Assessing the quality of potentially reclaimed mine soils: environmental implications for the construction of a nearby water reservoir

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Abstract

The cementation complex of Las Viñas (SW Spain) is a partially reclaimed abandoned mine site located in the drainage basin of a water reservoir currently under construction. The aim of this investigation was to analyze these mine soils to evaluate their potential environmental impact, especially on the final reservoir water quality. Results evidence the extremely high acidity of soils (pH of 3.4 and maximum potential acidity of 47 kg $CaCO_3$/ton), with high concentrations of trace elements, especially As, Pb and Cu. Sequential extraction data reveal the potential release of significant quantities of Mn, Cd, Cu and other easily-soluble trace elements by rainfalls. The weathering and transport of soils to the bottom sediments of the planned reservoir could lead to the release of significant quantities of toxic trace elements to the water column if anoxic (mainly As, Sb, Cr, Ni, Cu and Pb) or oxic (mainly Hg, Pb, V, Cu and As) conditions are found in the sediments. The acidity and metals released from these soils could jeopardize the quality of the reservoir waters. Remediation measures must be therefore adopted, focused on the cleanup and liming of soils in order to promote colonization and vegetation succession, thus avoiding soil erosion and limiting metal release to the hydrosphere. This study proposes the use of different low-cost materials to improve the soil quality, limiting the metal transfer to the planned reservoir water. The information contained in this study could be of great importance in other watersheds affected by abandoned mine sites.

Keywords: soil pollution; acid mine drainage; Iberian Pyrite Belt; restoration measures

1. Introduction

Mining is an important source of metals into the environment, leading particularly to appreciable soil pollution (e.g. Adriano 2001; Li et al. 2014; Beattie et al., 2017; Abraham et al., 2018). As a result of mining and mineral processing activities, soil is generally degraded and may continue causing environmental damage long after the cease of operations. The disposal of mine wastes may even produce a deeper impact than mining operations themselves (Fernández-Caliani et al., 2009). In many industrialized areas, the majority of mining environmental problems are legacies from the past (Lottermoser, 2010). This is the case of the Iberian Pyrite Belt (IPB, SW Iberian Peninsula) which hosts one of the largest concentrations of massive sulfide deposits in the world (Sáez et al., 1999), resulting in intense mining activities in the region dating back since prehistoric times (Nocete et al., 2005). This intense mining activity in the IPB has left a legacy of huge volumes of sulfide-rich mine wastes and flooded open pit and underground mining installations in more than one hundred abandoned mines. According to Grande (2016), around 4800 ha of surface are occupied by waste rock piles, pits, tailings impoundments and other mining facilities in the Spanish sector of the IPB. The exposure of these sulfide-rich materials to atmospheric conditions causes the oxidative dissolution of sulfide minerals, leading to a very long-lasting and pollutant process known as acid mine drainage (AMD). Mining wastes and the subsequent AMD production promotes a profound impact on the quality of the surrounding soils (EPA, 2016). The impact of mining activities in the IPB is evidenced by the water quality deterioration observed in the Tinto and Odiel rivers, the main watercourses draining the region, which transport huge loads of metals such as Fe (7900 t/yr), Al (5800 t/yr), Zn (3500 t/yr), Cu (1700 t/yr), and Mn (1600 t/yr) (Nieto et al., 2007).

These abandoned mine sites must be therefore restored to avoid impacts on the environment. The successful rehabilitation of a mine site requires the adoption of different measures such as the removal of all mine facilities, the sealing and securing of mine workings, ensuring long-term stability of waste repositories, modelling future water quality in underground workings, construction of suitable landforms, development of a suitable plant growth medium and establishment of a vegetation cover (Lottermoser, 2010). The different components of a mine site require a complete characterization, prediction, monitoring and treatment in order to adopt the most effective measures. One example of derelict mine site in the IPB is the Las Viñas mineral processing complex, which treated since 1909 the sulfide minerals extracted in the nearby mines of Sotiel and Tinto Santa Rosa (Fig. 1). Due to the high pollutant load released from this abandoned processing plant and to the planned construction of a water reservoir in this basin (today still in construction), this mineral-processing site was partially restored in 2009 and 2010. There are reasonable doubts about the final quality of the reservoir water due to the high number of AMD inputs along the drainage basin (Olías et al., 2011; Macías et al., 2017a). The huge volume of stored water (274 hm^3) requires a detailed assessment of the metal transference from the mine soils located in the drainage basin to the planned reservoir. This study is focused on assessing the already-implemented restoration measures in Las Viñas processing plant and to assess its environmental impact. The main aims of the present study are the following: (1) to determine the mobility of elements in the impacted soils under different weathering mechanisms, (2) to evaluate the current potential environmental impact, and (3), based on the results obtained, to propose alternative restoration measures in order to avoid the release of pollutants after the construction of the reservoir. The information obtained in this study could also be of great interest for decision-makers implied in the restoration of other degraded mine sites worldwide.

2. Site Description

The Las Viñas mineral processing complex is located in the Spanish sector of the IPB, intensively mined since ancient times due to its mineral richness (Sáez et al., 1999; Tornos, 2006). The IPB, whose dimensions are around 200 km in length by 40 km in width, belongs to the South Portuguese Zone of the Hercynian Iberian Massif. Slates, quartzites and greywackes, with interbedded acidic and intermediate tuffs, mainly characterize the lithology of the site. The most extensive group of soils in the study area are leptosols, which are poorly developed showing an AC profile of less than 20 cm depth, occurring over a wide variety of parent rocks (Fernández Caliani et al., 2009). Cambisols are also be found on the bottom of valleys over basic volcanic rocks, while regosols are the dominant soils over colluvial materials accumulated on foot slopes (Fernández Caliani et al., 2009). The Las Viñas mining facility is located in the middle stretch of the Odiel River, on its right bank. The climate in the area is typically Mediterranean, which includes long periods of drought and intense rain events. The mean annual rainfall in the Odiel basin is close to 700 mm, 60% of which occurs from October to January (Galván et al., 2014).

The Las Viñas mineral processing plant processed since 1909 sulfide minerals extracted in Sotiel and Tinto Santa Rosa Mines by cementation to obtain copper (Fig. 1A). Sulfides were roasted and stockpiled with a drainage and chimney aeration system called “terreros”. The piles were watered with stored acid water to obtain a metal-rich leachate that run through the cementation channels, where steel scrap was added to promote copper precipitation. Thus, iron oxidizes, and the copper ions are reduced through the transfer of electrons, in a process commonly known in hydrometallurgy as cementation. Finally, untreated water was discharged into the river with a high load of dissolved metals. The volume of minerals treated in the cementation plant of Las Viñas decreased with the interruption of transport from Tinto Santa Rosa mine since the final closure of the site in the 60’s. Since then, the complex remained abandoned and generating AMD until the present. Due to the planned construction of the Alcolea Reservoir (274 hm^3) in this drainage basin and the partial flood of the polluted soils by the stored waters (Fig. 1B), the regional authorities performed restoration measures in 2009 and 2010 in order to decrease the pollutant load into the future reservoir. The most important measure was the transport of the waste piles to the tailing impoundment of Almagrera (Fig. 1A) (Macías et al., 2017b). A volume of approximately 650,000 m^3 was removed and transported to this nearby pond, which was subsequently treated and is still being restored by dry covers.

Nonetheless, restoration measures were not completely effective as this abandoned site is still characterized by metal pollution of the soils and generation of AMD. This contaminated area is largely barren and supported only a limited number of plant species, among which endemic heather of the IPB Erica *andevalensis* is the most interesting by its tolerance to extreme conditions (Abreu e al., 2008; Pérez-López et al., 2014). The absence of vegetation may increase the release rates of pollutants and transport of mine soil particles during rain events, which are especially intense in this type of climates (e.g. Cánovas et al. 2008; 2012), causing severe episodes of pollution that could potentially affect the quality of the Alcolea reservoir (Fig. 1B).

3. Material and Methods

3.1 Sampling and analytical procedure

Thirty-eight soil samples (at 20-30 cm depth) were collected (Fig. 1B) in the Las Viñas area. The spatial distribution of the samples followed a systematic random grid. A composite sample of 2 kg was collected from each grid with a plastic shovel and transferred to plastic bags. Then, the samples were immediately transported to laboratory in secure containers. Samples were air-dried, homogenized and sieved. The fraction <2 mm was used to perform the particle size analysis (sand: 2–0.02 mm, silt: 0.02–0.002 mm, clay: <0.002 mm) by the hydrometer method (Gee and Bauder, 1986). Soil pH was determined in distilled water (1:2.5 soil/solution). Exchangeable base cations in soils were determined after leaching with an extracting solution (1 N NH_4Cl) and subsequent determination of Ca, Mg, Na and K by atomic absorption spectrometry. The exchangeable acidity in the leachate was determined by extraction with 1N KCl followed by titration against standard solutions of sodium hydroxide solution (0.01 N NaOH). Finally, the effective Cation Exchange Capacity (CECe) was calculated as the sum of exchangeable base cations and exchangeable acidity. Base saturation is considered as the percentage of the CECe occupied by exchangeable bases (Ca^{2+}, Mg^{2+}, K^+, and Na^+).

The acidity generation potential of soils was determined by the Acid Base Accounting (ABA) test using the modified method of Sobek et al. (1978) (Lawrence and Wang, 1997). The ABA involves the subtraction of an acid neutralizing capacity from a maximum potential acidity of a sample. The maximum potential to generate acid (MPA) is determined from the difference in the content of total S and sulfate S using a LECO analyzer. The neutralization potential (NP) is determined after digesting the sample with HCl and back titration with NaOH up to pH 8.3 (Lawrence and Wang, 1997). Then, the net neutralization potential (NNP) is obtained as the difference between NP and MPA, and the neutralization potential ratio (NPR) as NP/MPA. In addition, the net acid generation (NAG) of soils was determined by adding 250 mL of 15% H_2O_2 to a 2.5 g of sample (Sobek et al, 1978). The sample is allowed to react overnight, and then, the sample is heated for 2 h to remove excess H_2O_2 and encourage release of inherent neutralizing capacity. Once the sample has cooled to room temperature, the pH is measured.

The pseudo-total content of metals (i.e. Al, Sb, As, Ba, Be, B, Cd, Co, Cu, Cr, Sn, Sr, Fe, Li, Mn, Hg, Mo, Ni, Ag, Pb, Ti, V and Zn) was determined after extraction with *aqua regia* at 95° C for 1 h by inductively coupled plasma atomic emission spectroscopy (ICP-AES). A triplicate analysis was performed in order to evaluate the analytical precision, showing differences below 5% in all cases. In addition, the affinity of metals to the different geochemical fractions in soils was studied using the sequential extraction method proposed by Dold (2003) for matrices affected by mining. This method is composed of several steps. Step 1 (soluble fraction): 50 mL of distilled water during 1 h of stirring at room temperature. Step 2 (exchangeable fraction): 50 mL of NH_4-acetate at pH 4.5 during 2 h of stirring at room temperature. Step 3 (associated to non or poorly crystalline

Fe oxyhydroxides): 50 mL of ammonium oxalate at pH 3 during 1 h of stirring in dark conditions. Step 4 (associated to crystalline Fe oxides): 50 mL of ammonium oxalate at pH 3.2 h in a water bath at 80 °C. Step 5 (associated to organic matter and secondary sulfides): 35% hydrogen peroxide during 1 h in a water bath at 80 °C. Step 6 (associated primary sulfides): $KClO_3$ and HCl, followed by HNO_3 boiling at 80 °C. Step 7 (residual fraction): Attack with HF, $HClO_4$, HNO_3, open digestion on a hotplate. The affinity of the different elements to certain geochemical fractions is indicative of its mobility and therefore its availability and the potential risk involved. Soluble, exchangeable, iron oxyhydroxides, organic matter, secondary and primary sulfides fractions represent the potentially mobile amount of each element under different environmental conditions. On the contrary, the residual fraction corresponds to those metals strongly associated with crystalline structures of minerals, which are therefore unlikely to be released from the soils.

The mineralogical characterization of samples was carried out by X-ray diffraction (XRD, powder method) using a Bruker diffractometer (model D8 Advanced). Working conditions were slit fixed at 12 mm, Cu Kα monochromatic radiation, 20 mA and 40 kV. Samples were run at a speed of 0.3º 2θ/min (5–60º).

The quality control of the results was performed by analyzing homemade solutions from commercial standards. Differences between measured and standardized values were below 10% in all cases. In addition, duplicates were analyzed and the Relative Percentage Difference or %

RPD (De Vivo et al. 2008) was calculated, based on the proportional difference of the results of two samples and two corresponding duplicates, according to the following expression:

$$\%\,RPD = \frac{(S - D)}{(S + D)/2} \times 100$$

where, S are original samples and D duplicates.

The maximum permissible value for RPD is 30%. This value was below 10% in the whole sequence of analysis, which indicate the goodness of the analytical procedure.

3.2 Metal enrichment calculation

The metal enrichment in Las Viñas soils has been studied through the calculation of the index of geoaccumulation (I_{geo}), which was originally stated by Müller (1969) in order to determine metal contamination in bottom sediments by comparing current concentrations with pre-industrial levels. However, it can also be applied to the assessment of soil contamination, thus I_{geo} is calculated as follows (Loska et al., 2004):

$$I_{geo} = \log_2 [Cn/1.5Bn]$$

, where Cn is the measured concentration in the sediment/soil for the metal n, Bn is the background value for the metal n, and the factor 1.5 is used because of possible variations of the background data due to lithological variations. As background values, those reported by Galán et al. (2008) for the South-Portuguese zone were selected.

4. Results and discussion

4.1. Soil properties

Contrary to previous studies in mine soils with similar characteristics in the IPB (e.g. Fernández-Caliani et al., 2009), this study did not find a high proportion of coarse-grained components in soils. This fact may be due to both chemical alteration of the bedrock by AMD and mechanical size reduction produced during previous clean-up operations. Soil samples contain a high abundance of quartz and clay minerals such as muscovite and clinochlore, although a strong influence of mining activities is observed as evidenced by the presence of pyrite and secondary minerals from oxidation such as hematite and jarosite (Fig. 2). The presence of efflorescent hydrated metallic sulfate salts cannot be ruled out; however, their identification by XRD is often difficult since they tend to precipitate within a set of more abundant crystalline minerals and requires a detailed examination of samples.

The soils studied are extremely acidic, with a median pH value of 3.4 (Table 1). Acidity in soils may limit nutrient availability and nitrogen fixation, slowing down the humification and mineralization of organic matter as a consequence of low microbial activity (Zhang and He, 2004). Another acidity-related consequence is the toxicity that these soils may present, since most of the trace elements will tend to be more available because they are less strongly adsorbed on soil (Madejón et al., 2018).

The CECe of these acidic mine soils was medium, ranging from 10 to 28 Cmol(+)/kg (Table 1 and S1). As expected in acidic soils, the base saturation percentage was very low (median value of 8.4%; Table 1). Such low percentage may cause difficulties in plant nutrition and therefore the addition of liming is recommended (Fernández-Caliani and Barba-Brioso, 2010). The dominant basic cation in the exchange complex was Ca (median value of 0.44 Cmol(+)/kg), followed by Na (0.37 Cmol(+)/kg), Mg (0.33 Cmol(+)/kg) and K (0.12 Cmol(+)/kg). Thus, the content of these cations in the exchange complex was low to very low and the practically desaturation of the exchange complex was due to the excessive amounts of exchangeable H^+. The exchangeable sodium percentage, i.e. percentage of Na^+ over other adsorbed cations in the exchange complex, is less than 15% in all samples, so it is considered that these soils would not suffer sodification problems neither dispersion of its clay fraction (Rengasamy et al., 2003).

As stated before the CECe of the studied soils was medium, but resulted to be higher than soils present in the region (AMA, 1984), which confer them a higher capacity to retain metals (e.g. Pb^{2+}, Cu^{2+}, etc.) than these soils. However, CECe decreases with soil pH as shown by the positive linear correlation (R^2=0.66) between CECe and pH (Fig. 3), so if the soil acidification process continues, the CECe will be lower. Another important problem in acidic soils such those found in Las Viñas is that much of the exchangeable cations are hydrogen and aluminium, and this can lead to processes of phytotoxicity by aluminium or hydrogen protons (Yang et al., 2015).

4.2. Potential AMD generation

Exposure of sulfides, particularly pyrite, to atmospheric conditions inevitably causes its oxidation leading to AMD generation, which promotes the release of acidity, sulfate and metals to the environment (e.g. Cánovas et al., 2007). Therefore, it is of critical importance assessing the balance of soils between their potential to generate acidity by oxidation and their neutralization capacity, which will limit the long-term release of hazardous substances to the environment.

Mine soils studied have an average sulfur content of 3.6% (Table 2), although they exhibited a high variability (0.1-28%). Pyritic sulfur was the main form of sulfur in almost all samples (median value of 79%). This high value can be attributed to the inefficient cleanup efforts, which failed owing to the presence of mine waste minerals in these soils, showing a site-to-site variability (Table 2 and Fig. 2). Pyritic sulfur content is a useful parameter in the assessment of cleanup and remediation measures in affected soils by metallic mining. For example, a reference level of 0.3% (and exceptionally 1%) of pyritic sulfur was established to determine the effectiveness of cleanup and restoration measures after the spill of the Aznalcóllar mine (Mediavilla et al., 2001). If the same approach is followed to assess the restoration measures adopted in Las Viñas, it can be noted that around half of soil samples contain pyritic S values below 1% and only 3 of them reach values below 0.3%. The lowest values of pyritic S samples were observed on the west side of Las Viñas, where cleanup works seem to have been more efficient. In fact, the average pyritic S content in soils on the eastern side is four times higher than that found on the western side.

In order to evaluate the possible generation of AMD in the studied soils, the NNP and the NPR were calculated. Mine soils studied show a high MPA with a median value of 47 kg $CaCO_3$/tonne, reaching maximum values of up to 855 kg $CaCO_3$/tonne (Table 2). On the other hand, these soils exhibited a very low potential of acid neutralization as evidenced by the low values of NP (median value of 0.25 kg $CaCO_3$/tonne) (Table 2). As a result, more than 75% of samples showed NNP values below -20 kg $CaCO_3$/tonne (Table 2). If NNP presents values below -20 kg $CaCO_3$/tonne, sample will generate AMD while if values range between -20 and +20, the capacity to generate AMD is uncertain (EPA, 1994). In the same way, if NPR is greater than 3 the risk of AMD generation is low, uncertain risk for values between 3 and 1, and really high risk if values are above 3 (EPA, 1994). Therefore, as can be seen in Table 2, Las Viñas mine soils would have a high potential to generate AMD despite the preliminary remediation actions performed in 2009 and 2010.

In any case, ABA tests provide a prediction of AMD generation based on the content of sulfide, irrespective of the reactivity of sulfides contained in the samples. NAG tests provide a complementary improved approach based on the reactivity of sulfides by enhancing sulfide oxidation with an oxidant, measuring the final pH. This pH value is a good indicator of short-term acidification, mimicking the sulfide oxidation in the samples. Values of NAG-pH in Las Viñas soils ranged from 2.0 to 4.8 (Table 2) with half of samples exhibiting pH values equal to or below 2.0.

As a consequence, 94% of soil samples have a potential to generate acidity (Fig. 4), and therefore new remediation measures must be adopted.

4.3. Metal concentration

The trace element concentrations in collected samples are presented in Table 3. Elements with a significant number of samples found below the detection limit were not included (i.e. Ba, B, Cd, Mn, Se, Ti, Sn, Be, and Sr). Mine soils are characterized by very high total concentrations of Fe, ranging from 2.1% to 26% (Table 3). In comparison to Fe, concentrations of Al were relatively low, ranging from 0.3% to 4.4%, and reaching mean concentrations to 12 g/kg.

Elevated concentrations of As, Pb, and Cu were also observed, with median values of 787 mg/kg, 709 mg/kg, and 321 mg/kg, respectively. In the case of Pb, such high concentrations recorded in Las Viñas agree well with those found by Fernández-Caliani et al. (2009), who reported the maximum Pb concentration in mine soils of the IPB in this mineral processing plant. Lower concentrations were found in other elements such as Zn, Cr, V, Li, Sb, and Co were found (from 66 mg/kg of Zn to 11 mg/kg of Sb and Co; as median values, Table 3). On the other hand, the occurrence of other elements such as Hg, Mo, and Ag was almost negligible (below 10 mg/kg). No concentration patterns were observed along the mine site, except in the case of those areas with a higher slope where the access of machinery turned to be difficult and thus, the cleaning efficiency was lower. Except for Cr, V, and to a lesser extent Co, the trace metal content (median values) in mine soils of Las Viñas is higher than those reported in Andalusian, European and worldwide soils (Table 3).

However, these values must be compared with background values with similar lithological characteristics. In this sense, median values observed in this study are slightly higher for Pb and As than those reported by Fernández-Caliani et al. (2009) in other mine soils of the IPB. On the other hand, the content of Cu, Ni, Hg, Cr, Zn and to a lesser extent Co in Las Viñas soils is lower than in other soils of the IPB. If compared to the background values of the South-Portuguese zone, concentrations are noticeably greater in Las Viñas for As, Pb and Cu; around 31, 18 and 10 times higher than background values (Table 3). In the case of Ni and Zn, values observed in Las Viñas are similar to those reported in the South-Portuguese zone. Considering the regional regulation on contaminated soils (BOJA, 2015), Las Viñas soils would exceed the generic reference values (GRV) for industrial, urban and other land uses in As and Pb (except for industrial use; Table 3).

Figure 5 shows the index of geoaccumulation (I_{geo}) calculated for Las Viñas soils. As can be seen, Las Viñas soils are extremely or heavily polluted by As and Pb. A lesser degree of pollution is observed for Cu, with most samples showing a moderate to heavy contamination. On the other hand, the studied soils are practically uncontaminated by Co and Ni (Fig. 5). The lowest pollution level is observed for Cr, with all samples practically uncontaminated compared with background values. However, these latter elements may not be expected to occur according to the local lithology. Such high level of acidity and metals could limit recolonization and vegetation succession on these supposedly reclaimed soils. Saiz-Díaz and Ceacero-Ruiz (2008) proposed Fe (5.9%), Pb (1180 mg/kg) and As (532 mg/kg) as tolerance limits for plants in acid mine soils amended with alkaline by-products to some of the typical species in the surrounding mining areas of the IPB (i.e. *Cistus ladanifer*, *Pinus pinea* and *Pinus pinaster*). As can be seen in Table 2, values in Las Viñas soils are well above to the tolerance limits proposed by Saiz-Díaz and Ceacero-Ruiz (2008).

4.4. Metal mobility under weathering agents

The content of trace metals in Las Viñas soils can be considered high, especially for As, Pb and Cu, as stated before. However, these high levels could not pose an environmental concern if metal mobility from the soils is limited. Trace elements with a high mobility can cause huge environmental problems by accumulating in flora and fauna and reducing the quality of water bodies (Siegel, 2002), such as the planned Alcolea Reservoir, whose drainage basin reach Las Viñas (Fig. 1B). In order to address this issue, a sequential extraction method proposed by Dold

(2003) specifically for acid mine wastes was performed and results can be observed in Figure 6. The water-soluble fraction of an element is the most easily transferable to a living plant or organism (Galán et al., 2008) and may constitute the main source of metals to the reservoir. The soil water-soluble fraction was relatively low for most trace elements (below 10%), except for Mn (31%), Cd=Co (22%), Ni (18%), and Cu (15%). Although the water-soluble content of Al was below 10% (9.4%; Fig. 6), Al toxicity, mainly associated with soluble Al (EPA, 2003), is one of the major factors that limit plant growth and development in many acid soils (Mossor-Pietraszewska, 2001).

Metals accumulated in the exchangeable fraction (F2 in Fig. 6) can return to waters in the suspended or dissolved form and represent a potential risk for an aquatic ecology as well as the environment (Kassir et al., 2012). In addition, the release of exchangeable elements may cause a displacement of base cations from exchangeable sites in the soil, which would result in pronounced nutrient deficiency and toxic effects on plants. Nickel (9.8%), Mn (9.4%), Co=Cd (6.4%) and Cu (4.3%) were especially sensitive to exchange processes with soil solution. The soluble plus exchangeable fraction characterizes the mobile content of metals in soils (Kabata-Pendias, 2011) and corresponds to the available fraction for plant uptake (Pérez-López et al., 2014). Considering these fractions, Mn (40%), Cd=Co (28%), Ni (27%), and Cu (19%) would be especially available. Among them, the availability of Cu is especially concerning in Las Viñas soils (Table 3) and may cause toxicity to aquatic organisms (Gonçalves et al., 2018).

The content of Fe in the studied soils was around 9% (median value; Table 3). In this sense, Fe oxides and oxyhydroxides are known to be excellent adsorbents of trace metals, especially for As, Pb or Cr. If these minerals are subject to reductive transformation, these elements can be released back to the environment. These conditions can be met if weathered materials end in the bottom sediment of the planned reservoir. Metal transport by the colloidal/particulate matter has been proved to be important in mining areas (e.g. Gómez-González et al., 2016). Other reservoirs located in the region are stratified during the summer period, with an upper oxic layer and an anaerobic deeper layer in the bottom (Torres et al., 2013). Around 50% of Mo, 44% of Sb, 42% of As, 36% of Cr and Ni, 26% of Cu and lesser percentages of Mn, Pb and other trace elements are contained in the reducible fraction (Fe oxides and oxyhydroxides; F3 and F4; Fig. 6). Therefore, it exists environmental concern associated to the reducible fraction of As and Cu, found in higher concentrations in the soil, that could be released to the water column of the planned reservoir if reductive conditions are found in the bottom sediment.

Another route of metal transfer from eroded soils to the reservoir waters would be the oxidation of reduced species contained in the soils. Such oxidation conditions are observed in the reservoirs of the region in the shallowest zone during stratification periods or in the whole water column during mixing and turnover processes in winter (Torres et al., 2013). Under these circumstances, the weathered materials will be continuously exposed to water and air, leading to the release of metals to the water column by sulfide oxidation. Around 90% of Hg, 70% of V, 56% of Pb, 44% of Fe and Sn, 40% of Cu, 35% of As and Cu, and lesser percentages of other trace metals (Fig. 6) are found in the oxidizable fraction (organic matter and sulfides; F5 and F6) and would be released if exposed to oxidation conditions. Finally, the elements less reactive in the sediments seem to be Sb (48%), Al (43%), Mo and Cr (30%), with a significant presence in the residual fraction (Fig. 6).

Considering the total surface affected by mining in Las Viñas (0.26 km^2), the soil depth (30 cm) and the density of soils (1.2 kg/m^3), it can be quantified the potential metal release from the derelict processing plant of Las Viñas if remediation measures are not implemented. Table 4 shows the metal and metalloid pool contained in Las Viñas mine soils (65.3 tonnes) within the different available geochemical fractions. Aluminum (95 kg) and Fe (52 kg) are the metals with a higher abundance in the bioavailable fraction (soluble and exchangeable), which could lead to acidification processes in the reservoir due to the potential of both metals to generate acidity (Cánovas et al., 2007). The bioavailable pool of Cu (7.2 kg) and Pb (4.9 kg) is also striking, while the rest of metal and metalloid accounts for less than 1 kg. These elements would therefore be immediately released upon intense rainy events. Concerning the reducible fraction, around 2732 kg of Fe, 87 kg of Al, 32 kg of As, 29 kg of Pb, 9.5 kg of Cu, 1.3 kg of Zn and lesser amounts of other metal and metalloids (less than 1 kg; Table 4) would be readily available if these soils are exposed to reductive conditions, such as those found in bottom sediments of stratified reservoirs. Again, Fe is the most abundant metal in the oxidable fraction (2732 kg), followed by Al (264 kg), Pb (75 kg), As (24 kg), Zn and V (1 kg). A minor part of the soils (the lower areas; Fig. 1) will be periodically flooded by the reservoir waters, leading to the alternation of reductive and oxidative conditions. However, the main concern is the weathering and transport of mine soil particles to the reservoir sediments that could lead to the release of hazardous levels of meta and metalloids into the water column if remediation measures are not adopted.

4.5. New remediation strategies

Restoration measures in disturbed mining soils are usually challenging due to their severe alteration such as compacted structure, disordered stratigraphic sequence and degraded soil properties (Zhang et al., 2015). Mine soils are often extremely acidic, exhibiting deficiencies in P, N, Mg and Ca (Mingorance et al., 2017), which avoids the growth of vegetation and limits water retention, enhancing the water shortage in the area. The addition of alkaline substances to sulfide-rich materials is the most commonly employed technique to prevent AMD production. The presence of these alkaline substances favours acid neutralization, decrease of metal solubility and consequent removal of metals by precipitation (Pérez-López et al., 2007a). The application of adequate amounts of Ca and Mg to acidified soils reduces the metal phytotoxicity, easing the nutrient absorption of plant and develops the optimal conditions for the settlement of microfauna and microflora (Fernández-Caliani and Barba-Brioso, 2010). In addition, the restoration of mine soils is commonly approached by the combination of alkaline materials and organic matter.

Therefore, the optimal amendment must fulfil several requirements. From a chemical point of view, this amendment must have high alkalinity, adequate Ca/Mg ratio and, to a lesser extent, organic matter and nutrients such as N, P and K, but a low content in Na. However, in terms of operational and cost-effectiveness factors, these amendments must be located close to the mine sites, low-cost, available in enough quantities, have a high efficiency per unit of volume and not to provide additional harmful substances to the soil.

Different wastes have been tested to reduce soil acidity and mitigate the release of metals. For instance, Fernández-Caliani and Barba-Brioso (2010) assessed the use of waste sludge generated during the processing of marble stone in mine soils of Tharsis, also in the IPB. These authors showed that this amendment, joint with lime, significantly reduced the water-soluble concentrations of Cu, Zn, Pb and Cd. However, the large extension of acidic soils in the IPB requires the existence of huge quantities of available materials to be used. The use of different low-cost amendments has been explored considering its availability close to the mine sites. One alternative would be the use of coal combustion fly ash, a waste generated at power stations (Pérez-López et al., 2007a). Around 780 million tonnes of fly ash are annually generated worldwide from coal combustion (Izquierdo and Querol, 2012), and are available at a power plant located relatively near the IPB (Pérez-López et al., 2007a). Other potential alkaline materials, available in the study area, could be sugar foam generated in the sugar refinery industry and ashes from biomass combustion (ABC). Both industrial wastes have been successfully tested as amendment in acidic soils and mine tailings (e.g. Rodriguez-Jordá et al., 2010; Rodriguez et al., 2018). Table 5 shows the main chemical characteristics of the explored materials. Both type of ashes (biomass and fly ashes) showed pH values above 12 while the sugar foam recorded pH values of 8.6. The highest acidity neutralization potential (NP) corresponds to ABC (13,6 moles of H^+ per kg), with slightly lower values for sugar foam (Table 5). The lowest NP corresponds to fly ash (9,9 moles of H^+ per kg) despite reaching pH values above 12. Sugar foam exhibits the highest C and Ca content (16.5 and 6,4%), while fly ash has the highest Ca/Mg ratio. The content of impurities in the amendments is relatively low if compared with the high values observed in soils; only fly ash has significant concentrations of Cu, Cr, and especially Zn and Mn.

The approach proposed in this study to restore the Las Viñas area quality is similar to that followed by Saiz-Díaz and Ceacero-Ruiz (2008), and based on adding enough alkaline amendment to neutralize the acidity contained in the soil. Thus, the amount estimated to be added to the soils would stem from the ratio between the potential acidity of soils (MPA) and the neutralization potential of alkaline amendments (Table 5). According to this estimation, around 433 ton/ha of fly ash, 330 ton/ha of sugar foam and 315 ton/ha of ash from biomass combustion would be needed to restore these mine soils, avoiding the transference of metals and acidity into the planned reservoir. However, these figures may be considered as an upper level due to the occurrence of coating processes on the pyrite surface. As reported by Pérez-López et al. (2007b), the precipitation of iron-bearing phases upon the pyritic surface forming Fe-coatings during the mixing of sulfide-rich materials with alkaline amendments may halt pyrite oxidation, and therefore, the amount of alkaline material to raise the soil pH and promote revegetation should be lower. On the other hand, the formation of such coatings may also reduce the plant revegetation. In any case, cleaning up activities in Las Viñas soils must be resumed as application rate is directly related with the amount of mining wastes present. This would allow reducing the application of the amendment to around 80 ton/ha.

The amendments should be applied once if the amount of amendment is lower than 40 ton/ha, mainly during summer. In the opposite case, like in Las Viñas, the application should be performed twice, with a difference of at least, 6 months between each application. The amendments should be mixed with the soils aiming at the maximum possible homogenization. Due to the low-cost of the amendments proposed, the main expenditure would correspond to the material transport and machinery works.

On the other hand, impurities contained in the amendment could be released during the reaction with the acidic soils. However, as can be seen in Table 5, the level of impurities in these materials is very low if compared to those observed in the soils. The highest level of impurities (i.e. Cu, Zn, Cr, and Mn) are found in fly ash, and despite this, the application of this material seems to be safe as reported by some authors (e.g. Pérez-López et al., 2007a; Izquierdo and Querol, 2012), which demonstrated that most elements are tightly bound to fly ash and may not be easily released to the environment, irrespective of the nature of the ash. Although the release of metals from these amendments must be monitored, this study evidences that the use of these amendments could notably improve the soil quality of this derelict processing plant, limiting the metal release to the surrounding water bodies. On the other hand, a greater effort on clean-up operations would reduce the costs associated to the application of the amendments. The establishment of a vegetation cover on the amended soils would additionally be of paramount importance to speed up the revegetation process, avoiding the erosion and therefore, increasing the efficiency of the adopted measures. In this sense, Abreu et al. (2008) reported the suitability of Erica *andevalensis* and Erica *australis* to stabilize chemically soils affected by mining in a nearby mine site of the IPB. Both plants are found in Las Viñas mine site and could be used to set a vegetation cover. Other species commonly found in the area are *Cistus ladanifer*, *Pinus pinea* and *Pinus pinaster* (Saiz-Díaz and Ceacero-Ruiz (2008), which could be also used.

The long lasting nature of AMD processes could cause the water reservoir deterioration in the medium term if remediation measures are not adopted. This process was already observed in other water reservoir built in the 60s for industrial purposes, which water quality worsened progressively due to the AMD pressure from the Tharsis mine, with pH values below 3 and high metal concentrations (Cánovas et al. 2016).

Conclusions

The derelict cementation complex of Las Viñas (SW Spain) is a partially reclaimed abandoned mine site located in the drainage basin of a water reservoir currently under construction. Clean up operations performed in the past were inefficient and the mine soils can be a significant source of metals and acidity to the future planned reservoir. Las Viñas mine soils evidence an extremely high acidity (pH of 3.4 and maximum potential acidity of 47 kg $CaCO_3$/ton). Also, extreme values of trace element concentrations were observed in these soils. The average concentrations of Pb, As, Cu and Zn were well above the background values of the lithological and regional provinces, especially As, Pb and Cu.

Results obtained from sequential extraction of soils evidence the potential release of significant quantities of Mn, Cd, Cu and other easily-soluble trace elements by rainfalls. The weathering and transport of soils to the bottom sediment of the planned reservoir could lead to the release of significant quantities of toxic trace elements to the reservoir water column if anoxic (mainly As, Sb, Mo, Cr, Ni, Cu and Pb). In turn, if conditions in the water column-sediment interface turns to be oxic, then, the release of toxic elements such as Hg, Pb, V, Cu and As may be enhanced. This study quantifies a bioavailable pool of 95 kg of Fe, 52 kg of Al, 7.2 kg of Cu and 4.9 kg of Pb. The amount of metal and metalloids released if exposed to reducible conditions is even higher and similar figures are stored in the oxidable form Then, the acidity and metals released from these soils could jeopardize the quality of the reservoir waters.

Remediation measures must therefore be adopted, focusing on the cleanup and liming of soils in order to promote recolonization and vegetation succession, thus avoiding soil erosion and limiting acidity and metal release to the hydrosphere. Consequently, it would be necessary to take actions to reduce soil acidity and trace elements mobility. The general solution for remediation of these sites is to add an alkaline amendment. Therefore, these soils should be limed in order to raise the pH (4.5 or above). This study proposes the use of different low-cost materials to improve the soil quality, limiting the metal transfer to the planned reservoir water. For instance, the use of biomass combustion ashes seems to be the most efficient material to restore the mine soils. Other alternative materials successfully tested in other mine sites of the IPB are sugar foam wastes and fly ashes that could be obtained easily in the surroundings of the mine sites of the IPB. The longevity of AMD processes could cause the water reservoir deterioration in the medium term if remediation measures are not adopted. This process was already observed in other nearby water reservoirs of the IPB, which waters show a poor quality after decades of AMD pressure. The information contained in this study could be of great importance in other watersheds affected by derelict mine sites.

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Tables

	pH	Exchangeable acidity (Cmol(+)/kg)	Exchangeable cations (Cmol(+)/kg)					CECe (Cmol(+)/kg)	Base saturation (%)
			Na	K	Mg	Ca	Sum		
n	38	37	37	37	37	37	37	37	37
Minimum	2.2	5.2	0.18	0.03	0.16	0.34	0.89	10	3.2
Maximum	7.0	27	1.6	0.34	5.6	5.4	9.4	28	59
Mean	3.6	16	0.43	0.14	0.77	1.0	2.3	18	14
Median	3.4	16	0.37	0.12	0.33	0.44	1.4	18	8.4
Percentil 25	3.0	12	0.28	0.08	0.23	0.42	1.1	14	5.9
Percentil 75	3.7	18	0.47	0.18	0.54	0.75	2.0	20	14

Table 1. Basic statistics of pH, exchangeable acidity and cations, base saturation and exchange capacity of soils studied.

	Acidity	Pyritic Sulfur	Total Sulfur	NAG pH	MPA	NP	NNP	NPR
	Cmol(+)/kg	%	%		kg $CaCO_3$/tonne			
n	38	38	38	38	38	38	38	38
Minimum	0.50	0.02	0.09	2.0	0.52	0.25	-855	0.0003
Maximum	27	27	28	4.8	855	11	5.7	12
Mean	15	3.0	3.6	2.4	94	1.1	-93	0.36
Median	15	1.5	2.1	2.1	47	0.25	-47	0.005
Percentil 25	12	0.69	1.1	2.0	21	0.25	-106	0.002
Percentil 75	18	3.4	4.4	2.3	107	0.25	-20	0.014

Table 2. Basic statistics of some variables controlling the potential of generating acidity (i.e. acidity pyritic and total sulfur, net acid generation (NAG pH), maximum potential acidity (MPA), neutralization potential

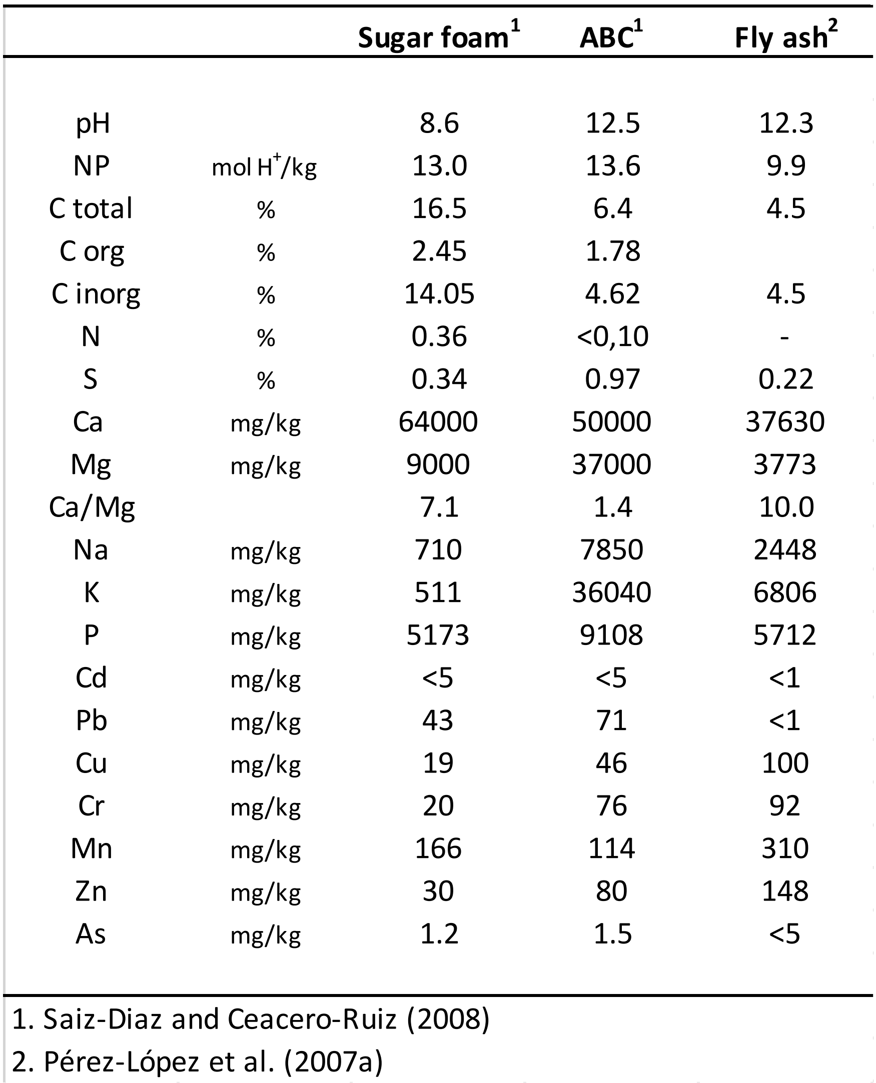
(NP), net neutralization potential (NNP) and neutralization potential ratio (NPR); see text for explanation) in soils studied.

	Al	**Sb**	**As**	**Co**	**Cu**	**Cr**	**Fe**	**Li**	**Hg**	**Mo**	**Ni**	**Ag**	**Pb**	**V**	**Zn**
n	38	38	38	38	38	38	38	38	38	38	38	38	38	38	38
Minimum	3239	0.50	31	2.5	32	13.7	21490	2.5	0.54	1.04	6.29	0.25	55	10.9	10
Maximum	43958	98	6081	34	2515	50	257791	51	68	20	60	34	9765	38	692
Mean	12064	18	1170	11	569	30	95841	19	8.0	3.7	35	6.7	2049	23	124
Median	8773	10.3	787	11	321	30	90360	15	3.9	2.7	33	4.3	709	24	66
Percentil 25	5908	2.64	296	7	175	22	45713	8.9	1.69	1.8	29	0.99	371	18	10
Percentil 75	17082	27	1650	15	630	35	124883	28	9.1	3.7	44	9.3	3103	29	204
Mine affected soils in the IPB [1]		-	621	16	726	71	-	-	34	-	1794	-	640	-	621
South Portuguese soils [2]			25	19	32	95	-	-	-	-	35	-	38	-	76
Andalusian soils [2]			10	12	24	70	-	-	-	-	29	-	24	-	56
European soils [3]			7	8	13	60	22	-	0.061	-	18	-	23	38	52
World soils [4]			5	10	25	80	-	-	-	-	20	-	17	-	70
Generic Reference values (GRV) [3]															
Industrial		4700	40	250	10000	10000	-	-	250	3900	10000	-	2750	3650	10000
Urban		470	36	25	3130	10000	-	-	25	390	1530	-	275	365	10000
Other uses		90	36	24	595	10000	-	-	25	115	1530	-	275	50	10000
Geochemical Index (I_{geo})			4.4	-1.4	2.7	-2.3					-0.7		3.7		-0.6

Table 3. Basic statistics of metal concentrations in studied soils and comparison with other soils affected by mining and different areas at local, regional, European and worldwide level.

	Fe	As	Pb	Cr	Cu	Co	Mo	Ni	Zn	V	Hg	Ag	Sb	Al
Average Concentration (mg/kg)	95841	1170	2049	30	569	11	3.7	35	124	23	8.0	6.7	18	12064
Total Pool (kg)	6258	76	134	1.9	37	0.75	0.24	2.3	8.1	1.5	0.52	0.44	1.2	788
Available pool (kg)														
Bioavailable	52	0.18	4.9	0.10	7.2	0.21	0.004	0.62	0.06	0.05	0.02	0.03	0.01	95
Reducible	2257	32	29	0.70	9.5	0.20	0.12	0.81	1.3	0.19	0.02	0.04	0.51	87
Oxidable	2732	24	75	0.58	15	0.21	0.04	0.77	1.2	1.1	0.47	0.33	0.08	264

Table 4. Metal and metalloid pool contained in the bioavailable fraction of soils studied (see text for explanation).



		Sugar foam[1]	ABC[1]	Fly ash[2]
pH		8.6	12.5	12.3
NP	mol H^+/kg	13.0	13.6	9.9
C total	%	16.5	6.4	4.5
C org	%	2.45	1.78	
C inorg	%	14.05	4.62	4.5
N	%	0.36	<0,10	-
S	%	0.34	0.97	0.22
Ca	mg/kg	64000	50000	37630
Mg	mg/kg	9000	37000	3773
Ca/Mg		7.1	1.4	10.0
Na	mg/kg	710	7850	2448
K	mg/kg	511	36040	6806
P	mg/kg	5173	9108	5712
Cd	mg/kg	<5	<5	<1
Pb	mg/kg	43	71	<1
Cu	mg/kg	19	46	100
Cr	mg/kg	20	76	92
Mn	mg/kg	166	114	310
Zn	mg/kg	30	80	148
As	mg/kg	1.2	1.5	<5

1. Saiz-Diaz and Ceacero-Ruiz (2008)
2. Pérez-López et al. (2007a)

Table 5. Chemical characteristics of amendments considered in this study to ameliorate the quality of mine soils.

Figures

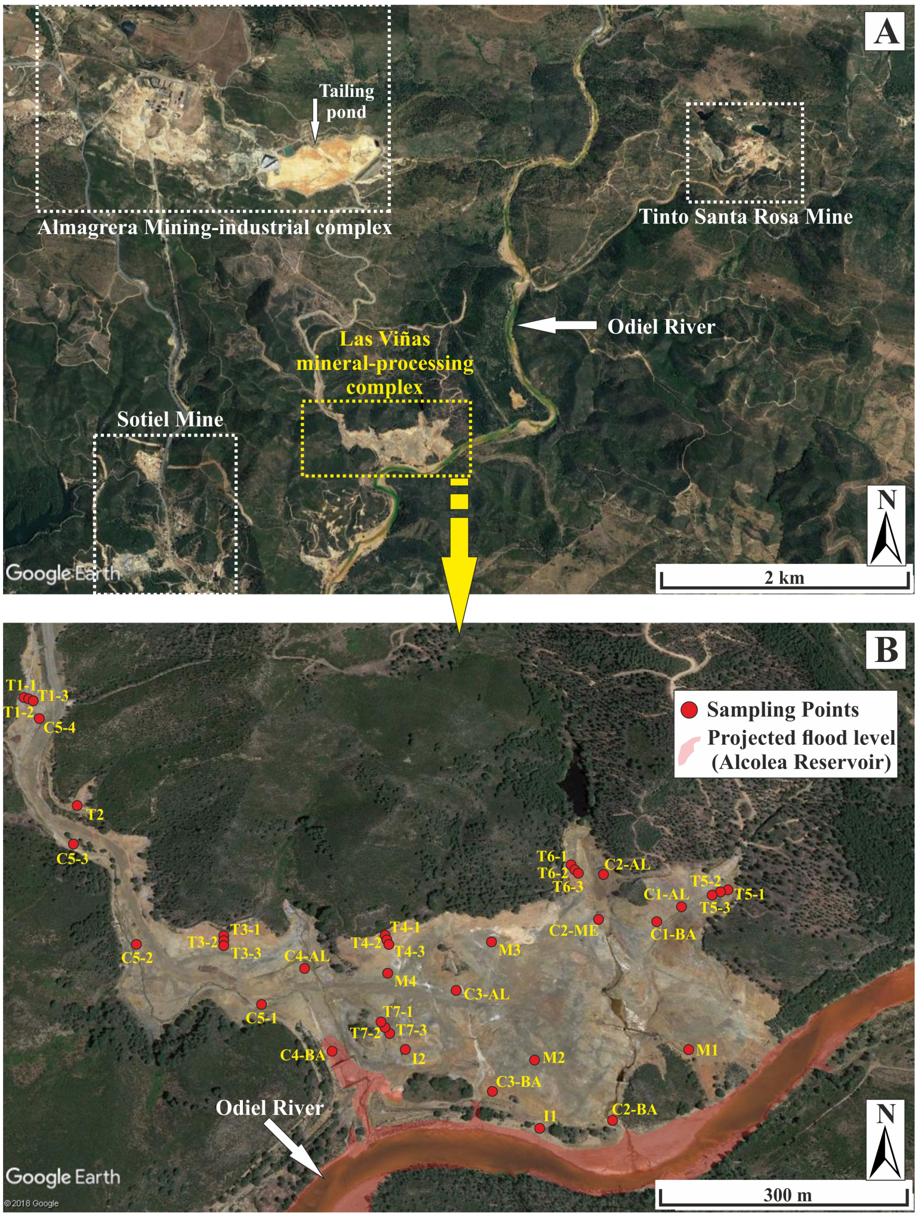


Figure 1. Location map of the derelict Las Viñas processing plant (A), showing the different samples collected during this study (n=38) and the water level in the projected reservoir.

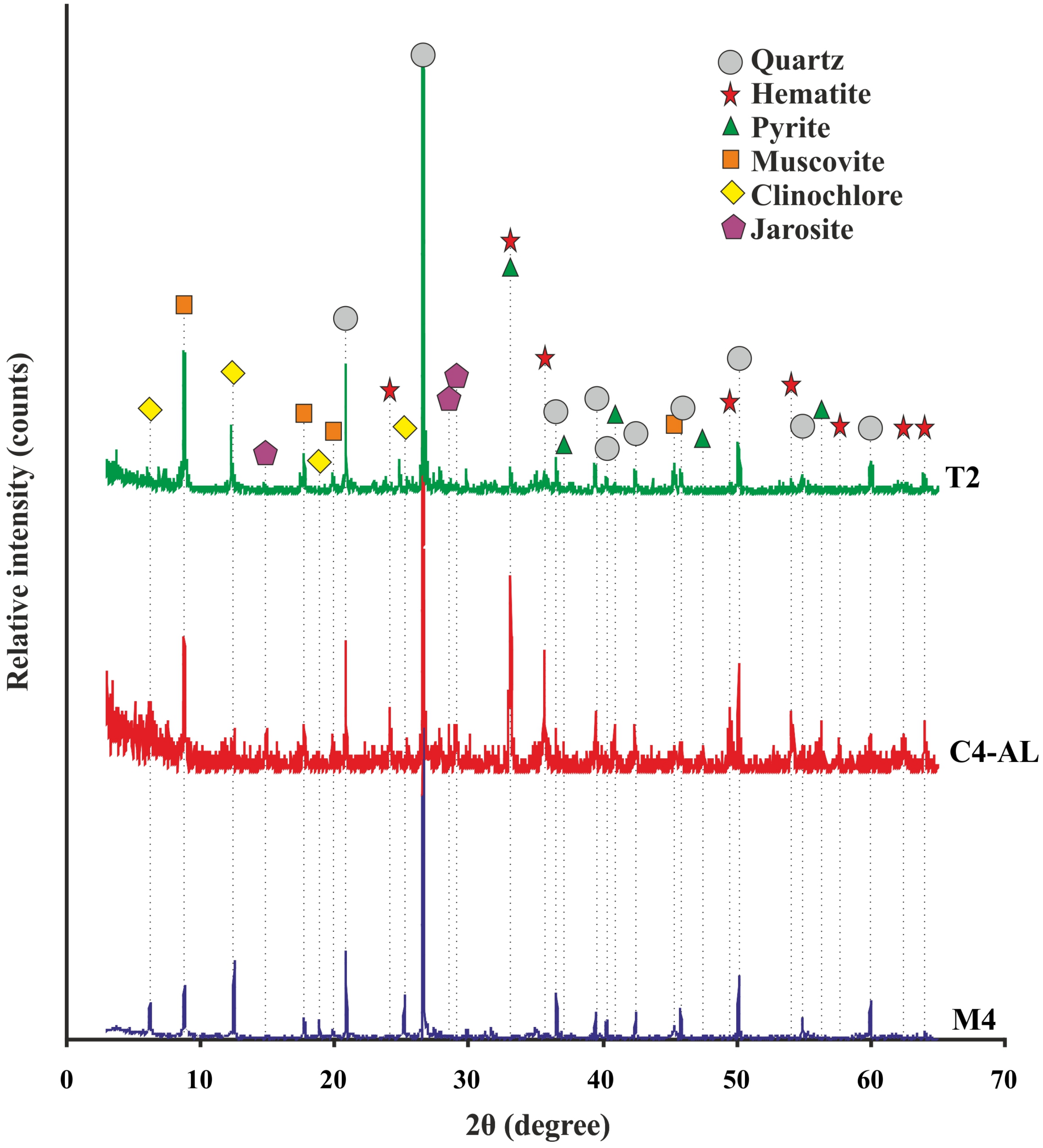


Figure 2. X-ray diffraction patterns of representative soils of this study.

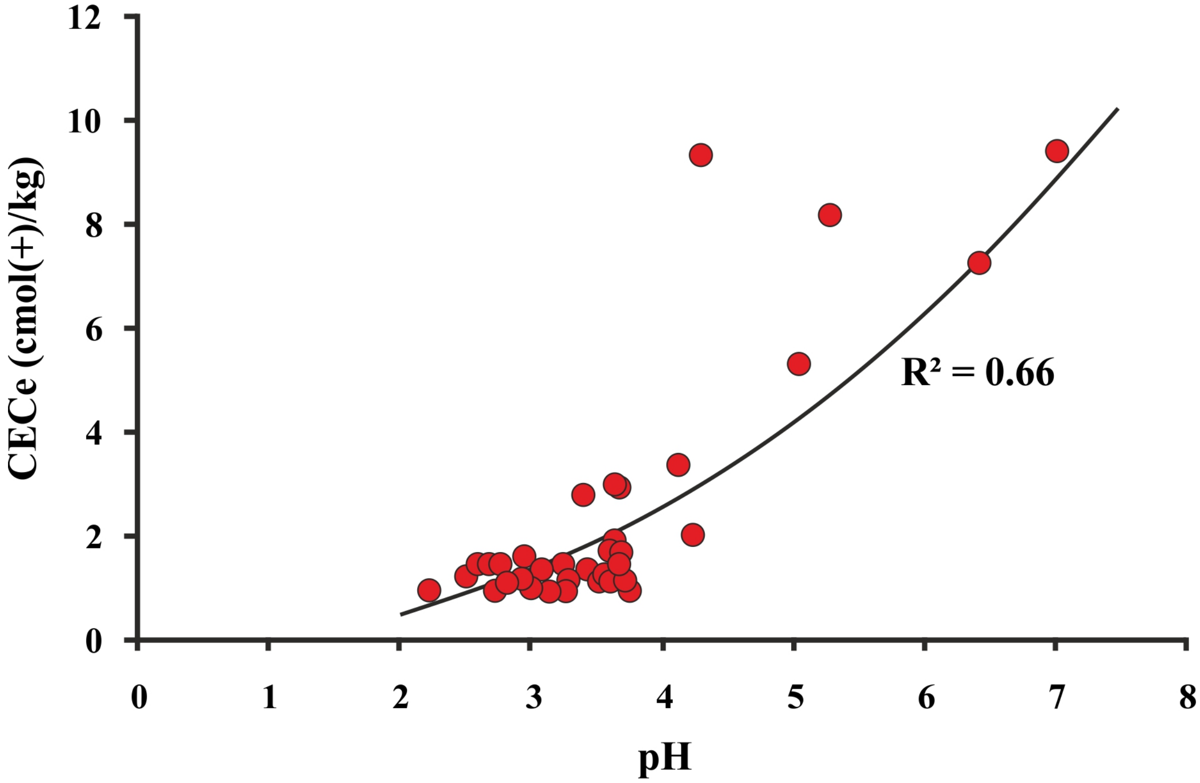


Figure 3. Relationship between CECe and pH in studied soils.

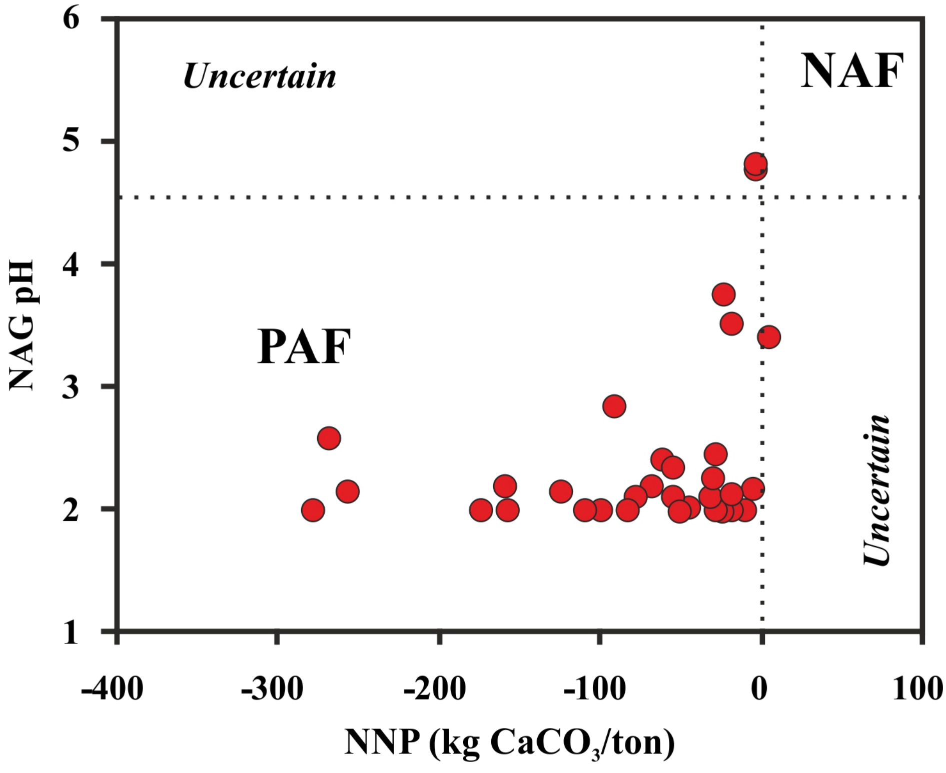
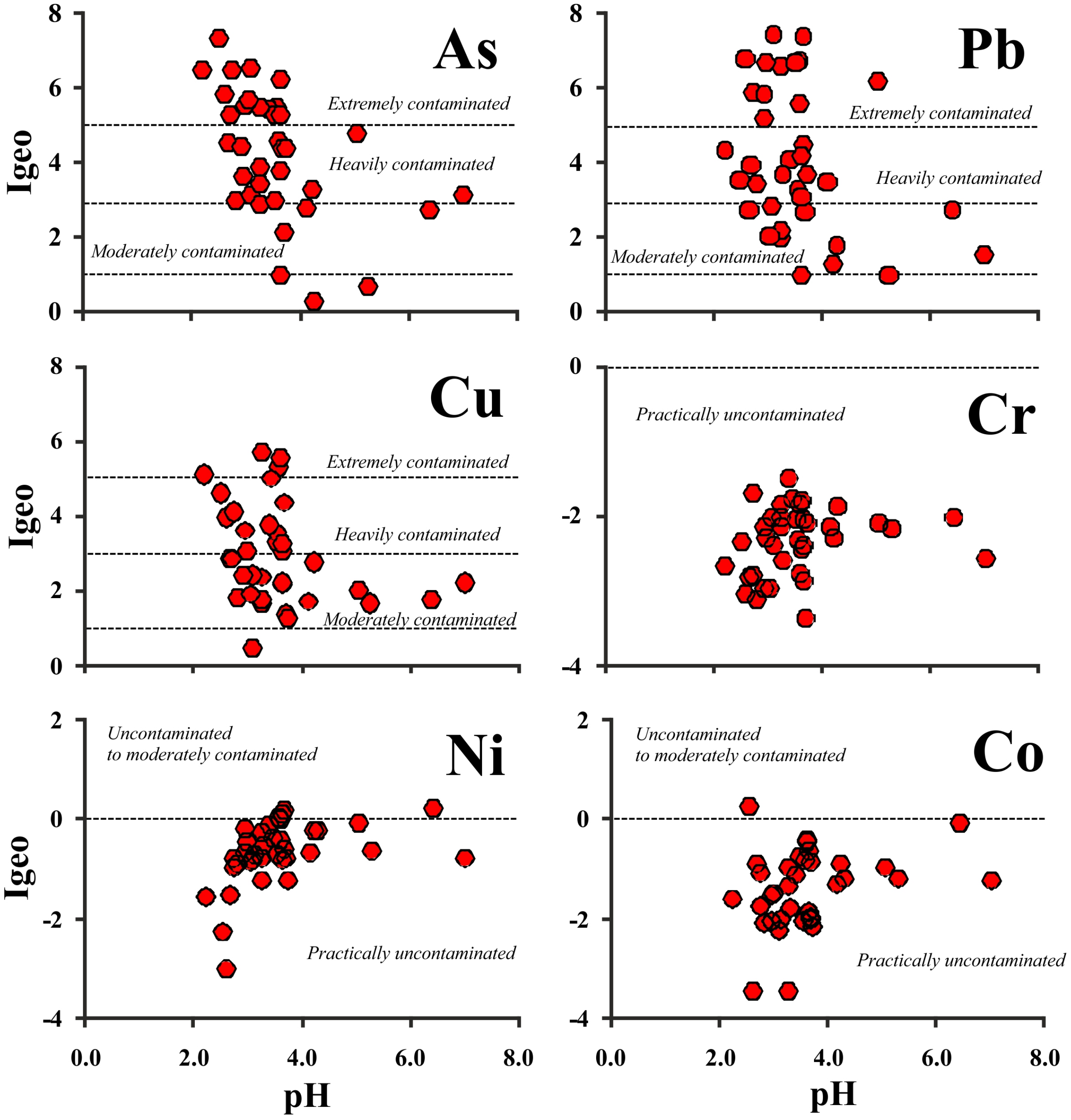


Figure 4. Acidification potential of studied soils (see text for explanation).



815

816 **Figure 5.** Index of Geoaccumulation (I_{geo}) of studied soils according to Müller (1969).

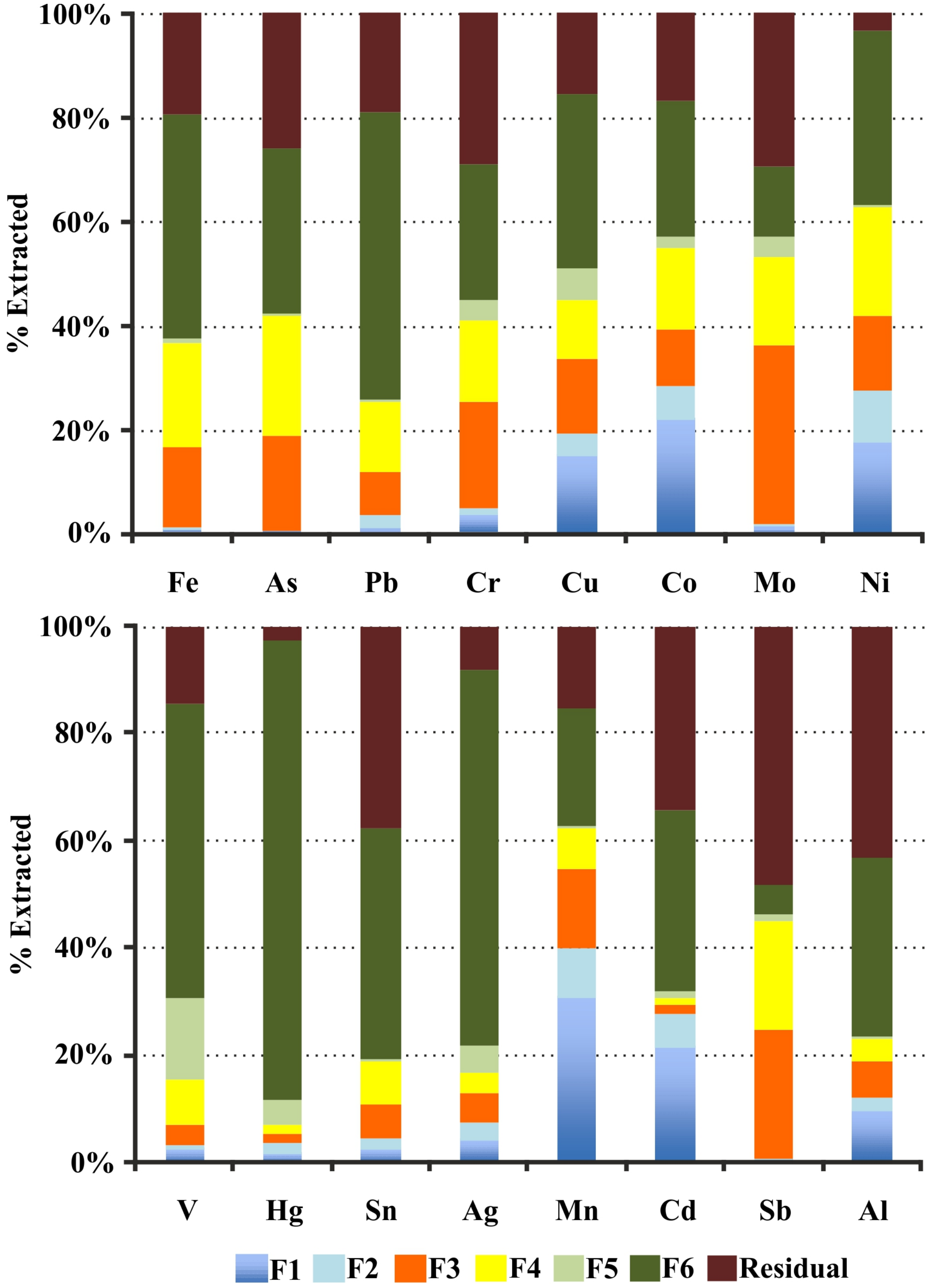


Figure 6. Results of the sequential extraction method proposed by Dold (2003) applied to the studied soils.