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Heavy metal contents in soils and native flora inventory at Mining Environmental Liabilities in the Peruvian Andes

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Abstract

Inadequate waste management in Mining Environmental Liabilities (MEL) represents a risk for the environment and human health and generates social problems. The aim of this article is twofold: i) to evaluate the environmental quality of soils from a geo-ecological perspective; and ii) to inventory native flora around two MEL in the Hualgayoc district in the Peruvian Andes. Soil samples collected for topsoil (upper 30 cm; i.e., soil arable layer) and subsoil (30-60 cm) were classified as Gleyic Cambisols and showed extremely acid pH (3.50 - 4.19 in site #1 and 2.74 - 4.02 in site #2). The mineralogical composition of soils is dominated by illite, kaolinite, quartz, and jarosite. The concentrations of six potentially toxic elements (Pb, Zn, As, Cu, Ag, and Cd) were determined. High concentrations of Pb (4683 mg kg^{-1}), Zn (724.2 mg kg^{-1}), Cu (511.6 mg kg^{-1}), Ag (33.4 mg kg^{-1}), and As (3611 mg kg^{-1}) exceeded the maximum permissible limits for agricultural soils according to Peruvian and Canadian

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regulations. Applied geochemical indexes classified some of the soils as extremely polluted and therefore the studied MEL represent a very high ecological risk. Twenty-two species of native flora belonging to 12 family species were inventoried in such contaminated sites thus having the potential to be used for phytoremediation purposes.

Keywords: Soil pollution, Contamination indices, Ecological risk, Native plants, Cajamarca, Peruvian Andes

1. Introduction

Mining has been one of the economic pillars of the Peruvian economy over the last decades (Figueroa et al., 2010) so that in 2018 it represented almost 10% of national GDP and about 61% of the total value of exports. Peru is the second largest producer of copper, silver and zinc, and is the first producer of gold, zinc, lead and tin in Latin America (Ministerio de Energía y Minas, 2018). Inadequate waste management during mining activity and the lack of clear regulations concerning mine closure have, however, led to the accumulation of Mining Environmental Liabilities (MEL sites) potentially causing environmental and social problems (Lam et al., 2017). MEL sites refer here to the environmental impact caused by abandoned mine activities with or without a responsible identified (Yupari, 2003). In Peru, MEL sites (*Pasivos Ambientales Mineros*, in Spanish) are defined as those installations, effluents, emissions, remains or residue deposits produced by mining operations, abandoned or inactive, that constitute a permanent and potential risk to human health, environment and patrimony (Ministerio de Energía y Minas, 2004). In 2019, the number of MEL sites in the Peruvian territory was of at least 8448, most of them without an identified responsible (Ministerio de Energía y Minas, 2019). The regions of Ancash, Apurímac, Arequipa, Cajamarca, Huancavelica, Junín, Pasco and Puno are the areas that concentrate the greatest number of MEL sites (Chappuis, 2019; Ministerio de Energía y Minas, 2019). Even though Peru was the first Latin American country to establish a legal framework for MEL sites back in 1993 (Oblasser and Chaparro Ávila, 2008), a significant number of MEL sites originated prior to this date, when mining environmental regulation and community

expectation standards were much lower than those set out in the present (Unger et al., 2015).

Soil contamination with heavy metals is a major potential damage caused by MEL sites, which may seriously compromise the alternative use of abandoned mine sites (Vassilev et al., 2004; Zhang et al., 2018; Li et al., 2019; Liu et al., 2020; Manjate et al., 2020). Heavy metals tend to accumulate, in general, in the upper part of soil profiles (surface horizons) and subsequently migrate into deeper horizons (Mazurek et al., 2019). Elevated concentrations of heavy metals in soils can be introduced to flora, fauna or human beings through food chains thus representing direct or indirect threat to human health (Midhat et al., 2019; Zhang et al., 2018). Assessment of the degree and toxicity of soil pollution is important to control contaminated site risks, prevent further soil damage and delineate plan remedial strategies (Liu et al., 2020; Mazurek et al., 2019). Pollution indices provide a useful tool for the quantification of soil quality and the identification of pollution sources. Also, they may help during management and remediation endeavors (Mazurek et al., 2019).

For the restoration of functional ecosystems at post-mining sites, soil recovery is essential (Angst et al., 2018) and the removal of heavy metals using plants represents an often viable alternative (Chaabani et al., 2017). In contaminated areas, the use of phytoremediation with native plants provides natural rehabilitation generating, in addition, a positive visual impact. Plants, by growing roots in contaminated soil, can help immobilize pollutants (Moreno-Jiménez et al., 2011). Native species have been identified often as of high potential to withstand high concentrations of pollutants (Hauptvogl et al., 2019) with the advantage that they grow without human intervention (Gajić et al., 2018).

In the watersheds of the Cajamarca region, where our study has been developed, conspicuous pollution problems derive from the leaching of heavy metals from alteration zones and MEL sites at high altitude. The Andes mountain range is affected by erosive processes leading to soil dragging to agricultural valleys and rivers during the rainy season (Santos-Francés et al., 2017a). Hualgayoc is a mining district of the Cajamarca region with a

long mining history that dates back to the times of the Spanish Colony. Metal production includes chiefly Ag and to a lesser extent, polymetallic ore (Zn, Pb and Cu; Canchaya, 1990). Because of the long mining history, the Hualgayoc district embraces a large number of MEL sites (Ministerio de Energía y Minas, 2019) potentially affecting the Tingo-Maygasbamba, Hualgayoc-Arascorgue and Llaucano river basins, their flora, fauna, and human beings (Pinto Herrera, 2014) and is a source of socio-environmental conflict (Chappuis, 2019).

The main objective of the present study is to evaluate the environmental quality of the soil in and next to MEL sites in the Hualgayoc district in the Peruvian Andes by assessing the environmental risk of heavy metal pollution. To do so, various pollution indices have been used in order to determine the correlation of physicochemical properties of soils and calculate the average content of metals. In addition, we offer an inventory of native flora that grows in such contaminated sites and that, therefore, has potential to be used for phytoremediation purposes.

2. Materials and methods

2.1. Description of the study site

The Hualgayoc district is located between the Chugur and Bambamarca districts, to the west of the Hualgayoc province, in the Cajamarca department in the Andes of northern Peru (**Fig. 1**), and has an extension of 226 km² (Padilla, 2019). The Hualgayoc city is located at an altitude of 3502 m above the sea level (m.a.s.l.), at 866 km N of Lima. The area of study is located between 6°44'46" S - 78°35'49.7" W and 6°44'46.2" S - 78°35'33.2" W. Apart from mining, the population of Hualgayoc has an agricultural tradition dedicated to the cultivation of corn, beans, potatoes, peas, oca, and olluco (Padilla, 2019).

Basement geology in the study area is largely composed of Cretaceous platform sedimentary rocks that were intruded during several magmatic episodes (Fig. 1; Canchaya, 1990; Macfarlane et al., 1994; Macfarlane and Petersen, 1990). The oldest sedimentary rocks belong to the lower Albian – Turonian Goyllarisquizga Group, which crops out in the

core of a northwest–trending anticline. Rocks of the Goyllarisquizga Group comprises mostly quartzites and lesser amounts of interbedded shales and are conformably overlain by a thick carbonate sequence of lower Albian – Turonian age. Bottom to top, carbonate rocks include massive calcareous siltstones and shales of the Inca Formation, grey fossiliferous limestones and shales of the Chulec Formation and dark grey to black bituminous limestones of the Pariatambo Formation. Volcanic rocks cropping out in the Hualgayoc district are of Late Cretaceous and Miocene ages, basic to intermediate in composition and calc-alkaline in affinity according to Canchaya (1990). Dacites from the so-called Hualgayoc intrusion were dated at 14.5 ± 0.5 Ma, sills in the Hualgayoc river canyon at 10 ± 0.5 Ma, and dacite extrusive rocks in the Hualgayoc hill at 7.2 ± 0.4 Ma (Borredon, 1982). Geologically, the studied MEL sites are located on the north-western limb of a regional anticline and deposited on quartzites of the Goyllarisquizga Group (**Fig. 1**).

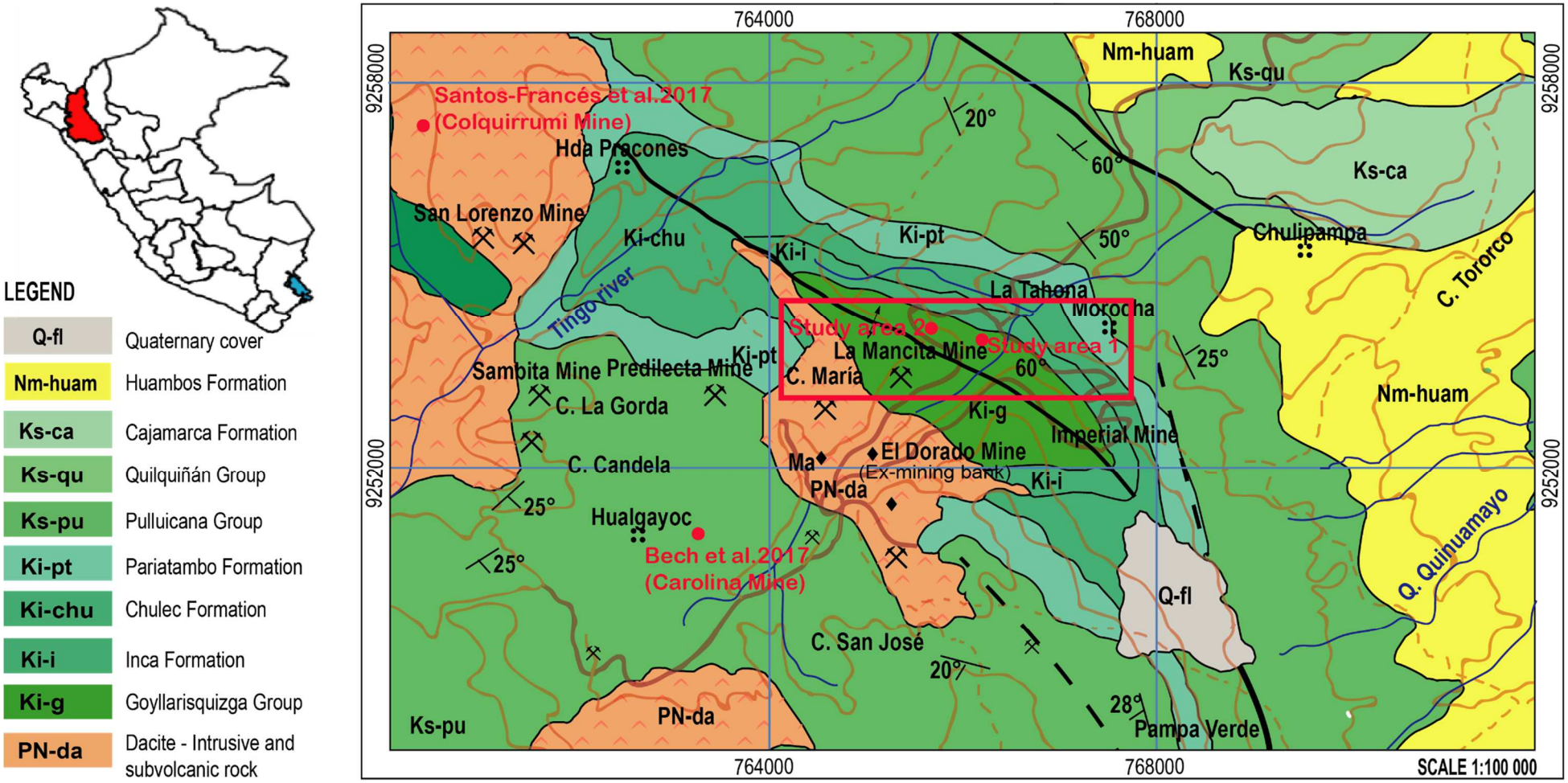

Fig. 1. Geological map of the study area in the Hualgayoc district, Cajamarca region, Peru. Adapted from INGEMMET (2017) and Padilla (2019).

The main mineralized structures in the Hualgayoc district are mantos and veins hosted largely in the upper Goyllarisquizga Group, the Inca Formation and lower Chulec Formation rocks (Canchaya, 1990; Macfarlane et al., 1994; Macfarlane and Petersen, 1990). The ore mineralogy of both mantos and veins is composed mostly of pyrite, sphalerite, and galena and lesser amounts of arsenopyrite, chalcopyrite, marcasite, pyrrhotite, fahlore, and a wealth of Cu-Ag-Pb sulfosalts. The main gangue minerals in both types of mineralization are quartz, barite and Ca-Mg-Fe-Mn carbonates (Canchaya, 1990; Macfarlane et al., 1994; Macfarlane and Petersen, 1990).

There are 943 cataloged MEL sites in the Hualgayoc district, most of them without an identified responsible (Ministerio de Energía y Minas, 2019). In the present investigation, soils and flora from two MEL sites belonging to the Ex-Mining Unit Los Negros have been sampled. Sampling site #1 corresponds to a leach pad, which is located on top of a mine waste deposit and has no drainage. Sampling site #2 corresponds to a mine dump without stabilization, drainage or human-driven revegetation. Both studied MEL sites lie in the flank of the Llaucano river valley. The Mansita, El Dorado, and Morocha mines are located around the studied MEL sites (Padilla, 2019).

2.2. Sampling

Soils and plants were collected around sampling sites #1 (6°44’49” S - 78°35’36” W, 3249 m.a.s.l.) and #2 (6°44’53” S - 78°35’49”, 3399 m.a.s.l.) in July 2018 (dry season; **Fig. 2**) following a criteria based on the distance from the point of contamination, wind direction, slope, vegetation cover and soil texture (Bech et al., 2002). The location of the points for soil sampling in both sites was fixed at 0, 15, 30, 45, and 60 m away from the point of contamination, along a downhill slope. For the determination of soil profile characteristics, samples were taken at four depths between 0 and 60 cm at 15 cm intervals. Following this scheme, a total of 40 soil samples of the topsoil (upper 30 cm; a.k.a. soil arable layer) and of the subsoil (30 to 60 cm downhole) were collected between the two sites. Soil colour was determined in situ with Munsell Colour Charts.

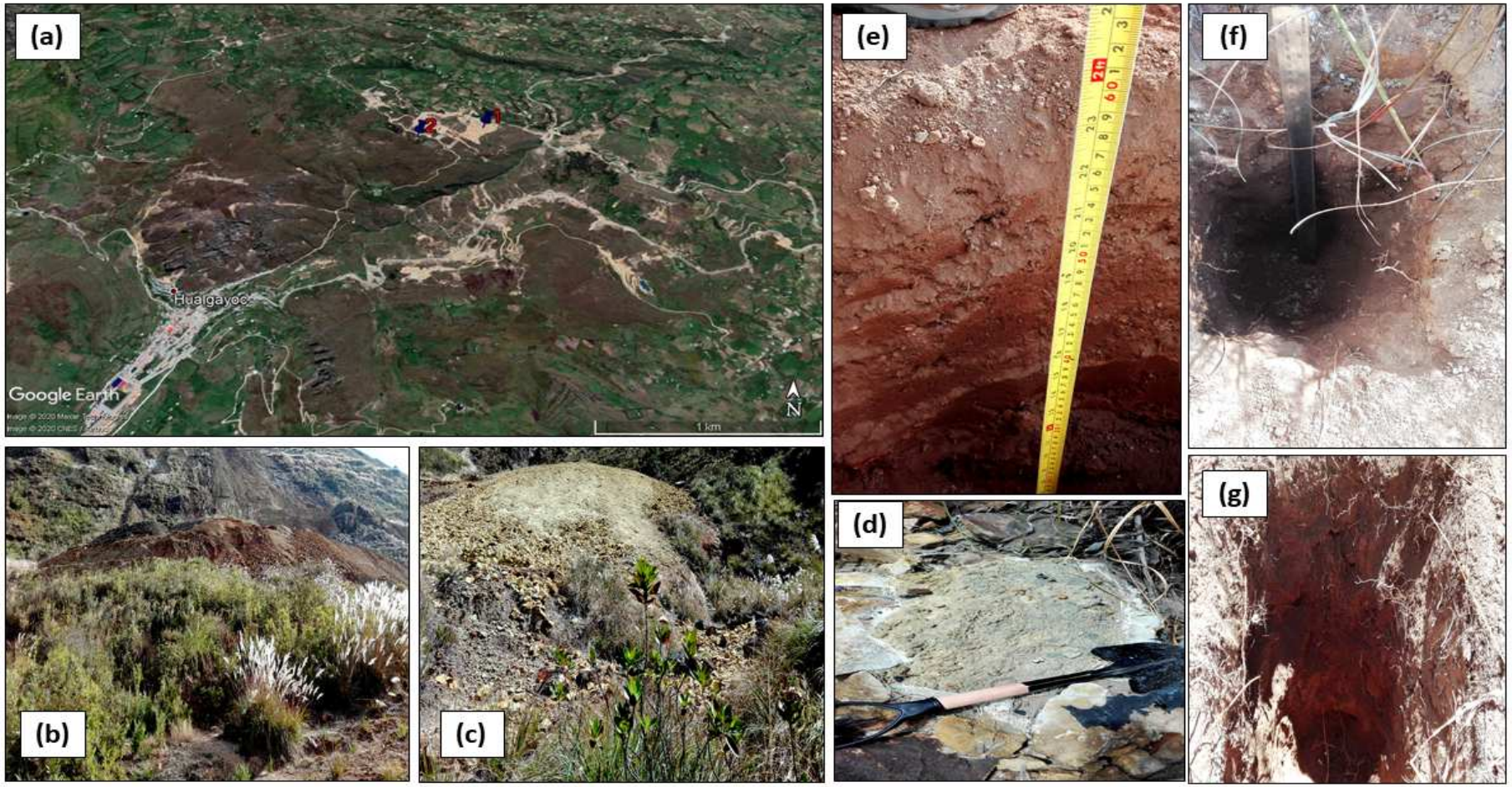

Fig. 2. (a) Localization of the study area in the Hualgayoc district, Cajamarca region, Peru. (b) Site 1- Leach pad and (c) Site 2 - Mine dump Mining Environmental Liabilities. (d) Lixiviate sample from site 1. (e), (f), and (g) soil profiles.

The sampling of flora specimens was carried out in the same locations as for soil sampling. Around each soil sampling point, an area of 4 m^2 was delimited for flora sampling. Flora samples were carefully placed inside a sheet of paper without damaging the main characteristics of the plant. A total of 29 plants in the sampling site #1 and 19 plants in the sampling site #2 were collected. It should be noted that some specimens represented biological replicates and that five species were found in common in both studied areas, thus resulting in a total of 22 species of native flora.

2.3. Chemical analysis of soils samples

Soil samples were analysed at the Soil, Plant, Water and Fertilizer Analysis Laboratory of the Universidad Nacional Agraria La Molina in Lima, Peru. Soil pH was measured using a suspension of soil in deionized water at a 1:1 ratio. The organic matter content was determined by means of the Walkley and Black method (i.e., oxidation of organic carbon with potassium dichromate) (Walkley and Black, 1934). Calcium carbonate content was determined by gas-volumetric method using a calcimeter. The electrical conductivity was measured in aqueous extract of soil in the water at a 1:1 ratio. The texture of soil samples was determined using the Bouyoucos Hydrometer method (i.e., mechanical analysis of soils by means of the suspension of solids for the quantification of the content of sand, silt, and clay in percentage; Bouyoucos, 1936). The soil available phosphorus was determined by the Olsen method (modified extraction with $NaHCO_3$ 0.5N, determination of available potassium content with NH_4OAc 1N extraction by atomic absorption spectrophotometry). The capacity cation exchange was determined using the saturation method of the clay-humic complex with ammonium acetate at pH 7, and nitrogen distillation by Kjeldahl (Sparks, 1996).

The concentration of metals in soils was analysed at the SGS Geochemical Assays Laboratory in Lima, Peru. Approximately 0.20 g of soil with particle size below 106 µm were analysed by digestion in two steps in a Hot Block (Environmental Express). The first digestion step was developed at a temperature of 90 °C for 30 min after the addition of 1 ml of concentrated nitric acid; the second digestion step was developed at a temperature of 90

°C for 1 hour after the addition of 3 ml of concentrated hydrochloric acid. Once it cooled to room temperature, 2 ml of concentrated hydrochloric acid was added and diluted with ultrapure water (18.2 MΩ.cm) to 20 ml (variation from EPA 3050-B method). The concentrations of metals were determined by inductively coupled plasma emission spectrometer (ICP-OES) using a Perkin Elmer Model Optima 8300 DV equipment. The concentration of the following 34 metals and metalloids was determined (detection limits, in ppm, are given in parentheses): Ag (0.2), Al(0.01), As (3), B (10), Ba (1), Be (0.5), Bi (5), Cd (0.4), Co (1), Cr (1), Cu (0.5), Fe (0.01), Hg (1), K (0.01), La(0.5), Li (1), Mg (0.01), Mn (2), Mo (1), Ni (1), P (0.01), Pb (2), S(0.01), Sb (5), Sc (0.5), Se (10), Sn (10), Sr (0.5), Te (10), V (2), W (10), Y (0.5), Zn (0.5), and Zr (0.5) (**Supplementary table 1**). The certified soil reference materials OREAS 906, OREAS 907, and OREAS 522 were used for quality control.

2.4. X-ray diffraction

Mineralogy of 2 soil samples was determined by means X-ray diffraction (XRD). A portion of about 50 g of soil after homogenization was selected for each sample. The clay fraction of soils was analysed as oriented mounts (Moore and Reynolds, 1997). XRD data were collected with a Bruker D8 Discover diffractometer in Bragg-Brentano θ/2θ geometry of 240 mm of radius, nickel filtered Cu Kα radiation (k = 1.5418 Å), and 40 kV–40 mA at the Centro de Caracterización de Materiales of the Pontifical Catholic University of Peru (CAM-PUCP). The patterns of samples on oriented mounts were collected as follows: (i) air dry, scanning from 2 to 80° (2θ); (ii) on samples saturated with ethylene glycol and scanning from 2 to 30° (2θ), (iii) by heating the sample up to 550 °C and scanning from 2 to 30° (2θ), and (iv) by heating the sample up to 550 °C and scanning from 2 to 30° (2θ) at a step size of 0.017° and a scan time of 50 s.

2.5. Electron probe microanalysis (EPMA)

The chemical composition of sphalerite grains from one ore sample picked up in the leach pad belonging to the Ex-Mining Unit Los Negros was analyzed by means of EPMA with a

particular interest in the concentration of Cd (i.e., sphalerite is the main Cd-bearing mineral in polymetallic hydrothermal mineralizations). Analyses were performed on a polished thick section using a five-channel JEOL JXA-8230 electron microprobe equipment (Jeol Ltd., Tokyo, Japan) available at Centres Científics i Tecnològics of the Univeristy of Barcelona (CCiT-UB), operated at 20 kV acceleration voltage, 20 nA beam current and with a beam diameter of 5 μm. Analytical standards and lines used for analyses were: sphalerite (Zn, Kα), chalcopyrite (Cu, Kα), FeS_2 (Fe and S, Kα), Ag (Ag, Lα), Sb (Sb, Lα), CdS (Cd, Lβ), PbS (Pb, Mα), GaAs (As, Lα), Sn (Sn, Lα), InSb (In, Lα) and Ge (Ge, Lα).

2.6 Pollution indices

2.6.1. Index of geo-accumulation (Igeo)

The geo-accumulation index (Igeo), first introduced by Muller (1969), has been successfully applied to the measurement of soil contamination (JI et al., 2008). The Igeo allows the assessment of the soil contamination based on the ratio between the content of metals in a soil sample and the content of metals of a specific geochemical background (Różański et al., 2018). The Igeo is calculated using the following equation:

$$I_{geo} = log_2 \frac{C_i}{1.5 * B_i}$$

where C_i is the measured concentration of the *i* metal examined in the soil; B_i is the background level of the *i* metal. The Igeo discriminates between 7 soil groups or classes (JI et al., 2008; Różański et al., 2018): unpolluted (Igeo ≤ 0), unpolluted to moderately polluted (0 < Igeo ≤ 1), moderately polluted (1 < Igeo ≤ 2), moderately to strongly polluted (2 < Igeo ≤ 3), strongly polluted (3 < Igeo ≤ 4), strongly to very strongly polluted (< Igeo ≤ 5) and very strongly polluted (Igeo > 5).

2.6.2. Nemerow pollution index (NI) and Improve Nemerow index (INI)

The Nemerow pollution index (NI) measures levels of pollution by metals and can estimate the effects of various metals in the soil quality and the environment (Zhang et al., 2018). It is defined as:

$$I = \sqrt{\frac{Pi_{\ ave}{}^{2} + Pi_{\ max}{}^{2}}{2}}$$

where, *Pi* is *the Pollution factor*, which quantifies the contamination of one individual metal, $Pi = C_i/B_i$, where C_i is the concentration of the measured contaminant and B_i is the geological background level (Santos-Francés et al., 2017b). Likewise, Pi_{ave} is the average value of single pollution indices, and Pi_{max} is the maximum value of single pollution indices. The quality of the soil environment is classified as class 0 (NI < 0.7) non-contamination, 1 (0.7 < NI < 1) slight contamination, 2 (1 < NI < 2) low contamination, 3 (2 < NI < 3) moderate contamination, and 4 (NI > 3) heavy contamination (Li et al., 2019).

According to Santos-Francés et al. (2017a, 2017b) and Mazurek et al. (2019) the Improved Nemerow index (INI) reflects more accurately soil reality using other similar pollution indexes, such as the geo-accumulation index (Igeo) in substitution of the pollution factor (*Pi*). INI is calculated using the following equation:

$$INI = \sqrt{\frac{1}{2}\left(Igeo_{\ max}{}^{2} + Igeo_{\ ave}{}^{2}\right)}$$

where, $Igeo_{max}$ is the maximum value of the Igeo of all metals in a sample and $Igeo_{ave}$ is the arithmetic mean of the Igeo. INI discriminate between class 0 - uncontaminated (INI < 0.5), class 1- uncontaminated to moderately contaminated (0.5 ≤ INI < 1), class 2 - moderately contaminated (1 ≤ INI < 2), class 3 - moderately to heavily contaminated (2 ≤ INI < 3), class 4 - heavily contaminated (3 ≤ INI < 4), class 5 - heavily to extremely contaminated (4 ≤ INI < 5) and Class 6 - extremely contaminated (INI > 5) soils.

2.6.3. Potential ecological risk (RI)

The method considers the potential impact of heavy metals on ecosystems and is used for the assessment of soil in large regional areas (Zhang et al., 2018). It is capable of assessing potential risks of one or multiple toxicological elements to the surrounding ecology (Liu et al., 2020). The Ecological Risk Index (Er) evaluates the toxicity of individual metals in soils, and the Potential Ecological Risk (RI) reflects the general situation of contamination caused by the simultaneous presence of the metals (Santos-Francés et al., 2017b). It is calculated following equations:

$$Er = Tr \cdot Pi$$

$$RI = \sum_{i=1}^{n} Er$$

where Tr is the toxicity coefficient of each metal (standard values are Pb = 5, Zn = 1, As = 10, Cu = 5, Ag = 50, and Cd = 30; Duodu et al., 2016; Santos-Francés et al., 2017a). Er classifies the situation of the contamination as low contamination risk (Er < 40), moderate contamination risk (40 ≤ Er < 80), considerable contamination risk (80 ≤ Er < 160), high contamination risk (160 ≤ Er < 320) and extreme contamination risk (Er > 320). The categories for the RI are: low ecological risk of contamination (RI < 150), moderate ecological risk (150 ≤ RI < 300), considerable ecological risk (300 ≤ RI < 600) and very high ecological risk (RI > 600).

2.7. Identification of plant species

Herbarium samples were taxonomically identified in the Laboratory of Floristics of the Herbarium of the Natural History Museum of the Universidad Nacional Mayor de San Marcos in Lima, Peru. The procedure was carried out by comparing specimens of unknown plants with reference botanical samples of the local flora.

3. Results and discussion

3.1. Soil properties

Morphological and physicochemical properties of studied soils are shown in **Table 1.** Soil profiles of the two sampling sites are complex and characterized by the presence of several horizons with contrasting colour, structure, particle size, compactness, and mottling. The colour of soils in site #1 ranged from dark reddish brown (2.5 YR 3/3) to brownish yellow (10 YR 6/8), while in site#2 ranged from brown (7.5 YR 4/3) to dark yellowish brown (10 YR 4/4). As for soil texture, the sand fraction was prevailing. In site #1, particle-size distribution classifies the studied soils as sandy clay loam (e.g., 50 % sand and 32 % silt) to clay loam (e.g., 42 % sand, 38 % clay), akin to soils in site # 2 (60 % sand and 22 % silt to 54 % sand, 28 % clay). Soils from both sampled sites yielded extreme acidity with similar pH values between 3.50 - 4.19 in site #1 and 2.74 - 4.02 in site #2. The soils were identified as non-saline yielding low electrical conductivity (EC) with an average value of 0.11 dSm^{-1} in site #1 and 0.21 dSm^{-1} in site #2. The organic matter (OM) content was moderate to high, between 1.1 and 7.59 % in site #1, and between 1.71 and 10.57 % in site #2, showing higher values in the topsoil. Available P was relatively low, in the range between 1.8 and 4.9 mg kg^{-1} in site #1 and between 1.8 and 3.9 mg kg^{-1} in site #2. Available K was low, in the range from 36 to 106 mg kg^{-1} in site#1, and 36 to 134 mg kg^{-1} in site #2. Both topsoils and subsoils had low capacity cation exchange (CEC) with mean values of 14.94 cmol kg^{-1} in Site#1 and 16.56 cmol kg^{-1} in Site#2. The cations of Ca^{2+}, Mg^{2+}, Na^{+} and K^{+} have been practically removed from the soil (**Table 1**) and no carbonate was found ($CaCO_3$ is systematically 0).

Distance (m)	Depth (cm)	Munsell Colour	pH	EC (dS m^{-1})	O.M (%)	P (mg kg^{-1})	K (mg kg^{-1})	CEC (cmol.kg^{-1})	Exchangeable cations (cmol.kg^{-1})					Particle-size (%)		
									Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	Al^{3+} + H^{+}	Sand	Silt	Clay
Site 1																
0	0 -15	2.5 YR 3/3 (dark reddish brown)	4.02	0.08	7.59	3.4	101	20.32	1.11	0.33	0.27	0.14	5.00	66	22	12
	15-30	2.5 YR 3/3 (dark reddish brown)	3.97	0.09	4.26	2.7	88	19.20	0.90	0.32	0.27	0.17	3.50	50	24	26
	30-45	2.5 YR 3/4 (dark reddish brown)	4.02	0.1	3.13	2.2	78	14.40	0.78	0.30	0.29	0.18	2.30	54	24	22
	45-60	2.5 YR 4/4 (reddish brown)	3.93	0.07	2.34	1.8	60	13.76	0.74	0.28	0.18	0.12	2.50	50	22	28
15	0 -15	10 YR 5/6 (yellowish brown)	4.19	0.05	4.39	3	106	12.80	0.89	0.33	0.35	0.13	2.70	52	26	22
	15-30	10 YR 6/8 (brownish yellow)	3.89	0.07	2.48	2.6	87	14.08	0.90	0.32	0.27	0.10	3.30	42	22	36
	30-45	10 YR 5/6 (yellowish brown)	3.5	0.12	1.38	2.1	72	12.80	0.84	0.30	0.25	0.11	3.40	42	20	38
	45-60	10 YR 4/6 (dark yellowish brown)	3.51	0.39	1.02	1.9	75	13.12	1.45	0.30	0.23	0.17	4.80	50	18	32
30	0 -15	10 YR 3/6 (dark yellowish brown)	3.63	0.13	3.45	3.6	62	15.20	0.64	0.27	0.20	0.16	3.00	52	24	24
	15-30	10 YR 3/6 (dark yellowish brown)	3.84	0.15	3.76	4.6	66	16.00	0.63	0.25	0.19	0.13	2.10	54	28	18
	30-45	10 YR 4/6 (dark yellowish brown)	3.76	0.12	2.87	4.9	59	16.96	0.59	0.23	0.17	0.12	1.70	50	30	20
	45-60	10 YR 4/6 (dark yellowish brown)	3.59	0.13	1.95	3.6	36	17.60	0.54	0.25	0.14	0.15	1.90	70	18	12
45	0 -15	10 YR 5/8 (yellowish brown)	3.63	0.08	5.72	4.1	78	18.88	0.86	0.30	0.24	0.15	4.30	66	18	16
	15-30	10 YR 6/6 (brownish yellow)	3.67	0.08	1.79	2.2	40	10.88	0.63	0.28	0.15	0.17	2.50	52	22	26
	30-45	10 YR 6/6 (brownish yellow)	3.68	0.08	1.26	1.9	39	8.00	0.63	0.28	0.14	0.14	1.60	46	24	30
	45-60	10 YR 7/8 (yellow)	3.63	0.08	1.1	1.9	40	7.52	0.61	0.27	0.16	0.12	2.00	50	22	28
60	0 -15	10 YR 6/8 (brownish yellow)	3.76	0.05	4.21	3.8	84	15.20	0.58	0.23	0.22	0.11	3.80	54	28	18
	15-30	10 YR 3/6 (dark yellowish brown)	3.59	0.09	4.51	2.6	81	19.20	0.66	0.28	0.24	0.14	4.40	50	24	26
	30-45	10 YR 3/6 (dark yellowish brown)	3.68	0.07	3.51	2.7	57	16.64	0.54	0.23	0.18	0.11	3.30	58	22	20
	45-60	10 YR 3/6 (dark yellowish brown)	3.8	0.08	3.16	2.2	54	16.32	0.58	0.27	0.17	0.14	2.60	46	24	30
Site 2																
0	0 -15	7.5 YR 4/4 (brown)	3.42	0.08	10.57	3.6	92	22.08	0.63	0.30	0.24	0.13	6.90	60	22	18
	15-30	7.5 YR 4/3 (brown)	3.37	0.11	4.98	3.2	65	18.72	0.57	0.27	0.20	0.13	6.50	56	24	20
	30-45	7.5 YR 4/3 (brown)	3.67	0.06	3.31	2.7	61	12.80	0.61	0.28	0.16	0.12	4.60	58	20	22
	45-60	7.5 YR 4/3 (brown)	3.72	0.06	2.43	1.8	56	11.68	0.60	0.27	0.09	0.16	3.20	52	18	30
15	0 -15	10 YR 4/4 (dark yellowish brown)	4.02	0.02	4.36	4	85	14.40	0.83	0.32	0.25	0.13	3.00	54	20	26

Distance (m)	Depth (cm)	Munsell Colour	pH	EC (dS m^{-1})	O.M (%)	P (mg kg^{-1})	K (mg kg^{-1})	CEC (cmol.kg^{-1})	Exchangeable cations (cmol.kg^{-1})					Particle-size (%)		
									Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	Al^{3+} + H^{+}	Sand	Silt	Clay
	15-30	10 YR 4/4 (dark yellowish brown)	3.89	0.02	4.37	3.4	78	16.32	0.63	0.28	1.03	0.12	2.80	62	20	18
	30-45	10 YR 4/4 (dark yellowish brown)	3.76	0.04	5.22	3.3	75	17.92	0.62	0.30	0.22	0.11	4.40	54	22	24
	45-60	10 YR 4/4 (dark yellowish brown)	3.72	0.04	6.09	2.7	77	17.60	0.64	0.28	0.22	0.12	4.60	60	22	18
30	0 -15	7.5 YR 5/4 (brown)	3.37	0.14	2.48	3.2	83	16.48	0.67	0.25	0.24	0.11	6.00	52	18	30
	15-30	7.5 YR 3/3 (dark brown)	3.46	0.14	2.88	2.2	71	17.60	0.66	0.28	0.25	0.12	4.50	54	18	28
	30-45	7.5 YR 4/4 (brown)	3.5	0.22	3.13	1.8	68	16.00	0.61	0.28	0.21	0.13	4.00	54	20	26
	45-60	7.5 YR 3/3 (dark brown)	3.03	0.61	4.62	1.8	70	20.00	0.55	0.27	0.19	0.12	7.50	52	22	26
45	0 -15	7.5 YR 4/4 (brown)	3.85	0.05	4.92	3.9	134	19.20	0.78	0.30	0.37	0.12	5.70	56	22	22
	15-30	7.5 YR 4/4 (brown)	3.72	0.05	3.28	3	91	16.48	0.65	0.28	0.29	0.17	5.10	58	22	20
	30-45	7.5 YR 4/4 (brown)	3.46	0.08	2.87	2.6	75	15.36	0.63	0.28	0.24	0.13	4.80	54	24	22
	45-60	7.5 YR 4/4 (brown)	2.9	0.4	1.99	2.7	50	15.52	0.60	0.25	0.16	0.10	4.50	50	22	28
60	0 -15	7.5 YR 5/4 (brown)	2.94	0.32	2.15	4	53	16.00	0.57	0.27	0.16	0.13	4.20	54	24	22
	15-30	7.5 YR 5/4 (brown)	2.77	0.57	1.71	3.4	40	14.08	0.66	0.32	0.13	0.15	4.60	54	20	26
	30-45	7.5 YR 4/4 (brown)	2.74	0.61	1.88	3	37	16.32	0.59	0.23	0.12	0.12	4.40	56	18	26
	45-60	7.5 YR 4/4 (brown)	2.82	0.56	2.1	2.9	40	16.64	0.54	0.30	0.15	0.17	6.00	56	20	24

EC: Electrical Conductivity, OM: Organic Matter, CEC: Cation Exchange Capacity

Table 1. Properties of soil samples from sites #1 and #2 in the Hualgayoc district, Cajamarca region, Peru.

According to the moderate to high organic matter content, brown to dark yellowish-brown colour and extreme acidity, most studied soils showed Andic properties (IUSS Working Group WRB, 2015). Considering the morphology and analytical data (taxonomy of the World Reference Base; IUSS Working Group WRB, 2015), and the soil colour with Munsell Colour Charts, the studied soils are classified as Gleyic Cambisols. In the study performed by Santos-Francés et al. (2017), in the Colquirrumi mine and in the mining project of the Zanja in the Cajamarca region, soils were classified as Haplic Umbrisols, and Umbric Andosols; in addition, these authors also identified Dystric Regosols and Gleyic Cambisols.

The limited availability of P and K in the studied soils can be attributed to the low pH and associated low CEC (Claveria et al., 2019). The soil particle-size, though variable, is relatively coarse (sandy clay loam and clay loam), a fact that is commonly observed in mining waste environments (Delplace et al., 2020). Soils are very poor in essential nutrients when the cations of calcium, magnesium, sodium, and potassium are released and replaced by hydrogen and aluminum instead (Gardi et al., 2015). Our results show that low clay content is directly correlated with decreasing CEC, which has been also described by Kodirov et al., 2018. The bioavailability of nutrients could have been affected by low pH in soils (Claveria et al., 2019) and the unbalanced content of macronutrients points to poor soil management (Egerić et al., 2019). Mining-affected soils show low fertility and low ability to hold cations thus facilitating metal lixiviation, which is further accelerated by the acidic character of soils (Delplace et al., 2020) pointing out the need to introduce corrective measures.

Soils at the Carolina mine, located 4 km SW of the study area (Fig. 1) and studied by Bech et al. (2017) showed basic pH values (up to 8.0) and high calcium carbonate levels, moderate organic carbon contents and silt loam texture. Soils studied by Santos-Francés et al. (2017) at the Colquirrumi mine, located 6 km NW of our study area were acid (pH = 4.6), had low organic matter content (5.04 %), moderate CEC (31.7 $cmol.Kg^{-1}$) and silt sand texture (41.5 silt, 30.8 % clay, and 29.5% sand). It is noteworthy that soils at the Carolina mine are on a substrate of carbonate rocks with intercalation of black shales (Pulluicana

Group; **Fig. 1**) that may have exerted an important role in the neutralization of acidity and increased carbonate levels in soils (Crozier and Hardy, 2003; Webb and Sasowsky, 1994). In contrast, the studied soils at Hualgayoc and Colquirrumi are on quartzite and dacite substrates, respectively, which are much less reactive.

3.2. Soil mineralogy

Identification of minerals in B-1 and D-1 samples was achieved by comparison of XRD diffractogram with ICDD database (2007 release) using Diffrac plus Evaluation software. The following minerals were identified: illite, kaolinite, quartz, and jarosite; in addition, a maximum of X-ray diffraction at 4.3Å was detected, which coincides with the most intense diffraction peak of cristobalite; however, the presence of this mineral in not expected in the studied soils (**Fig 3**). Two very wide and low-intensity diffraction maximum were observed for B-1 at 22.5 Å and 13.3. Å, and for D-1, at 25.1 Å and 12.6 Å, which were identified as interstratified minerals from the clays group possibly as an illite-smectite interstratified. The B-1 sample showed greater abundance of the interstratified clay relative to the sample D-1. The weight proportions of the minerals were difficult to determine due to the presence of amorphous material, identified by the high background (see **Fig. 3**). In both samples, the diffractograms obtained in the oriented mounts with the treatments showed and confirmed the presence of illite, due to the fact that this mineral did not show any change in the 00l spacings with the ethylene glycol (ETG) and 550 °C treatments (Moore and Reynolds, 1997). Also, the presence of kaolinite was confirmed since the diffraction maximum disappeared when the sample was heated to 550 °C. On the other hand, the diffraction maximum identified as illite-smectite interstratified disappeared when the sample was heated and no clear displacement of the diffraction maximum was observed when the sample was treated with ETG, which made its identification unclear. Semiquantitative analysis from the RIR (Davis et al., 1990) of the minerals identified in the studied samples showed that illite was very abundant in B-1 (71 wt. %), other phases occurring in minor amounts (kaolinite, 21 wt. %; quartz, 6 wt. %; jarosite and cristobalite (<2 wt. %) akin to sample D-1 (illite/sericite, 55 wt. %; kaolinite, 27 wt. %; quartz, 9 wt. %; jarosite, 7 wt. %; cristobalite, 3 wt. %; **Fig 3a-b**). It is worth noting that

studied soils lack detectable amounts of carbonate minerals, which agree with the nil calcium carbonate contents according to the calcimetry assay (**Table 2**).

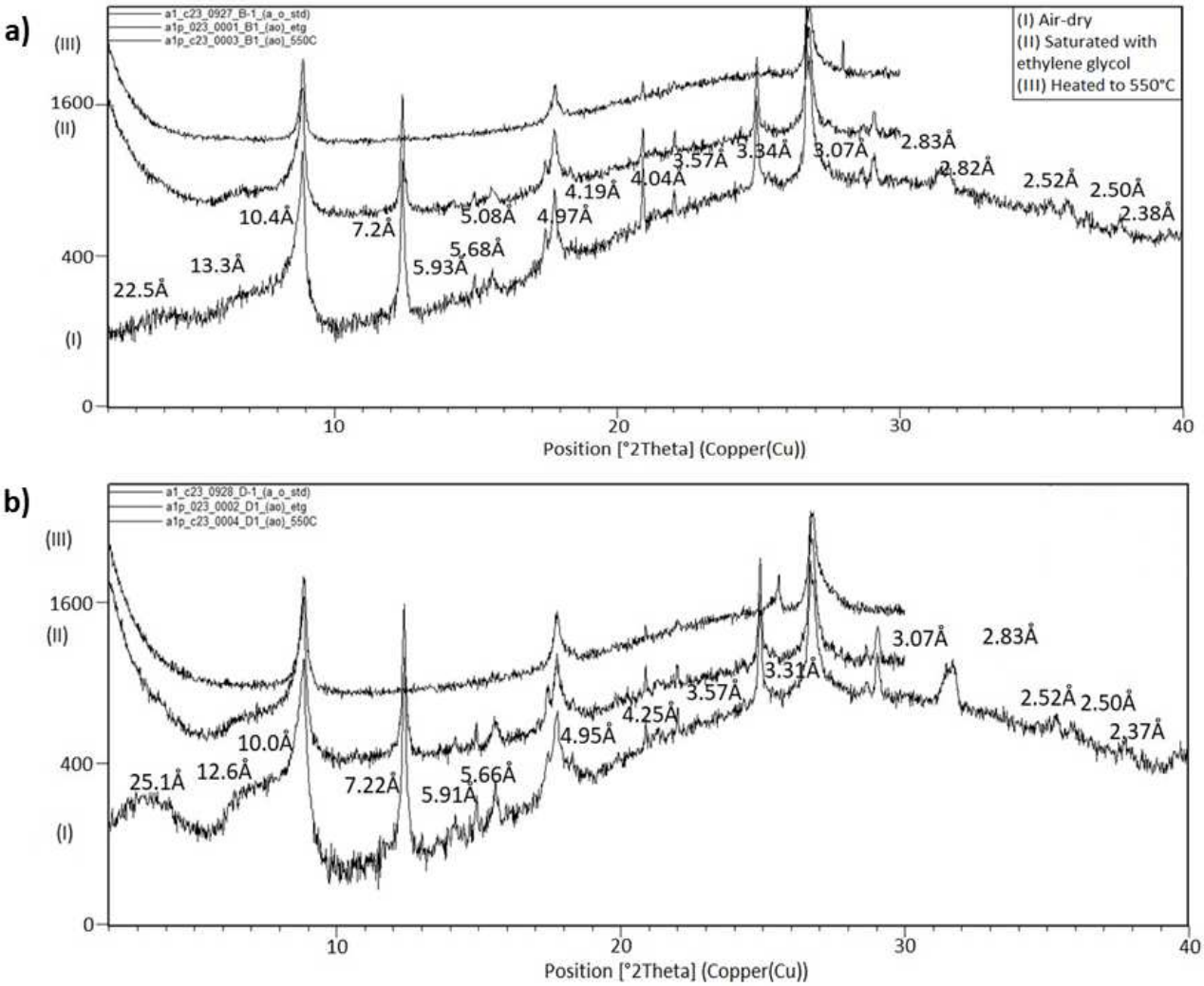

Fig. 3. Diffractogram of soil samples B-1 and D-1 in the site #1 and #2 in the Hualgayoc district, Cajamarca region, Peru**.**

3.3. Soil elemental composition

Potentially toxic concentrations of Pb, Zn, As, Cu, Ag and Cd were found out of a total of 34 elements analysed. Metal and metalloid concentrations in soils from site #1 are provided in **Table 2** and graphically shown in **Supplementary Fig. S1**. Concentrations are

relatively highly variable among the studied samples. In general terms, Pb was the metal showing the highest concentrations, which were in the range between 1129 and 4683 mg kg^{-1}. Although the distribution pattern of Pb is rather erratic, it is maximum in the topsoil with the exception of the soil profile sampled at 0 m from the contamination point, in which the concentration of Pb is maximum at a depth of 45-60 cm. There is also a general enrichment trend in Pb with decreasing distances to the contamination point, with the notable exception of the soil profile sampled at 60 m from the contamination source, which registers indeed the highest Pb concentration. Zinc concentrations were in the range between 167.8 and 724.2 mg kg^{-1}, with the highest values recorded in topsoil samples located at a distance of 15 and 60 m from the contamination point (724.2 and 696.3 mg kg^{-1}, respectively) and general enrichment on the topsoil. Exceptionally, the sample collected at the contamination point (0 m) at a depth of 45-60 cm yields a higher concentration of Zn regarding upper soil layers. The concentration of As was in the range from 85 to 3611 mg kg^{-1} and is normally higher in the topsoil regarding the subsoil. Nevertheless, soil sampled at 30 m of distance to the contamination point yields extremely high As concentrations (1123 to 3611 mg kg^{-1}) in the subsoil. Copper concentrations varied between 183.9 and 511.6 mg kg-1, showing a slight increase in topsoil samples at distances of 15 and 45 m from the contamination point (462.1 and 511.6 mg kg-1). Copper concentrations remain relatively constant in the other studied soil samples regardless their location and depth of sampling. Silver contents were relatively low, between 0.4 and 33.4 mg kg^{-1}, and Cd presented the lowest concentrations in the range between 1 and 5 mg kg^{-1}.

Distance (m)	Depth (cm)	Pb	Zn	As	Cu	Ag	Cd
			Site 1				
0	0 -15	2523	287.2	287	273.8	14.9	1.143
	15-30	2370	290.8	305	267.5	7.7	1.072
	30-45	1944	529	85	183.9	2.3	1.79
	45-60	3278	432.8	400	271.5	6.7	1.472
15	0 -15	2322	724.2	395	462.1	13.3	1.759
	15-30	1951	243.9	274	246.9	4.2	0.949
	30-45	1504	241.5	255	230.6	3	1.075
	45-60	1328	167.8	234	202.1	4.2	0.799

30	0 -15	1949	375.9	390	333.7	9.2	1.743
	15-30	1506	287.6	343	317.3	4.2	1.284
	30-45	1517	240	1123	369.2	4.1	2.306
	45-60	1493	214.8	3611	302.2	2.2	5.017
45	0 -15	1607	353.2	385	369.7	20.7	1.895
	15-30	1129	523.2	252	511.6	4.1	1.64
	30-45	1912	216	168	353.4	0.4	1.054
	45-60	2205	212.3	155	361.1	2.5	1.234
60	0 -15	4683	696.3	401	351.9	33.4	4.703
	15-30	3061	368.8	321	307.3	16.3	2.298
	30-45	1535	300.2	336	361.5	4.9	1.909
	45-60	1482	358	346	329.2	3.2	2.05
Site 2							
0	0 -15	2367	277.2	295	277.1	20.4	1.584
	15-30	969	304.6	197	241	3.7	1.116
	30-45	884	122.6	171	168.4	3	0.859
	45-60	814	122	184	166	2.7	0.914
15	0 -15	670	230.1	119	117.5	2.7	0.989
	15-30	932	198.1	165	131.3	4.2	0.873
	30-45	1007	239.8	183	156.6	7.2	1.056
	45-60	988	215.5	159	150.2	6.5	0.972
30	0 -15	1025	193.7	226	252.7	4.2	0.754
	15-30	934	198.6	213	283	4	0.856
	30-45	906	233.4	216	314.4	3.6	0.952
	45-60	960	201.7	165	247.9	3.5	0.893
45	0 -15	1327	145.8	343	255.4	9.7	0.985
	15-30	1086	120.7	292	189.4	11.5	0.761
	30-45	1135	96.7	253	238.3	13.9	0.79
	45-60	1138	73.8	200	237.3	8.4	0.698
60	0 -15	1772	120.4	728	149	7.5	0.788
	15-30	1919	138.2	736	146.7	6.5	0.898
	30-45	1155	113.3	846	154	3.8	0.832
	45-60	1086	100.9	924	151.7	7.5	0.808

Table 2. Concentration of Pb, Zn, As, Cu, Ag and Cd (mg kg^{-1}) in soil samples from sites #1 and #2 picked at distances between 0 and 60 m from the contamination points and at depths of 0-15, 15-30, 30-45 and 45-60 cm in the Hualgayoc district, Cajamarca region, Peru.

In soils from sampling site #2, Pb was the most concentrated metal with values between 670 and 2367 mg kg^{-1}. The highest concentration was found in the upper soil layer located adjacent to the contamination point. In the soil sampled at 15 m from the contamination point, however, samples in the subsoil yielded higher Pb concentrations than samples in the topsoil. The values of Zn varied in the range between 73.8 and 304.6 mg kg^{-1}.

Akin to Pb, Zn concentration was maximum in soil sampled adjacent to the contamination point and its concentration in the topsoil steadily decreases at increasing distances from the contamination point. The concentrations of As were in the range between 119 and 924 mg kg^{-1}, and in general, increased progressively at increasing distances from the contamination point, so that, the highest concentrations were obtained at 60 m of distance. Copper contents in studied soils were in the range between 117.5 and 314.4 mg kg^{-1}. Soils sampled at 0 and 45 m from the contamination point had higher Cu concentrations in the topsoil regarding samples from deeper sampling levels; in contrast, soils sampled at 15, 30 and 60 m from the contamination point showed the opposite trend. The Ag concentrations varied between 2.7 and 20.4 mg kg^{-1} and Cd concentrations were systematically very low and rather constant for all samples with an average concentration of 0.9 mg kg^{-1}.

The heavy metals concentrated in the studied soils are in close linkage with the ore mineralogy of the Ex Mining unit Los Negros in the Hualgayoc district, which includes abundant iron sulphides (mostly pyrite, but also marcasite, and pyrrhotite), galena, sphalerite and arsenopyrite. EPMA analyses on sphalerite grains, in addition, show moderate concentrations of Cd in the range between 0.28 and 0.63 wt. % (**Table 3**).

	Sample	**2018-**	**2018-**	**2018-**	**2018-**	**2018-**	**2018-**
d.l.	Analysis	Circle E-sl	Circle D-sl-001	Circle D-sl-002	Circle C-sl-001	Circle B-sl-001	Circle A-sl-001
0.0	S	32.87	32.89	32.58	32.57	32.79	32.66
0.1	Pb	0.19	<d.l.	0.26	0.22	<d.l.	<d.l.
0.0	Zn	66.38	66.48	66.84	66.96	67.10	66.12
0.0	Fe	1.06	0.94	0.68	0.80	0.54	1.02
0.0	Cd	0.46	0.29	0.30	0.28	0.38	0.63
	Total	100.95	100.60	100.65	100.83	100.82	100.43

Sb, In, As, Ga, Ge, Cu, Ag, Sn <d.l.: below detection limit.

Table 3. Representative analyses of sphalerite in the sampling sites from the Hualgayoc district with chemical composition in wt. % (EPMA data).

According to the Peruvian Environmental Quality Standards (PEQS) for agricultural soil, the maximum allowed contents of Pb, As, and Cd are of 70, 50, and 1.4 mg kg^{-1}, respectively (Ministerio del Ambiente, 2017), tantamount to Canadian Soil Quality Guidelines (CSQG; Canadian Council of Ministers of the Environment, 2007) for Pb and Cd. The CSQG, however, establishes a maximum allowed value of 12 mg kg^{-1} for As. In sampling sites #1 and #2, measured concentrations of Pb and As exceeded the maximum allowed values by environmental regulations. Cadmium concentrations were mostly below maximum allowed concentrations in both sites. PEQS does not establish maximum concentrations for Ag, Cu, and Zn whereas CSQG contemplates maximum values of 20, 250, and 63 mg kg^{-1}, respectively (Canadian Council of Ministers of the Environment, 2018, 2007). According to Canadian standards, Zn concentrations exceeded the maximum allowed values in samples from site #1, mainly in the topsoil and in samples from site #2 at 0 m in the topsoil. Copper concentrations in both sites considerably exceeded the maximum values allowed according to CSQG, and the maximum allowed content of Ag was only exceeded at 45-60 m from the contamination point for site#1 and at 0m from the contamination point for site #2. High concentrations of heavy metals largely exceeding maximum allowed concentrations according to both PEQS and CSQG are reported in soils from neighbouring Colquirrumi (Pb = 2068.76 mg kg^{-1}, Zn = 1893.06 mg kg^{-1}, As = 428.32 mg kg^{-1}, Cu = 197.70 mg kg^{-1}, Cd = 13.03 mg kg^{-1}; Santos-Francés et al., 2017a) and Carolina (Pb = 3992-16060 mg kg^{-1}, Zn = 11550-28059 mg kg^{-1}, As = 256-2070 mg kg^{-1}, Cu = 280-1030 mg kg^{-1}; Bech et al., 2017) mining areas (**Fig. 1**).

3.4. Indices of soil pollution

3.4.1. The Geoaccumulation Index, the Nemerow Pollution Index and *Improved Nemerow Index*

Geochemical baselines for Pb, Zn, As, Cu, and Cd were established in soils from the La Zanja mining project, which is located 30 km SW of our sampling sites, in 2006 (i.e., before its exploitation; Santos-Francés et al., 2017a). For Ag, we considered the natural abundance in the Earth's crust (Yaroshevsky, 2006). All indices were calculated for topsoil and subsoil portions (**Tables 4 and 5**). The Igeo values revealed that the level of soil pollution ranged from unpolluted to extremely polluted in both sampling sites (**Table 4**). Considering the Igeo, studied soils were unpolluted with Cd, but moderately to highly polluted (site#1), and moderately polluted (site #2) with Zn. Regarding Cu, soils were highly polluted in site#1 and moderately to highly polluted in site#2, and regarding As, soils were highly polluted in both sampling sites. Studied soils are extremely polluted in site #1 and highly to extremely polluted in site #2 with Pb, and extremely polluted with Ag in both sites. Calculated Igeo values here are mostly equivalent to other studied mining soils in the region. Bech et al. (2016) reported Igeo values for soils in the Carolina mine (**Fig. 1**) pointing to extreme contamination with Pb and Zn, and slight to moderate contamination with As and Cu. Santos-Francés et al. (2017) stated that soils in the Colquirrumi mining area (**Fig. 1**) ranged from uncontaminated to extremely contaminated.

Metals	**Pb**	**Zn**	**As**	**Cu**	**Ag**	**Cd**
Geochemical baseline values in a natural region - From the mining project La Zanja (2006)[1]	44.87	47.42	27.5	22.2	-	4.36
Abundances of Chemical Elements in the Earth's Crust[2]	16	83	1.7	47	0.07	0.13
Geo-accumulation index (Igeo)						
Site 1						

Samples						
Minimum (Min)	4.07	1.24	1.04	2.47	1.93	-3.03
Maximum (Max)	6.12	3.35	6.45	3.94	8.31	-0.38
Average	5.09	2.29	3.75	3.20	5.12	-1.71
Site 2						
Minimum (Min)	3.32	0.05	1.53	1.82	4.68	-3.23
Maximum (Max)	5.14	2.10	4.49	3.24	7.60	-2.05
Average	4.23	1.08	3.01	2.53	6.14	-2.64

[1] Santos-Francés et al. (2017a)

[2] Yaroshevsky (2006)

Table 4. Geo-accumulation index (Igeo) for soils sampled at five distances from the contamination points and at four depths (topsoil: 0-15 and 15-30 cm; subsoil: 30-45 and 45-60 cm) in sampling sites #1 and #2 in the Hualgayoc district, Cajamarca region, Peru.

NI values of trace metals in soils were relatively high, ranging in sampled soils from site #1 between 31.41 and 345.41, and in soils from site #2, between 28.43 and 210.72 (**Table 5**) corresponding to heavy contamination (NI > 3); however, the high IN figures could be due to used background values. INI values were of 5.09 (class 6: extremely contaminated) in soils from site #1 and of 4.67 (class 5: heavily to extremely contaminated) in soils from site #2. It should be noticed that INI is considered much more accurate in assessing the environmental risks of the contamination compared with NI (Li et al., 2019). In

short, the presented heavy metal analyses in mining soils from both studied sites indicate high indices of contamination and the need for effective contamination control and remediation (Li et al., 2018).

Samples	***Pi***						**NI**	**INI** (based in Igeo values)
	Pb	**Zn**	**As**	**Cu**	**Ag**	**Cd**		
Site 1								
Minimum (Min)	25.16	3.54	3.09	8.28	5.71	0.18	31.41	3.66
Maximum (Max)	104.37	15.27	131.31	23.05	477.14	1.15	345.41	6.52
Average	46.02	7.45	18.30	14.43	115.36	0.43	188.41	5.09
Site 2								
Minimum (Min)	14.93	1.56	4.33	5.29	38.57	0.16	28.43	3.53
Maximum (Max)	52.75	6.42	33.60	14.16	291.43	0.36	210.72	5.80
Average	25.71	3.63	12.03	9.07	96.07	0.21	119.58	4.67

Table 5. Nemerow Pollution Index (NI) and Improved Nemerow Index (INI) calculated for soils sampled at five distances from the contamination points and at four depths in the sampling sites #1 and #2 in the Hualgayoc district, Cajamarca region, Peru.

3.4.2. Ecological risk assessment

Soils contaminated with heavy metals may cause severe ecological risks and negatively impact human health though different forms of interaction (agriculture, cattle breeding, etc.) since highly toxic metals can get introduced into the food chain (Li et al., 2019). Therefore, the potential ecological risk for Pb, Zn, As, Cu, Ag, and Cd in soils were evaluated (**Table 6**).

Samples	**Er**						**RI**
	Pb	**Zn**	**As**	**Cu**	**Ag**	**Cd**	
Site 1							
Minimum (Min)	125.81	3.54	30.91	41.42	285.71	5.50	651.27
Maximum (Max)	521.84	15.27	408.36	115.23	23857.14	34.52	24651.10
Average	323.82	9.41	219.64	78.32	12071.43	20.01	12651.18
Site 2							
Minimum (Min)	74.66	1.56	43.27	26.46	1928.57	4.80	2084.63
Maximum (Max)	263.76	6.42	336.00	70.81	14571.43	10.90	15021.62
Average	169.21	3.99	189.64	48.64	8250.00	7.85	8553.12

Table 6. Individual ecological risk index (Er) and Potential Ecological Risk Index (RI) calculated for the studied soils from the Hualgayoc district, Cajamarca region, Peru.

According to the Er index, levels of metal contamination in the subsoil and topsoil were similar in both studied sites and varied from low to extreme ecological risk. Cadmium and Zn represented a low contamination risk (Er < 40), Cu represented a moderate risk of contamination (40 ≤ Er < 80), As represented a considerable contamination risk (80 ≤ Er < 160), and Pb and Ag represented an extreme contamination risk (Er > 320). The impact of the metals coincides with Igeo impact (**Table 4**). On the other hand, considering the RI for all the studied metals and metalloids, there is a very high ecological risk (RI ≥ 600). The observed extreme accumulation of metals and metalloids in the soils (chiefly Pb and As) can impact ecosystems, affect the quality and safety of food, and increase the risk of serious diseases (cancer, kidney, liver damage, etc.; Li et al., 2019).

3.5. Inventory of native flora

The results of the ecological risk assessment revealed conspicuous soil contamination with heavy metals (Nouri and Haddioui, 2016), which may have a big impact on ecosystems (Swartjes et al., 2011). Native plants colonizing polluted sites must be evaluated as chief candidates for phytoremediation, because i) they are able to perform better than other species in terms of survival, growth, and reproduction as they are already adapted to the local climate; and ii) they have intrinsically demonstrated the capability of growing in soils contaminated with heavy metals (Marchiol et al., 2013).

In this study, an inventory of the native plants that grew at the contaminated sampling sites was conducted. A total of 15 species were inventoried in site #1 (**Table 7**) and a total of 12 species were inventoried in site#2 totaling 22 plants of native flora belonging to 12 family species (**Table 8**). **Fig. 4** shows pictures of some of the species identified. The following 5 species were found in both studied sites: *Achyrocline alata*, *Pernettya prostrata*, *Hypericum laricifolium*, *Brachyotum radula*, and *Cortaderia bifida*.

N°	Family name	Scientific name	biological replicates
1	Asteraceae	*Achyrocline alata*	2
2		*Ageratina fastigiate*	3
3		*Ageratina glechonophylla*	2
4		*Baccharis alnifolia*	1
5	Bromeliaceae	*Puya sp*	1
6	Caryophyllaceae	*Arenaria digyna*	1
7	Ericaceae	*Bejaria sp.*	1
8		*Pernettya prostrata*	1
9	Hypericaceae	*Hypericum laricifolium*	4
10	Iridaceae	*Orthrosanthus chimboracensis*	1
11	Melastomalaceae	*Brachyotum radula*	2
12	Poaceae	*Calamagrostis recta*	2
13		*Chusquea scandens*	2
14		*Cortaderia bifida*	5

15	Solanaceae	*Nicotiana thyrsiflora*	1

Table 7. Native flora with their family name in the sampling site #1 in the Hualgayoc district, Cajamarca region, Peru.

N°	Family name	Scientific name	biological replicates
1	Asteraceae	*Achyrocline alata*	1
2	Calceolariaceae	*Calceolaria tetragona*	2
3	Ericaceae	*Gaultheria glomerata*	1
4		*Pernettya prostrata*	2
5		*Vaccinium floribundum*	1
6	Hypericaceae	*Hypericum laricifolium*	1
7	Melastomalaceae	*Brachyotum radula*	2
8		*Miconia vaccinioides*	1
9	Poaceae	*Cortaderia bifida*	5
10		*Festuca sp*	1
11	Polygonaceae	*Muehlenbeckia tamnifolia*	1

12	Scrophulariaceae	*Buddleja interrupta*	1

Table 8. Native flora with their family name in the sampling site #2 in the Hualgayoc district, Cajamarca region, Peru.

Fig. 4. Native flora from sampling sites: (a) *Puya sp*, (b) *Bejaria sp*, (c) *Chusquea scandens*, (d) *Cortaderia bifida*, (e) *Nicotiana thyrsiflora*, (f) *Hypericum laricifolium*, (g) *Brachyotum radula*, (h) *Pernettya prostrata*, (i) *Buddleja interrupta*, (j) *Gaultheria glomerata*, (l) *Calceolaria tetragona*, (m) *Miconia vaccinioides.*

Bech et al. (2017) reported that in the Carolina mining area (**Fig. 1**), some native plants growing up in soils affected by mining activity accumulated considerable amounts of metals in their tissues. Of these plants, *Achyrocline alata*, common specie with our study,

accumulated high concentrations of Zn and was considered as a promising species for phytoextraction of Zn. **Table 9** contains native species of botanical families that coincide with those at our study and that have been described to grow in soils (either acidic or alkaline) with presence of toxic metals derived from active and abandoned mines in Latin America; native species in this table, in addition, have demonstrated ability to transport potential hazardous elements from roots to shoots, and are therefore considered suitable candidates for the phytoremediation.

Family	Native Species	Information on Publications about metals	Soils pH values	Name of the mine	Country	Reference
Asteraceae	*Ageratina sp.*	Phytoextraction of Zn Hyperaccumulator of Pb	6.8 - 8 (basic)	Carolina mine - Hualgayoc	Peru	Bech et al., 2017, 2016
	Achyrocline alata	As, Cu, Pb and Zn Phytoextraction of Zn				
	Baccharis latifolia	As, Cu, Pb and Zn				
		As, Ba, Cu, Fe, Mn, Zn and Hyperaccumulator of Pb	7,4±0,5 (neutro)			Durán Cuevas, 2010; Oyuela Leguizamo et al., 2017
	Baccharis amdatensis	As, Cd, Cu, Pb and Zn	< 4 (acid)	Bartolomé mine	Ecuador	Bech et al., 2017

	Baccharis rhomboidalis	Cu, Pb and Zn	3.9 (acid)	Teniente mine	Chile	
	Baccharis dracunculifolia DC.	Cd, Cr, Pb, V, Ba	6.2 (basic)	Camaquã mine	Brasil	França Afonso et al., 2020
	Baccharis trimera Less DC					
Melastomataceae	*Miconia lutescens*	As, Cu and Zn	4.8 (acid)	Turmalina mine - Piura	Peru	Bech et al., 2017
Poaceae	*Cortaderia Hapalotricha*	Hyperaccumulator of Pb	6.8 - 8 (basic)	Carolina Mine - Hualgayoc	Peru	
	Cortaderia nitida	As, Cd, Cu, Pb and Zn	< 4 (acid)	Bartolomé mine	Ecuador	
Polygonaceae	*Muehlenbeckia hastulata*	Cu, Zn and Pb	5.4	No mine - Los	Chile	Córdova et al., 2011

			(acid)	Maitenes area in the Puchuncaví Valley		
Solanaceae	*Nicotiana*	Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Sb, Hg and Pb	acid	Wadley antimony mine district - San Luis, Potosí	Mexico	Levresse et al., 2012

Table 9. Native plant species studied in terms of Phytoremediation in Latin America.

Also noteworthy is the fact that some of the inventoried species in the studied sites are used in traditional Peruvian medicine, such as *Hypericum laricifolium* (Vidal Ccana-Ccapatinta and Lino von Poser, 2015). In addition, Andean berries or wild berry of *Vaccinium floribundum* (known locally as "mortiño") are consumed as fruits, in juice and jam (Vizuete et al., 2016). This research through the identification of specific flora at MEL sites in the Andes is a first step to the identification of native plant species for phytoremediation in heavily contaminated soils.

4. Conclusions

Soil samples collected around two mining environmental liabilities (MEL sites) from the Hualgayoc district in the Peruvian Andes showed extremely acid pH values (3.50 - 4.19 in site #1 and 2.74 - 4.02 in site #2). Most soils showed Andean properties and classified as Gleyic Cambisol. Soil mineralogy was dominated by illite, kaolinite, quartz, and jarosite, and carbonates were systematically absent. The concentrations of Pb, Zn, As, Cu, and Ag (up to 4683, 724.2, 3611, 511.6, and 33.4 mg kg^{-1}, respectively) exceeded the maximum allowable values for agricultural soils according to the Peruvian and Canadian regulations. The geo-accumulation (Igeo), Nemerow Pollution (NI), Improved Nemerow (INI), and Potential Ecological Risk (RI) indexes were used to assess soil pollution. According to the Igeo index, studied soils are unpolluted to extremely polluted (increasing indexes are Cd<Zn<Cu<As<Pb<Ag). The Nemerow Pollution Index (NI) indicates heavy contamination, and the Improved Nemerow Index (INI), heavy to extreme contaminations. The RI points to a very high ecological risk reflecting serious impact caused by MEL sites and potential affectation to the ecosystems and the local communities. On the other hand, this research contributes with an inventory of native flora - 22 plants of native flora belonging to 12 family species - that grow up around the studied MEL sites and that, therefore, have potential to be used for phytoremediation purposes.

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