph depicting the situation of the sampling sites.

bioaccessibility of PTE.

2. Study area and background

2.1. Mine site description

The Poderosa mine site (37°44'55''N; 6°39'15''W) is a historical copper mine situated about 8 km north west of the world-renowned mining district of Rio Tinto, in western Andalusia, Spain (Fig. 1). It is a volcanic-hosted massive sulfide deposit capped by gossan, in which chalcopyrite occurs as an accessory mineral associated with pyrite. Modern mining started in the mid-19th century with the extraction of low-grade copper ores, although there is archeometallurgical evidence that ancient work dates back to Roman times and earlier. The cupriferous pyrites were converted into water-soluble sulfates by open-air heap roasting, leached out in place by covering the ore heaps with water, and then the solubilized copper was precipitated from the leaching solution by means of iron scrap. The most intense mining and mineral processing activities took place between 1875 and 1924, when the mine was closed due to copper price drop. During this period, over 580,000 tons of ore was mined (Pinedo-Vara, 1963). More recently, in the 1990s, the gossan overlying the massive sulfide deposit was exploited for gold and silver.

Large-scale open cast and underground mining operations and extensive metallurgical activities left a legacy of open pits, mine adits, hazardous waste rock dumps and pyrite-roasting residues that cause serious environmental damage to surrounding areas through the release of acidity and dissolved PTE. The mine site is located near the Odiel river, which receives highly acidic and heavy metal contaminated discharges emanating from the abandoned underground workings. Hence, the main adit of the Poderosa mine is still a major contributor to water pollution in the area (Sánchez-España et al. 2006; Ruiz-Cánovas et al. 2018). The original hilly topography and hydrologic conditions of the site have been altered dramatically by extensive surface mining operations, and the natural soil and vegetation of the land were destroyed by open cast excavation and overburden dumping. The current disturbance area comprises over 18 ha of mine waste dumps, and an open pit of 190 m length and 90 m width. Despite the mine is surrounded by poorly-developed soils (Leptosols), they are capable of supporting woody vegetation, both trees and shrubs.

A site remediation plan was implemented by the Regional Government of Andalusia during 1993 and 1994, involving removal of sulfidic mine wastes with disposal in the former open pit mine, backfilling and capping with a low-permeability sealing layer of compacted clay-rich materials (Saiz and Ceacero, 2008), in an attempt to prevent the generation of acid mine drainage. The clean-up left a barren landscape, largely devoid of any vegetation, until the site was revegetated in the framework of an experimental reclamation project initiated in December 1997 with the challenging objective of restoring the post-mining landscape. The post-reclamation land use is forestry and wildlife habitat.

2.2. Soil prior to reclamation

According to results from a surface material investigation prior to reclamation (Saiz, 2004), the mine soil was characterized by poor structure, low water-holding capacity, ultra-acid pH values and low nutrient status. The mean pH values were 2.7 (pH in water) and 2.6 (pH of oxidation), with sulfide oxidation being the dominant source of acidity. The content of pyritic sulfur was as high as 2.6% in places where sulfide minerals were present, whilst the soil was depleted in acid-neutralizing minerals. It had low levels of total organic carbon, with a median value of about 0.45%, total nitrogen (less than 0.1%) and available phosphorus (P_{Olsen} values typically below 5 mg kg^{-1}), thus limiting root growth and establishment of plants.

Effective cation-exchange capacity of the mine spoil was mostly lower than 10 cmol$_c$ kg^{-1}, and the percent base saturation measured prior to reclamation ranged between 12 and 26%, which is indicative of low fertility. Consistently, the soil exchange complex was clearly dominated by acid cations, such as Al^{3+} (up to 4.05 cmol$_c$ kg^{-1}) and H$^+$ (up to 2.56 cmol$_c$ kg^{-1}).

Acidity generated by the oxidative dissolution of sulfides, especially pyrite, led to concomitant release of associated PTE and their consequent accumulation in the mine spoil. Total median concentrations of PTE in soil, reported by Saiz (2004), were as follows: 4080 mg kg^{-1} of Pb, 536 mg kg^{-1} of As, 632 mg kg^{-1} of Cu, 1040 mg kg^{-1} of Zn, and 56.6 mg kg^{-1} of Hg (open pit area); and 2160 mg kg^{-1} of Pb, 542 mg kg^{-1} of As, 298 mg kg^{-1} of Cu, 174 mg kg^{-1} of Zn, and 4.22 mg kg^{-1} of Hg (waste dumps area).

2.3. Reclamation measures

The post-mining reclamation plan was carried out in line with the remediation strategy for soils impacted by the Aznalcóllar mining spill in 1998, a well-known example of a large-scale cleaning and effective remediation program intended to rehabilitate about 3000 ha of contaminated land (Madejón et al. 2018). Soil reclamation methods were tested in experimental plots before application (Saiz and Ceacero, 2008), including the following steps: 1) clean-up operations and other earthworks; 2) soil treatment by amendments addition; 3) planting with native vegetation and reforestation.

Clean-up operations consisted of removing sulfide-bearing waste material to a depth of 30 cm using bulldozers and backhoes. The removed material was stockpiled and sealed with a low-permeability layer of compacted clay. Perimeter channels were constructed at the base of the disposal areas to collect and convey the flows from the bench drains. Other earthworks, involving the reshaping and contouring of the overburden dumps, were undertaken to prevent soil erosion, reduce the slope instability hazard and facilitate the re-establishment of vegetation.

Under the strongly acidic condition of the mine spoil, revegetation would not be possible without any previous treatment to increase the soil pH, reduce metal mobility and improve nutrient availability, by adding liming and organic amendments from local sources. Sugar beet lime (SBL), a by-product of the sugar purification process, was the liming material used to alleviate soil acidity, and composted biosolids (CB) from a nearby wastewater treatment facility was added to supply organic matter and nutrients, and thus enhance soil fertility and productivity. Such low-cost amendment materials were applied in 2003, at a variable rate according to soil requirements (Saiz and Ceacero, 2008), and were thoroughly mixed into the soil by deep tillage or subsoiling to a depth of roughly 50 cm. This also helped to improve soil structure by reducing compaction.

After amendment addition and preparation of the land, the overburden area and the benches of the open pit were revegetated with drought tolerant trees and evergreen shrubs, native to the Mediterranean region. The tree species selected for planting was stone pine (*Pinus pinea*), a forest species widely used for reforestation in acidic and nutrient-deficient soils. Oleander (*Nerium oleander*) was planted in grounds along the banks of ephemeral streams and creeks to create a riparian effect. The lack of rains in the area delayed the planting until early 2005.

3. Materials and methods

Wherever possible, the sampling and analytical procedures followed in this study were the same as those used by Saiz (2004) to ensure comparability of data before and 15 years after soil reclamation.

3.1. Soil sampling and sample preparation

Fieldwork and soil sampling were carried out in the fall of 2018 at twenty sampling sites located throughout reclaimed and revegetated

zones of the open pit mine and the waste disposal area (Fig. 1), following a stratified random sampling design. The stratification was based on the aforementioned mining areas, as defined in Saiz (2004). At each sampling site, three samples with similar slope and drainage conditions were collected with an auger to a depth of 20 cm, and bulked in the field to make a composite sample of about 5 kg. The composite soil samples were air-dried, gently ground, homogenized, and passed through a 2-mm mesh sieve to separate coarse fragments from the soil fine-earth particles and remove visible roots. In addition, seven sites were selected to collect topsoil samples (0–10 cm depth) in sterile flask for microbial tests, which closely correspond with the samples for physical and chemical analysis except one sample located on the pit bottom (sample 4 in Fig. 1).

3.2. Analytical procedures

Soil minerals were identified by X-ray powder diffraction (XRD) analysis, using monochromatic Ni-filtered CuKα radiation at 40 kV and 30 mA. For clay minerals identification, oriented clay-size fractions were obtained from sedimentation of soil suspension, and analyzed in the air-dry state, after treatment with ethylene glycol solvation, and after heating at 550 °C for 2 h. Relative mineral abundance was semi-quantitatively estimated from the XRD patterns by using mineral intensity factors in combination with the 100% approach (Kahle et al., 2012).

Soil texture was determined using particle-size distribution data resulting from laser diffraction analysis (Mastersizer 2000 instrument). The combined silt and clay content and soil organic carbon (SOC) content were used to calculate the structural stability index (SI), as follows (Pieri, 1992):

$$SI = \frac{[1.72 SOC(wt\%)]}{[(clay + silt)(wt\%)]} x100$$

The SI is a way of assessing the risk of structural degradation, where $SI \leq 5\%$ indicates structurally degraded soil; $5\% < SI \leq 7\%$ a high risk of degradation; $7\% < SI \leq 9\%$ a low risk of structural degradation; and $SI > 9\%$ a stable structure.

Active soil reaction (pH_{H2O}), redox potential (Eh) and electrical conductivity (EC) values were measured after 30 min equilibration with deionized water at a soil-to-water ratio of 1:2 (v/v), using properly calibrated glass electrodes. Moreover, pH measurements with 1 M KCl (pH_{KCl}) were used to obtain the exchangeable acidity of the soil; the abrasion pH (pH_{ab}) was determined on the slurry produced by grinding the soil sample for 2 min with deionized water (Grant, 1969); the pH of oxidation (pH_{ox}) was measured by complete oxidation of the sample after 6 h of treatment with hydrogen peroxide (33% w/v, adjusted to pH 5.5), and then the net acid production (NAP) potential was obtained by titration of the extract using a 0.1 N NaOH solution adjusted to pH 7 (Monterroso and Macías, 1998).

Total carbon (TC) and total nitrogen (TN) contents in soil were quantified by dry combustion using a LECO SC-144DR analyser, total inorganic carbon (TIC) was measured by the Bernard calcimeter method, and the amount of SOC was calculated as the difference between TC and TIC. The concentration of plant-available phosphorus was determined following the Olsen's method (P_{Olsen}), which is based on the alkaline extraction of phosphate from the soil by a 0.5 N NaH(CO₃) solution (Olsen and Sommers, 1982). The content of pyritic sulfur was obtained by the ASTM D2492 standard test method, which provides a separation of sulfur into pyritic and sulfate forms based on their different solubilities in HCl and HNO₃. Effective cation exchange capacity (eCEC) was determined by leaching the soil samples with 1 M NH₄Cl solution. Base cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) released into solution were analyzed by flame atomic absorption spectroscopy (FAAS), and the amount of exchangeable acid cations (H^+ and Al^{3+}) was estimated by titration with 0.01 N NaOH. Base saturation was quantified by the percent of soil exchange sites occupied by the base cations versus all cations.

Total concentrations of major and minor elements (Fe, Al, Mn, Mg, Ca, K, Na, S and P) and selected PTE (As, Cd, Cu, Hg, Ni, Pb and Zn) were determined in soil samples by inductively coupled plasma-optical emission spectrometry (ICP-OES), after a four-acid digestion (HF-HClO₄-HNO₃-HCl). Quality assurance and quality control (QA/QC) were accomplished through the analysis of reagent blank samples, certified reference materials (GXR-4, GXR-6, SDC-1, SBC-1) and replicate samples. In order to assess the actually mobile and potentially mobile fractions of PTE in soil (Gupta et al., 1996; Houba et al. 1996), two commonly used single-reagent extraction tests with 0.01 M CaCl₂ and with 0.05 M EDTA (adjusted to pH 7.0) were applied, respectively. After chemical extractions, the suspensions were centrifuged for 10 m at 5000 rpm, and the PTE of concern were analyzed in the supernatant after filtration (0.45 μm), using an Agilent 7700 ICP-MS instrument. Furthermore, a recently developed single extraction method using 0.43 M HNO₃ was conducted to estimate the oral bioaccessibility of PTE in the <250 μm sieved fraction of soil (Rodrigues et al. 2018).

The precision of the analytical results was estimated by analyzing duplicate samples. The relative percent difference between the duplicate samples was within an acceptance range of variation (±10%).

3.3. Culture-based microbial tests

A one-gram aliquot of dried and crushed sample was resuspended in 10 mL of peptone water and centrifuged at 2000 rpm for 2 min. Supernatants were used as source of microorganisms. The assays were performed on petri dishes containing tryptone-soy-agar (TSA), which is used to cultivate a wide variety of microorganisms, or sabouraud agar-chloramphenicol (SAC), allowing specifically the growth of fungi and yeasts (Pepper and Gerba, 2004). The petri dishes were incubated for 5 days at 30 °C, and development of colonies was observed every day during the period.

4. Characterization of reclaimed mine soils

4.1. Soil properties

Particle-size distribution, electrochemical parameters and cation exchangeable capacity of the RMS samples are given in Table 1. Soil is predominantly silty loam in texture with less than 10% of clay-sized particles. The mean coarse fragment (gravel) content in this medium-textured soil is 28%-30% of total mass.

The pH_{H2O} values normally varied from 6.4 to 8.3 with a median value of 7.3, indicating that the lime-treated soil has a near neutral reaction when suspended in water, although some samples (4E and 6E) from the waste dump area showed moderately acid ($pH_{H2O} = 5.8$) and very strongly acid ($pH_{H2O} = 4.6$) reactions. Similar results were obtained when the soil pH was measured in a high ionic strength KCl solution. The pH_{KCl} values of most samples were in the range of 6.3 to 7.8, with a median of 7.2, so that exchangeable acidity is virtually absent, except in the above-mentioned samples which have pH_{KCl} values about one pH unit lower than pH_{H2O} values. The median pH of finely ground soil in water ($pH_{ab} = 7.6$) was slightly higher than the median pH_{H2O} and pH_{KCl} values, as a result of the creation of highly reactive surfaces of the liming material that are freshly exposed by abrasion. The median value of the pH measured after complete oxidation of the sample was 6.7, which is indicative of low potential sulfidic acidity. Nonetheless, the samples 4E ($pH_{ox} = 2.2$) and 6E ($pH_{ox} = 3.5$) revealed a latent acid-generating capacity after oxidation, which can be ascribed to the occurrence of pyrite. The NAP of these samples was 28.54 and 15.15 kg CaCO₃ t⁻¹, respectively.

The RMS seems to be well drained and aerated, spanning a range of positive Eh values (344–511 mV) that reflect moderately oxidizing conditions. There were remarkable differences in soil electrical conductivity (EC) among zones. In the open pit area, the EC values ranged

Table 1

Particle size distribution, electrochemical parameters and cation exchange capacity of the reclaimed soil samples. EC (electrical conductivity); Eh (potential redox); eCEC (effective cation exchange capacity); BS (base saturation).

Area	Sample	Particle size distribution			Electrochemical parameters						Cation exchangeable capacity						
		Sand	Silt	Clay	pH_{H2O}	pH_{KCl}	pH_{ab}	pH_{ox}	Eh	EC	Ca^{2+}	Mg^{2+}	Na^+	K^+	$Al^{3+}+H^+$	eCEC	BS
		%	%	%					mV	mS cm^{-1}	cmol kg^{-1}	cmol kg^{-1}	cmol kg^{-1}	cmol kg^{-1}	cmol kg^{-1}	cmol kg^{-1}	%
Open pit	1C	41.2	53.8	5.0	6.6	6.5	7.5	6.4	397	2.32	14.0	1.30	0.10	0.13	35.1	50.6	30.7
	2C	31.9	61.9	6.2	6.7	6.8	7.4	6.3	382	1.79	15.1	0.69	0.08	0.16	43.1	59.2	27.2
	3C	28.2	63.8	8.0	7.1	6.7	7.2	7.2	360	2.74	35.7	1.84	0.06	0.08	45.1	82.7	45.5
	4C	16.9	73.8	9.3	6.9	6.8	7.2	6.8	392	2.92	54.6	2.95	0.07	0.08	50.1	107.9	53.5
	5C	24.9	67.2	7.9	7.9	7.5	8.2	6.4	356	1.83	9.72	0.53	0.04	0.10	35.1	45.5	22.8
	6C	30.8	62.7	6.5	8.1	7.7	8.4	6.3	346	0.21	11.1	0.62	0.03	0.10	45.1	56.9	20.8
	7C	21.1	71.0	7.9	7.6	7.5	7.9	6.9	413	1.20	14.8	0.34	0.19	0.09	50.1	65.5	23.5
	8C	9.6	80.1	10.3	8.3	7.8	8.4	6.3	383	0.20	11.7	0.49	0.05	0.12	40.1	52.5	23.6
	9C	32.2	62.4	5.4	8.2	7.7	8.3	6.6	359	0.27	8.68	1.07	0.28	0.69	45.1	55.8	19.2
	10C	32.6	59.3	8.1	7.5	7.4	7.6	7.4	434	3.09	61.4	3.55	0.27	0.64	54.9	120.8	54.5
Mine waste dumps	1E	42.5	51.4	6.1	6.4	6.3	6.7	–	394	2.47	30.5	3.49	0.03	0.17	34.9	69.0	49.5
	2E	35.5	55.7	8.8	6.4	6.3	6.6	–	392	2.91	43.7	4.25	0.04	0.05	40.1	88.2	54.5
	3E	37.1	55.5	7.4	7.7	7.3	7.6	7.5	369	17.34	12.9	6.17	0.09	0.15	39.9	59.2	32.7
	4E	52.9	40.9	6.2	4.6	3.5	4.5	2.2	511	12.96	0.59	2.29	0.04	0.10	45.0	48.0	6.3
	5E	48.5	46.9	4.6	6.6	6.4	6.4	6.7	356	2.52	14.0	6.31	0.03	0.04	30.0	50.4	40.4
	6E	42.6	52.6	4.8	5.8	5.1	5.7	3.5	379	154.4	6.17	1.84	0.02	0.08	40.1	48.2	16.8
	7E	31.2	61	7.8	7.4	7.5	7.8	6.7	358	46.2	15.7	4.58	0.06	0.07	39.9	60.4	33.9
	8E	30.7	63.5	5.8	7.3	7.3	7.7	6.8	358	133.5	19.3	4.16	0.06	0.06	29.8	53.3	44.2
	9E	40.3	52.8	6.9	7.4	7.1	7.8	7.4	360	46	10.6	6.17	0.03	0.06	39.7	56.6	29.8
	10E	33.6	57.7	8.7	7.9	7.5	8.1	6.9	344	28	11.6	4.39	0.05	0.07	36.7	52.8	30.5

up to about 3.0 mS cm^{-1}, suggesting a relatively low soluble salt content in the soil solution, whereas the samples collected in the overburden dumps showed a highly variable salinity, from non-saline to moderately saline (EC values up to 15.4 dS cm^{-1}). The high salinity could be associated with position in the landscape and possible redistribution of salts by drainage and subsequent precipitation of transient soluble sulfate minerals.

The eCEC values obtained in the amended soil samples from the open pit area ranged broadly, from 45 to 120 cmol$_c$ kg^{-1}. The results showed that acid cations (H^+ and Al^{3+}) are the most prevalent cations in the soil exchangeable pool, accounting for about 68% of eCEC on average. The dominant base cation on the exchange sites was Ca^{2+} (from 8.7 to 61.4 cmol$_c$ kg^{-1}), followed by Mg^{2+} (up to 3.5 cmol$_c$ kg^{-1}). The amounts of exchangeable K^+ and Na^+ were practically negligible. The percent base saturation (BS), or proportion of eCEC in the soil occupied by base cations, was lower than 50% in most samples.

4.2. Soil constituents and nutrients

The RMS samples are mineralogically composed of quartz, clay minerals (mica, kaolinite, and more rarely chlorite), feldspars and carbonates in variable proportions. The carbonate content in soil samples, expressed as an equivalent calcium carbonate content, reached to a maximum of 34%. In addition, some samples contain XRD-detectable amounts of secondary sulfate minerals, namely jarosite and gypsum, and iron oxides. Exceptionally, hematite accounted for 25–30% of the sample 4E due to the occurrence of roasted pyrite ash (red wastes).

Soil carbon, nitrogen, phosphorus and sulfur contents are given in Table 2. There were significant differences (p < 0.05) among the zones. The total carbon content in samples from the open pit area (TC = 0.48–3.26%) was dependent mainly on the carbonate content, as the content of soil organic carbon in these samples was rather low (SOC = 0.31% on average). The mean percent SOC was about two times higher

Table 2

Soil nutrients and other constituents determined in the reclaimed soil samples.

Area	Sample	C_{total} %	SOC %	Carbonate %	N %	C/N -	P_{total} %	P_{Olsen} mg kg^{-1}	S_{total} %	S_{pyr} %
Open pit	1C	0.48	<0.1	4.8	0.02	24.0	0.068	12.7	0.51	0.02
	2C	0.61	0.12	4.1	0.04	15.3	0.085	23.2	0.29	0.01
	3C	1.09	0.08	8.4	0.08	13.6	0.105	25.8	1.86	0.02
	4C	1.41	0.47	7.9	0.06	23.5	0.137	50.0	1.57	0.02
	5C	1.09	<0.1	9.8	0.06	18.2	0.092	28.1	0.16	0.02
	6C	2.30	<0.1	19.9	0.14	16.4	0.190	61.3	0.24	0.07
	7C	1.14	0.40	6.2	0.06	19.0	0.112	27.5	0.42	0.02
	8C	1.37	0.65	6.0	0.06	22.8	0.111	28.7	0.23	0.05
	9C	3.26	0.84	20.2	0.14	23.3	0.212	49.4	0.19	0.03
	10C	2.18	0.42	14.7	0.10	21.8	0.238	39.1	3.19	0.02
Mine waste dumps	1E	1.66	0.98	5.70	0.10	16.6	0.084	3.5	1.06	0.39
	2E	1.05	0.24	6.74	0.07	15.0	0.156	4.2	3.32	0.59
	3E	1.93	0.54	11.6	0.10	19.3	0.070	4.9	0.09	0.07
	4E	2.88	2.59	2.45	0.12	24.0	0.043	2.8	0.55	0.55
	5E	0.71	0.12	4.91	0.04	17.8	0.051	2.4	0.58	0.21
	6E	0.95	0.38	4.78	0.05	19.0	0.064	2.2	0.35	0.32
	7E	7.86	6.14	14.3	0.21	37.4	0.340	33.2	0.66	0.65
	8E	7.27	6.58	5.76	0.18	40.4	0.382	22.3	1.14	0.62
	9E	2.33	2.18	1.25	0.13	17.9	0.072	1.8	0.39	0.40
	10E	4.05	2.25	14.9	0.14	28.9	0.203	18.8	0.83	0.84

in the overburden dumps than in the open pit, due to the high organic-matter level detected in the samples 7E and 8E, with SOC values above 6%. With few exceptions, total N content was very low throughout the mine site (TN about 0.10% on average). The sample 7E had the highest TN concentration too (0.21%). The C/N ratio fell in the range from 13 to 40, with a median value of about 20 in both sampling areas. The total content of P in the reclaimed soil was found below 0.40% in all the samples, and the amount of P_{Olsen} varied widely, from 1.8 to 61.3 mg kg^{-1}. The pool of available P was, therefore, less than 5% of the total P concentration. The total content of S ranged from 0.09 to 3.32%, with a mean value of about 0.90% in both reclaimed areas. However, the median content of pyritic S in the samples from the waste dumps area (S_{pyr} = 0.50%) was considerably higher than that recorded in the open pit area (S_{pyr} = 0.02%), which is in accordance with their high potential sulfidic acidity. Considerable differences in S_{total} and S_{pyr} proportions denote the occurrence of sulfate minerals detected by XRD, such as jarosite and gypsum.

4.3. Microbial test

An estimation on the amount of bacterial and fungal colonies that grew after five days of incubation on the TSA and SAC plates is given in Table 3. Filamentous fungi and yeasts were found in the reclaimed areas, with the exception of the open pit bottom (sample 4), and the fungal abundance varied among sampling sites. Combined growth of bacteria and fungi was most apparent in samples 1, 3, 5 and 7. Morphology of bacterial colonies was diverse indicating the occurrence of several strains. No bacterial colonies were identified in samples 2 and 4, and though they were barely developed in sample 6, abundant mycelial growth of fungi was observed. The samples 2 and 6 collected for microbial test at the locations 4E and 9C, respectively, showed limited microbial development. These sites are being affected by acidic seepages and runoff, as indicated by the low percent of base saturation (6.3% and 19.2%, respectively), which may limit the growth of bacterial colonies.

4.4. Major and trace elements concentrations

Major and trace element concentrations of bulk soil samples are listed in Table 4. Regardless of the silica content, the results showed that the geochemistry of major elements is dominated by Fe (up to 23.3%), Ca (up to 15.2%), and Al (up to 9%), and in an lesser extent by K (up to 3.35%), which is consistent with the mineral composition of the amended soil. The highest percentages of Fe and Ca reflect the abundances of hematite and calcite, respectively, whereas the Al and K concentrations are related to clay minerals (kaolinite, mica), and to some extent to jarosite in the case of K. The remaining major elements (Mg, Mn, Na) were all generally present at concentrations less than 1 wt %.

Interestingly, it was found high contents of PTE in some soil samples from the reclaimed zones. The most elevated concentrations of Pb, As, Cu, Ni, and Cd were found in the mine waste dumps area, with median values of 1260, 361, 779, 15, and 1.8 mg kg^{-1}, respectively. In particular, the sample 4E reached exceptionally high levels of Pb (more than 5000 mg kg^{-1}), As (504 mg kg^{-1}) and Cu (1470 mg kg^{-1}). The largest

median concentrations of Zn (463 mg kg^{-1}) and Hg (16 mg kg^{-1}) were recorded in samples from the open pit area.

4.5. Extractable trace element concentrations

The results of the PTE concentrations extracted by $CaCl_2$, EDTA and HNO_3 are presented in Table 5. For most soil samples, the metal content in the $CaCl_2$ extracts was virtually negligible. The extractable concentrations of Pb and Cd were lower than the detection limit by ICP methods in all or most samples. Of the other contaminants, the mean concentration of As extracted by $CaCl_2$ was 0.09 mg kg^{-1}, the Zn concentrations in the extracts varied among soil samples, from undetectable levels to 2.63 mg kg^{-1}, whereas Cu was generally present at concentrations less than 1 mg kg^{-1}, with the exception of a few samples. The maximum concentration of Cu (7.70 mg kg^{-1}) was measured in the extract of the sample 4E. Therefore, the average extractability of the metals by $CaCl_2$ followed the decreasing order of Cu > Zn > As > Cd > Pb.

The amounts of PTE obtained by the EDTA extraction method varied greatly depending on the PTE involved and the sampling site. On average, the EDTA treatment dissolved 97.9 mg kg^{-1} of Cu and 63.3 mg kg^{-1} of Zn, reaching exceptionally high values (up to 520 mg kg^{-1} of Zn and 280 mg kg^{-1} of Cu) in the sample E2. The soil extract from this sample also recorded the maximum content of Cd (5.0 mg kg^{-1}). The extractable content of Pb was generally below 20 mg kg^{-1}, but a concentration as high as 228 mg kg^{-1} was measured in the sample E9. For As, the EDTA-extracted amounts were relatively low, with an average about 3 mg kg^{-1}. The mean values of EDTA-extractable concentrations were in the order: Cu > Zn > Pb > As > Cd.

The use of 0.43 M HNO_3 as extracting reagent led to higher extraction yields than those quantified with $CaCl_2$ and EDTA, although it provides similar information about the relative mobilization of metals. The average amounts of PTE released upon acid treatment of the RMS samples were: 238 mg kg^{-1} of Cu, 161 mg kg^{-1} of Zn, 41 mg kg^{-1} of Pb, 5.6 mg kg^{-1} of As, and 0.63 mg kg^{-1} of Cd. Thus, the PTE displayed the same overall trend of decreasing extractability than that observed for EDTA.

5. Discussion

5.1. Effectiveness of soil reclamation

5.1.1. Soil texture and structural stability
The average percentage of fine earth (silt plus clay fraction) in the RMS was higher than that of the mine soil, and the mean sand content declined from 50% to 33% after 15 years of reclamation (Fig. 2a), due to mixing of the coarse-textured spoil with the different amendment materials. Therefore, the RMS now has an increased water-holding capacity, and can retain nutrients for plants more effectively.

The structural stability of soil is linked with the content of fine earth and SOC. Although the mean value of the structural stability index (SI) increased from 1.55% to 3.58% during the reclamation period, the RMS has a structurally degraded surface soil. This condition is similar to the one described by Spargo and Doley (2016), indicating that organic matter applied to coal mine spoil had been lost from the surface soil within 2.5 years after placement, with the result that the surface was bleached and exhibited surface seal, which reduced rainfall infiltration. In agreement with previous studies in other mine sites (e.g. Zhang et al. 2016), results also indicated that amendments and revegetation did not substantially improve the physical structure of the degraded soil, at least for a period of 15 years. However, the SI of various samples from the mine waste dumps area was higher than 9% (samples E7 and E8) indicating sufficient organic carbon to maintain the soil structural stability.

5.1.2. Soil acidity
Soil pH_{H2O} is a measure of active acidity of the sample and is the most commonly used indicator for estimating soil quality, especially in mine

Table 3
Relative growth of bacterial and fungal colonies.

Area	Sample	Bacteria	Fungi
Open pit benches	1	+++	++
	2	–	+
	3	++	+++
Open pit bottom	4	–	–
Mine waste dumps	5	+++	++
	6	+	+++
	7	+++	+++

+++ abundant; ++ common; + scarce; - not detected.

Table 4
Total concentrations of major and trace elements in the reclaimed soil samples.

Area	Element	Major elements (% wt)							Trace elements (mg kg^{-1})						
		Al	Fe	Mn	Mg	Ca	K	Na	As	Cd	Cu	Hg	Ni	Pb	Zn
	Detection limit	0.01	0.01	0.01	0.01	0.01	0.01	0.01	3	0.3	1	1	1	3	1
Open pit	1C	6.73	4.46	0.01	0.96	1.15	2.35	0.23	497	1.3	326	27	3	2130	576
	2C	7.48	3.13	0.01	0.44	0.95	2.40	0.42	460	1.1	384	81	4	2650	486
	3C	6.57	6.22	0.04	0.57	2.89	3.19	0.43	326	1.3	448	8	10	1450	453
	4C	5.36	6.47	0.01	0.49	4.47	1.90	0.33	224	0.7	494	14	7	1080	196
	5C	7.89	3.61	0.01	0.94	3.48	2.19	0.36	195	0.4	586	11	4	1060	418
	6C	6.49	3.85	0.01	1.06	8.41	2.06	0.26	151	BDL	1120	3	6	667	362
	7C	8.48	3.98	0.01	1.00	2.67	2.61	0.27	114	1.2	939	3	7	546	531
	8C	9.00	4.63	0.01	1.03	3.79	3.35	0.27	258	BDL	596	4	9	1110	201
	9C	6.40	4.40	0.09	0.58	8.05	2.68	0.15	127	2.7	373	2	22	377	916
	10C	4.89	5.38	0.01	0.52	8.95	1.73	0.22	368	2.3	1060	11	8	970	491
Mine waste dumps	1E	7.36	5.22	0.04	0.38	2.83	1.78	0.52	154	3.1	608	3	36	1260	766
	2E	7.40	8.02	0.03	0.20	4.25	1.53	0.12	361	5.3	1110	2	31	1100	1210
	3E	7.15	4.64	0.03	0.43	3.87	1.37	0.30	21	0.3	69	2	34	185	118
	4E	4.27	23.30	0.02	0.58	0.30	1.03	0.42	504	2.0	1470	12	15	>5000	304
	5E	5.08	3.33	0.01	0.24	0.95	2.22	0.12	275	0.3	168	8	14	790	98
	6E	7.01	5.51	0.01	0.43	0.66	2.63	0.27	324	BDL	195	2	12	679	75
	7E	3.68	6.76	0.01	0.34	13.60	0.96	0.30	378	1.8	845	5	8	2060	311
	8E	3.29	7.28	0.03	0.40	15.20	0.82	0.26	361	1.6	1550	3	14	3590	425
	9E	5.65	7.89	0.07	0.60	1.61	1.72	0.52	518	2.1	1370	3	23	3320	377
	10E	4.49	8.79	0.01	0.37	9.07	1.45	0.37	648	1.3	712	3	15	2130	300

Table 5
Trace element concentrations extracted with CaCl$_2$, EDTA and HNO$_3$ from the reclaimed soil samples.

Area	Element (mg kg^{-1})	As			Cd			Cu			Pb			Zn		
	Detection limit	0.001			0.002			0.002			0.007			0.006		
	Extractant	CaCl$_2$	EDTA	HNO$_3$	CaCl$_2$	EDTA	HNO$_3$	CaCl$_2$	EDTA	HNO$_3$	CaCl$_2$	EDTA	HNO$_3$	CaCl$_2$	EDTA	HNO$_3$
Open pit	C1	0.02	1.95	3.85	BDL	0.49	0.56	0.40	34.18	95.36	BDL	16.29	43.30	BDL	23.51	86.86
	C2	0.06	3.00	10.05	BDL	0.42	0.64	0.38	89.23	168.2	BDL	48.36	101.9	0.13	51.32	110.5
	C3	0.01	0.88	10.89	BDL	0.46	0.61	0.34	90.92	186.7	BDL	4.68	9.10	BDL	76.38	178.9
	C4	0.02	0.25	11.40	BDL	0.20	0.36	0.46	94.51	236.2	BDL	4.09	12.32	BDL	22.46	53.83
	C5	0.04	2.91	3.63	BDL	0.09	0.15	0.64	55.74	184.8	BDL	13.03	31.91	0.17	9.24	25.77
	C6	0.53	2.42	4.56	BDL	0.06	0.16	0.72	117.3	634.7	BDL	9.69	26.52	0.53	8.06	28.65
	C7	0.01	1.27	5.75	BDL	0.57	0.76	0.48	228.2	528.0	BDL	12.86	19.32	BDL	81.07	213.2
	C8	0.05	7.30	5.24	BDL	0.11	0.08	0.41	63.02	218.4	BDL	15.59	32.58	BDL	4.13	10.09
	C9	0.04	2.63	5.34	BDL	0.73	0.07	0.33	60.19	201.2	BDL	7.04	8.96	BDL	119.2	866.7
	C10	0.11	0.22	25.24	BDL	0.66	1.39	0.82	221.9	723.1	BDL	6.57	4.06	0.83	86.25	312.7
Mine waste dumps	E1	0.02	0.42	3.05	BDL	1.03	1.28	0.23	89.67	262.0	BDL	26.39	40.03	BDL	84.46	301.8
	E2	0.02	0.08	10.97	BDL	5.00	4.70	0.46	279.5	543.6	BDL	17.54	29.16	0.73	520.0	821.7
	E3	0.01	1.54	0.25	BDL	0.09	0.18	0.37	8.02	14.82	BDL	10.25	22.52	BDL	9.13	19.48
	E4	0.03	1.88	0.55	0.02	0.04	0.09	7.70	38.98	100.5	BDL	91.13	137.4	2.50	2.99	4.49
	E5	0.02	2.53	5.26	BDL	0.15	0.19	0.36	29.50	51.25	BDL	7.72	11.19	BDL	22.15	40.15
	E6	0.01	2.24	2.10	BDL	0.02	0.03	0.23	15.56	34.96	BDL	8.92	13.01	BDL	2.85	4.87
	E7	0.08	7.10	2.85	BDL	0.23	0.02	0.40	45.17	16.44	BDL	24.31	16.24	BDL	25.80	3.14
	E8	0.31	2.33	0.31	BDL	0.27	0.13	0.78	116.9	50.29	BDL	49.07	0.60	0.36	43.30	11.18
	E9	0.04	7.95	0.04	BDL	0.65	0.85	1.27	258.1	503.9	BDL	227.7	247.8	BDL	56.91	111.0
	E10	0.47	12.37	0.47	BDL	0.13	0.40	0.24	22.07	11.99	BDL	12.01	12.61	2.63	16.20	7.84

soils, since it has a great influence on key biogeochemical processes (Sheoran et al. 2010; Buta et al. 2019). Since low soil pH is commonly associated with heavy metal toxicity, enhancement of pH provides the basic condition necessary for metal attenuation at mine sites (Wilkin, 2008).

The SBL amendment had a strong effect on pH of the soil–water system. The amended soil experienced a pH$_{H2O}$ increase over the study period, from ultra-acid to slightly alkaline values (Fig. 2b), which coincide with the pH conditions required for effective precipitation/adsorption of most heavy metals. Given the long lapse of time since the amendment, the soil pH appears to be buffered by carbonate, and thereby the potential acid production by residual pyrite may be consumed with little or no decrease in pH through the following acid-neutralization reactions:

$$CO_3^{2-} + 2H^+ \leftrightarrow HCO_3^- + H^+$$

$$HCO_3^- + H^+ \leftrightarrow H_2O + CO_2$$
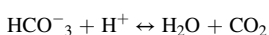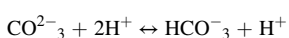
Similarly, the near-neutral values of the soil pH$_{KCl}$ suggest that the potentially available pool of acidic cations on soil exchangeable sites of the reactive soil particles is negligible in the RMS.

After SBL application, the pH$_{ox}$ values also sharply increased from a median value of 3.1 to 6.7 (Fig. 2b). This means that the amount of acidity derived from the oxidative dissolution of pyrite was not relevant in most RMS samples, which is consistent with the lack or low level of pyritic S (0.25% on average) in soil 15 years after the liming material was applied. Prior to reclamation, the mean content of pyritic S was 1.63% in the open pit area, and 1.78% in the mine waste dumps area. Therefore, acidity produced by oxidative dissolution of pyrite was neutralized by lime material, leading to an increase in pH that would promote soil fertility and nutrient cycling. Nonetheless, the acid-generating capacity of the samples E4 (571 mmol H$^+$ kg^{-1}) and E6 (303 mmol H$^+$ kg^{-1}) may require more lime (28.5 and 15.5 kg CaCO$_3$ t^{-1} according to their respective NAP values) to achieve a pH suitable for growing plants and for the improvement of other soil health indicators.
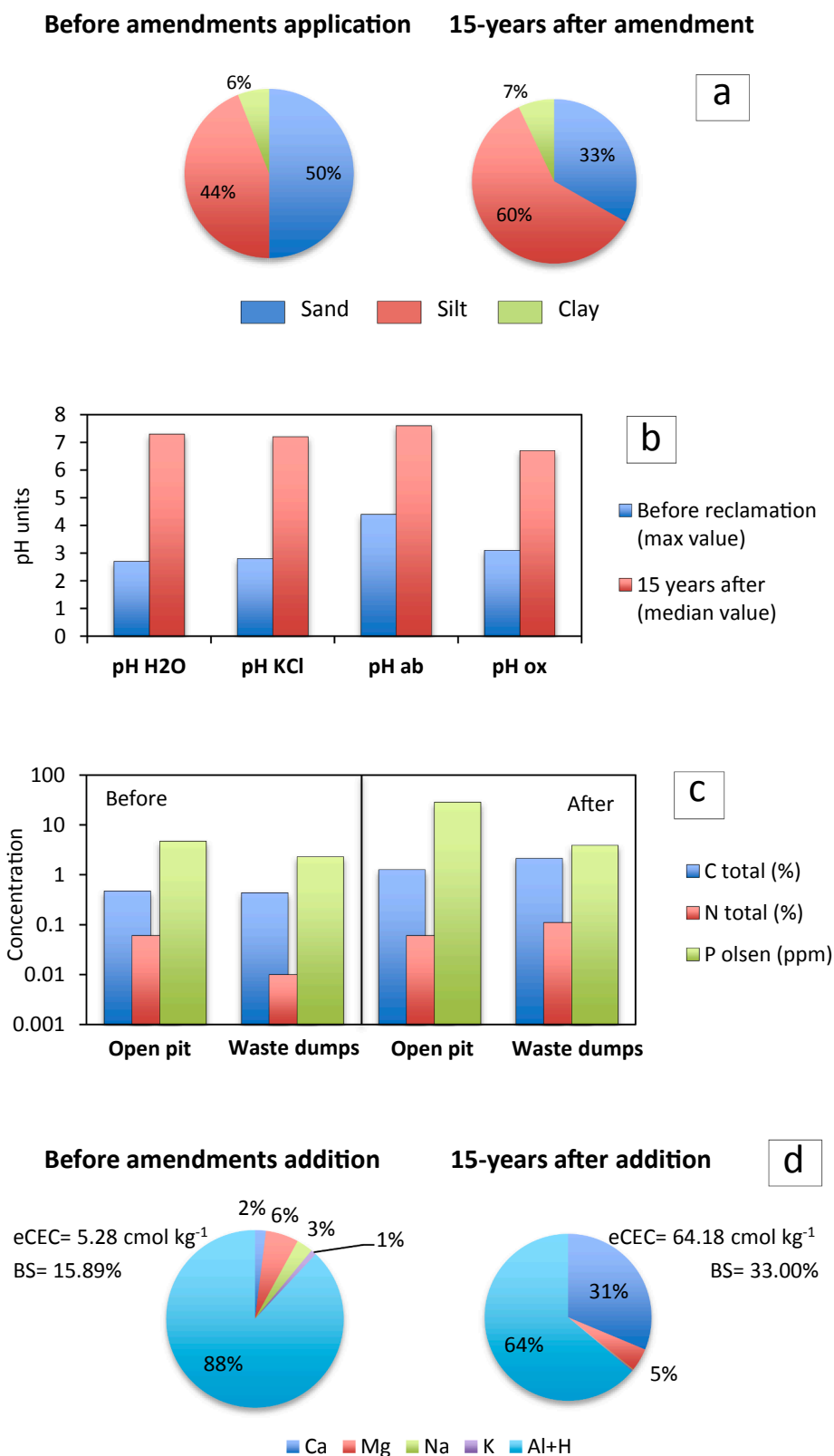
Fig. 2. Comparison charts of soil properties for before and after land reclamation: a) mean grain-size distribution; b) pH values; c) median concentrations of total C, total N and Olsen P; d) effective cation exchange capacity (eCEC), base saturation (BS) and percent of exchangeable cations (expressed as mean values).

5.1.3. Soil fertility

A supply of soil nutrients is critical for the establishment and maintenance of vegetation in reclaimed mine lands (Tordoff et al. 2000; Larney and Angers, 2012). In particular, C and N play an important role in the restoration of ecosystem functions (Shrestha and Lal, 2007). The median concentration of total C in the spoil was around 0.45% according to Saiz (2004), and it was increased in both the open pit area (1.26%) and the waste dumps area (2.13%) after soil reclamation (Fig. 2c). It

must be noted that most of this increase accounted for by carbonates. The combined use of SBL and CB as soil amendment has shown to increase the soil carbon storage and phosphorus availability. Seven of the 20 RMS samples showed a level of SOC greater than 0.75%, which is indicative of good fertility (Ghosh et al. 1983). The C/N ratio increased with amendments as the level of TN remained nearly constant in the open pit area (Fig. 2c). The median value of the C/N ratio in the RMS was about 20, that is, still somewhat below the optimal range for adequate soil functions (Shrestha and Lal, 2007). It is also apparent that the available P concentration in RMS was increased upon the treatment since the average value of P_{olsen} in the spoil (4.7 mg kg^{-1}) changed to 34.6 mg kg^{-1} in the RMS (Fig. 2c). According to the relatively high P_{Olsen} concentrations measured in the SBL (914 mg kg^{-1}) and CB (525 mg kg^{-1}) additives (Saiz and Ceacero, 2008), it can be argued that there has been a significant increase (p > 0.05) in the available P pool as a result of the amendments. This indicates that the nutritional status of the soil in relation to this important nutrient has improved considerably.

Effective CEC increased with SBL and CB addition, with mean values changing from 5.28 cmol$_c$ kg^{-1} (pre-operational situation) to 64.18 cmol$_c$ kg^{-1} after the treatment. This effect was induced by the soil pH increase, as a result of deprotonation of pH-dependent charge sites of clay minerals and organic matter. Under the slightly alkaline conditions prevailing in the RMS, clay minerals have negatively charged surfaces on both basal (0 0 1) and edge faces, thus providing exchange sites for cations. Soil organic matter has functional groups that can be deprotonated, resulting in enhanced cation adsorption through increased negative surface charge with raising soil pH. The dominant exchangeable base cation was Ca^{2+} (Fig. 2d). It can be assumed, therefore, that most of the newly-created exchange sites were occupied by Ca^{2+}. This cation has strong hydration spheres and is mostly adsorbed as outer-sphere complexes on negatively charged surfaces (Strawn, 2021).

5.1.4. Soil contamination

Reclamation activities caused some important changes in the trace element geochemistry of soil. Fig. 3 depicts the temporal variation of total concentrations of the most concerned PTE. As compared to the -prior to reclamation results, the median contents of As, Cu, Hg, Pb and Zn decreased in the RMS samples from the open pit area. This fact can be explained, in part, as a dilution effect due to the incorporation of amendment materials. Likewise, the median values of As, Hg and Pb decreased in the mine waste dumps area but, conversely, those of Cu and Zn were increased, probably as a result of transient precipitation of soluble sulfate minerals from acidic runoff from the waste overburden stockpiles.

Therefore, the RMS retains anomalously high concentrations of PTE, notably As, Cu, Pb and Zn, that are well above the soil geochemical baseline of the South-Portuguese Zone of the Iberian Massif (Galán et al. 2008), which reasonably represents the natural background levels of the IPB (Fernández-Caliani et al. 2009). Based on the Pollution Load Index (PLI) of Tomlinson et al. (1980), a quantitative evaluation of the degree of multielement soil contamination was made by calculating the fourth root of the product of their concentration factors (CF$_{As}$ × CF$_{Cu}$ × CF$_{Pb}$ × CF$_{Zn}$). Thus, over time, the PLI decreased remarkably in areas disturbed by open-pit mining, from median values around 28 (before amendments application) towards 13 (15-years after application), whilst the PLI values of the waste dumps area remained almost constant (around 13) or slightly higher when compared to soil prior reclamation (Table 6). The largest pollution load (PLI higher than 26) was recorded in the sample E4 indicating that there is still a severe and persistent contamination by PTE, especially in the soil contaminated with leachates from pyrite-

Table 6
Concentration factor (ratio between each trace element in the sample and its background value) and PLI values of the reclaimed soil samples.

| Area	Samples	Concentration factors (CF)				Pollution Load Index (PLI)
		As	Cu	Pb	Zn	
Open pit	1C	19.88	10.19	56.05	7.58	17.13
	2C	18.40	12.00	69.74	6.39	17.71
	3C	13.04	14.00	38.16	5.96	14.27
	4C	8.96	15.44	28.42	2.58	10.03
	5C	7.80	18.31	27.89	5.50	12.17
	6C	6.04	35.00	17.55	4.76	11.53
	7C	4.56	29.34	14.37	6.99	10.77
	8C	10.32	18.63	29.21	2.64	11.04
	9C	5.08	11.66	9.92	12.05	9.17
	10C	14.72	33.13	25.53	6.46	16.84
Mine waste dumps	1E	6.16	19.00	33.16	10.08	14.06
	2E	14.44	34.69	28.95	15.92	21.92
	3E	0.84	2.16	4.87	1.55	1.92
	4E	20.16	45.94	>131.6	4.00	>26.42
	5E	11.00	5.25	20.79	1.29	6.27
	6E	12.96	6.09	17.87	0.99	6.11
	7E	15.12	26.41	54.21	4.09	17.25
	8E	14.44	48.44	94.47	5.59	24.66
	9E	20.72	42.81	87.37	4.96	24.90
	10E	25.92	22.25	56.05	3.95	18.90
Regional baseline*		25	32	38	76	–

* Data from Galán et al. (2008).
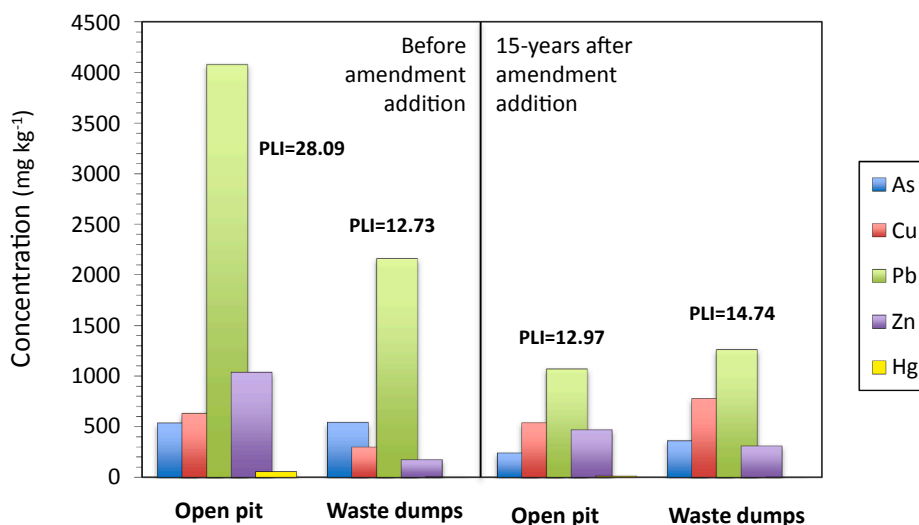
Fig. 3. Bar charts comparing the median total concentrations of trace elements in soil before and 15 years after the mine land reclamation, and the median values of PLI (Pollution Load Index).

roasting residues.

According to the Spanish regulation on contaminated soils, the RMS is potentially contaminated and requires site-specific quantitative risk assessment to predict hazards more precisely. Some contaminants like As, Cu and Pb are present at concentrations that could adversely affect human health and the environment. In fact, As and Pb concentrations exceeded their regulatory thresholds for forestry land use (36 mg kg^{-1} and 275 mg kg^{-1}, respectively) in all RMS samples except one. The reference level for Cu (595 mg kg^{-1}) was also exceeded in several samples from both sampling sites.

5.1.5. Microbial development and vegetation assessment

The results of the microbiological test indicated that soil reclamation measures promoted the development of both mycelial fungi and yeasts, and also of a variety of bacterial strains in most sampling sites, which is a good sign of healthy soil processes. Mycorrhizal fungi may have contributed to plant re-establishment by increasing the nutrient absorption capacity of roots and improving soil structure (Tordoff et al. 2000).

Re-establishment of the forest cover and associated spontaneous vegetation (grasses and shrubs) has been essential to mitigate the negative impact of the past mining on the landscape and reduce soil erosion. The success of the revegetation program was evaluated by Saiz and Ceacero (2008) through quantitative assessment of the plant growth and survival one year after planting was completed. The percent of pine trees that survived during this period was 72%, and the survival rate of oleander was higher than 90%. Recent studies have shown that this resistant shrub meets the criteria to be used for phytostabilization purposes of pyritic mine soils (Parra et al. 2016). On the basis of an allometric relationship, it was found a moderate positive correlation ($R^2 = 0.6$) between plant height and basal stem diameter, resulting in substantially improved vegetation growth.

Actually, a visual inspection of the reforested mine land verifies a general improvement in the ecological and aesthetic values of the landscape, which is currently in environmental harmony with its surroundings (Fig. 4). Based on the high survival and adaptability of plant species to the physical and physicochemical conditions of the RMS, it is apparent that most of the mine site has been successfully revegetated. Even so, there are localized areas subject to acidic runoff from sulfide-rich waste dumps where plants failed to establish and show signs of deterioration. This also applies in the case of soil contaminated with red wastes (sample E4), which has severe limitations for soil microbial turnover, species survival and vegetative growth, except for *Erica andevalensis*, an endemic heather that grows spontaneously only in extremely acid, metal enriched soils of the IPB, and *Erica australis* a similar, tolerant species able to growth in mine-impacted soils (Márquez-García et al. 2012; Pérez-López et al. 2014). Moreover, landslides and erosive processes have prevented adequate establishment of pine trees in some pit benches.

5.2. Ecological and human health concerns

The RMS contains residual high levels of PTE partitioned among the various solid phases, that could be released upon exposure to the surface environment. Since soil pH is a critical factor in controlling mobility and bioavailability of heavy metals, it can be hypothesized that the lime-induced increase in pH would favor metal retention through coprecipitation and adsorption mechanisms, as reported in similar mine soils of the IPB (Fernández-Caliani and Barba-Brioso, 2010). The opposite behavior can reasonably be expected for oxyanion-forming elements, like As. The rise in pH also increases the net negative charge of variable charge mineral surfaces, thus preventing the adsorption of As oxyanions, which may be released into soil solution under circumneutral conditions.

Therefore, it is paramount to evaluate the extent of metal mobilization and the potential concerns for ecological and human receptors. Two commonly used single reagent extraction tests with $CaCl_2$ and with EDTA were applied to assess, respectively, the mobile and potentially mobile (or mobilizable) fractions of PTE in the RMS, and the results of the 0.43 M HNO_3 test were used to estimate the oral bioaccessibility (Fig. 5).

The mobile and very active fractions of As, Cd, Cu, Pb and Zn predicted from the mean values of their contents in the $CaCl_2$ soil extracts (Houba et al. 1990; Madejón et al. 2011) were less than 0.15%,

Fig. 4. Field pictures of the Poderosa mine site showing a chronosequence of the post-mining forest restoration: a) before land reclamation; b) shortly after the tree planting; c) open pit area 15 years after the land reclamation d) wastes dumps area 15 years after the land reclamation.
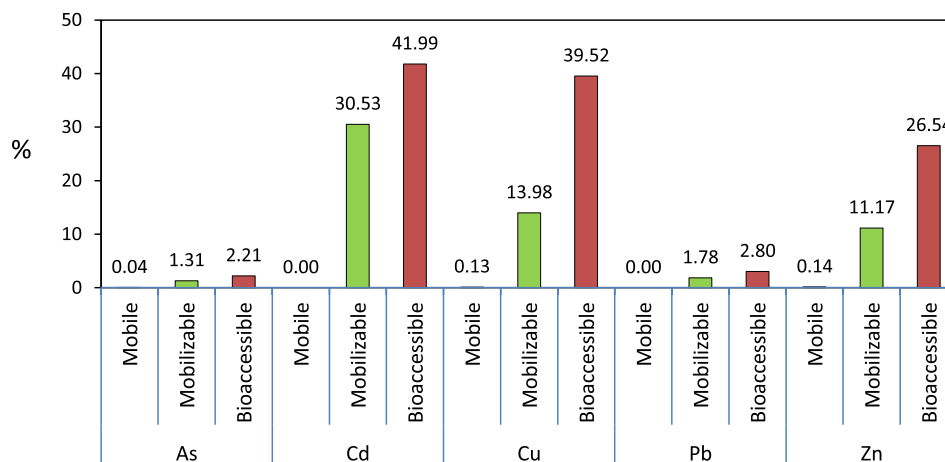
Fig. 5. Mobile (CaCl$_2$-extractable), potentially mobile (EDTA-extractable) and bioaccessible (HNO$_3$-extractable) fractions of trace elements in the reclaimed mine soil.

indicating that the amount of PTE freely dissolved in pore soil water and electrostatically weakly bound onto soil particles is very small in comparison with the total concentration in soil. Adsorption of PTE by cation exchange mechanisms could have been inhibited or limited in this carbonate buffered system, due to the competition with Ca^{2+} ions for sorption sites. Accordingly, the proportion of the total soil metal pool, which may be readily available for plant uptake and leaching into groundwater or nearby watercourses, was found to be negligible due to the low activities of soluble and exchangeable ions in the soil solution.

The potentially mobile metal fraction, assessed by single extraction with EDTA, accounted for a modest fraction of extractable As and Pb in relation to the fixed pool, with median values of 0.80 and 1.39%, respectively. Nonetheless, the EDTA-extracted portions of Zn (10.37%), Cu (13.18%), and especially Cd (29.94%) suggest that a considerable amount of such heavy metals is potentially able to move into the plant root system (Madejón et al. 2009). This complexing agent is capable to remove not only the exchangeable metal fraction but also can extract organically complexed metals, and those bound to iron oxyhydroxides and carbonates (Ure, 1996), likely reflecting the metal availability in the long-term. It can be inferred, therefore, that most heavy metals are effectively immobilized in the RMS under the current slightly alkaline and oxidizing conditions. This behavior is also applicable to As, despite the fact that liming has the potential to mobilize As in the form of relatively soluble oxyanions (Jones et al., 1997; Fernández-Caliani and Barba-Brioso, 2010). The very low fraction of As in potentially mobile forms could be due to scavenging onto poorly crystallized iron oxyhydroxides, which have the ability to strongly immobilize this metalloid through chemisorption and coprecipitation processes, after acid neutralization. Another plausible mechanism for As immobilization following lime addition could be formation of low-solubility calcium arsenates (Bothe and Brown, 1999).

The 0.43 M HNO$_3$ single extraction procedure provided similar information about the relative mobilization of metals although it showed a higher extraction capacity when compared to the other methods. The extraction efficiency of PTE in soil by using the 0.43 M HNO$_3$ test is related to that of *in vitro* methods for measuring human bioaccessibility (Rodrigues et al. 2018), although the results may be somewhat overestimated (Fernández-Caliani et al. 2019). The bioaccessible fraction varied within a broad range depending on the involved metal. According to their median values (shown in brackets), the relative bioaccessibility of PTE increased in this order: As (1.95%) < Pb (2.21%) < Zn (19.62%) < Cu (36.71%) < Cd (44.87%). The higher extractability of Cd upon acid treatment is consistent with the fact that a remarkable portion of this metal may be specifically bound to carbonates, as reported in lime-amended mine soils of the IPB (e.g. San Platon mine, cf. Fernández-

Caliani et al. 2009). The bioaccessible fraction of PTE can be remobilized under the acidic conditions prevailing in the stomach, thereby posing a potential health risk to human receptors via ingestion of contaminated soil particles.

6. Conclusions

This comparative study between pre- and post-reclamation conditions at the Poderosa mine site has shown that soil quality changed noticeably over the considered period (2003–2018), with overall improvements in key soil properties, such as structural stability, cation exchange capacity, degree of base saturation, soil organic carbon, available phosphorus and microbial growth.

Based on these findings, the combined application of SBL and CB as soil additives is an attractive option for assisting natural remediation of heavily contaminated acid mine soils, with proven long-term efficacy. Liming was highly effective in neutralizing soil acidity and for lowering the concentrations of PTE in the most labile metal pools, thereby reducing their leachability and transport to groundwater, plant uptake and bioaccessibility to human and ecological receptors. Soil pH is buffered by carbonate equilibria in most sampling sites, which guarantees both the retention of PTE in the soil matrix and the phytoavailability of essential nutrients.

The use of organic-based soil amendments, such as biosolids, showed promise in enhanced soil fertility, facilitating the re-establishment of a tree cover similar to what would have existed prior to mining, and thus contributing to soil carbon storage. Revegetation with *Pinus pinea* and *Nerium oleander* seems to be a successful and sustainable strategy for reclamation of the drastically disturbed mine soils under Mediterranean conditions, although further efforts should be made to control the phytotoxic levels of residual metals and ensure the maintenance of sufficient fertility to support vegetation.

Based on the progress achieved over the last 15 years in reducing soil acidity, metal leaching and bioaccessibility, and re-establishing vegetation, the insights gained from this land reclamation experience have potential for widespread dissemination and can be extrapolated to broader spatial scales for assisting natural attenuation in other extremely acidic mine soils of the IPB and elsewhere in the world.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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