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Potential use of *Erica andevalensis* and *Erica australis* in phytoremediation of sulphide mine environments: São Domingos, Portugal

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Abstract

The area around the São Domingos copper mine (Iberian Pyrite Belt) is subject of great environmental concern as acid mine water occurs several kilometres downstream of the mine. In addition thousands of tons of mine waste are present. *Erica australis* and *Erica andevalensis*, which are two spontaneous plant species of this area, have been studied with regard to their potential for phytostabilization.

Soils and plants from São Domingos and from a reference site (Moreanes) were analysed for soil characteristics, chemical element content in soils (total and AB-DTPA bioavailable fraction) and in plants. Superficial and seepage water as well as waste material leachates were also analysed. Seepage water showed high redox potential (mean 481 mV), high conductivity (mean 4337 $\mu S\ cm^{-1}$) and low pH values (mean 2.6), being classified as mining water. Leachate solutions possessed mainly high levels of Fe, Al and SO_4^{2-}. Soils in the mining area were highly contaminated in Pb, As and Sb. Locally also high values of Cu and Zn were encountered and the soil available fraction of the majority of the elements showed also quite high values.

E. andevalensis grows in soils with pH between 3 and 4, whereas *E. australis* was only found in soils with pH above 3.5. Both species grow spontaneously in soils, highly contaminated with Pb, As and Sb. These plants, even in the non contaminated soils, are Al-tolerant and Mn-accumulators. In contaminated soils these species are also As-tolerant.

Considering the tolerant behaviour in extreme environmental conditions, these *Erica* species may be of major importance for the recovery of the sulphide mining areas, with climate conditions compatible with its breeding and growing, by physical and chemical stabilization of contaminated soils and even waste materials.

Keywords: Phytostabilisation; acid mine drainage; sulphide mine waste; *Erica andevalensis*; *Erica australis*; Al and As tolerance; Portugal

1. Introduction

Mining activity was an important sector of the Portuguese economy during the 19th and the first half of the 20th centuries. The majority of the mining activity ceased due to the ore exhaustion, and the introduction of new and more profitable techniques elsewhere made the extraction unprofitable (Martins and Oliveira, 2000). Nowadays, only few mines are still active in Portugal.

São Domingos mine, south-east Portugal, is an abandoned copper mine situated in the Iberian Pyrite

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Belt. Exploitation has been known since the pre-roman times, and massive sulphides were exploited from 1868 until the exhaustion in 1966 (Custódio, 1996). Actually, the São Domingos area is subject of great environmental concern as acid mine drainage has acidified and contaminated sediments and soils along several kilometres of the water course (Quental et al., 2002).

The present condition of the São Domingos mining area suggests that phytoremediation should be considered one of the best solutions for recovering the soil characteristics and diminishing the risk for human health. The benefits of phytoremediation are quite obvious as it is non-expensive and non-disruptive to the landscape and to those living near the contaminated site (Rittmann, 2004; Adriano et al., 2004).

The phytostabilisation is a particular technology of the phytoremediation concept which could be the best strategy for the São Domingos mining area. The objective of phytostabilisation is not to remove metal contaminants from a site but rather to stabilise them and reduce the risk to human health and the environment. This is achieved using specific tolerant plants and can be improved by applying soil amendments in order to enhance the biogeochemical processes in soils that can contribute to immobilise trace elements (Adriano et al., 2004; Clemente et al., 2006). The presence of vegetation reduces water and wind erosion and may induce a soil hydraulic control, which can decrease the downward migration of contaminants into the groundwater. Furthermore, tolerant plants can help physical and chemical immobilisation of contaminants by root sorption or by inducing chemical retention in soil (Prasad and Freitas, 2003). Phytostabilisation has the advantage, over other phytoremediation techniques, to eliminate the need of treating harvested shoot residues as hazardous waste. Tolerant plant species used in phytostabilisation should not accumulate contaminants to parts of the plants (branches, leaves, fruits, seeds) that may be consumed by humans and animals (Prasad and Freitas, 2003).

In the São Domingos area several plant species have been recognized as tolerant to the mining environment (Veigas, 2005). Among these plants, two species of the genera *Erica* (*Ericacea* family) deserves special attention, *Erica australis* and *Erica andevalensis*. The latter species was described for the first time by Cabezudo and Rivera (1980). It grows on the banks of Tinto and Odiel rivers as well as on mining tailings in the same zone being its distribution limited, at the time, to the mining region of Andévalo (Spain). *E. andevalensis* was classified as an endangered species by the Andalusian (southern Spain) Regional Government, as its geographic distribution is limited to the pyrite mine environments (Aparício and García-Martin, 1996). In Portugal, this species was identified in the São Domingos mine for the first time by Capelo et al. (1998), where it grows exclusively on soils developed on the sediments along the bank of the São Domingos river that carries acid water from the abandoned mine (Quental et al., 2002). *E. australis*, the other species of *Ericaceae* family that grows at São Domingos, is endemic in the Iberian Peninsula and NW Africa. It is widely distributed in various climates and soil types, but it can also grow on soils with high concentrations of trace elements, such as As, Cu and Pb (Freitas et al., 2004).

The implantation of these plant species may be a valuable element for mining landscape restoration because of its compact growth as a shrub plant up to 1–2 m high, showing striking pink to crimson blossoms from June to December. In addition, *E. andevalensis* is the only angiosperm species adapted to extreme ecological conditions ($\mathrm{pH} < 2.5$, strong impoverishment in nutrients, high heavy metals content) (Soldevilla et al., 1992) and it has never been observed, at our knowledge, growing out of Iberian Pyrite Belt mining habitats. However, it is likely that *E. andevalensis* species may become extinct as soon as its habitat changes, which illustrates the importance of the habitat in species conservation (Aparício and García-Martin, 1996).

Despite the interesting characteristics of these species, there are limited published studies dealing with its potential use for recovering pyrite mining environments. Soldevilla et al. (1992) and Asensi et al. (1999) studied the metal content of both *Erica* species and also its metal-tolerant character, mainly for Cu. The relationship between soil characteristics and *E. andevalensis* growing on soils from the Spanish Pyrite Belt has been studied by Buján et al. (2006), which concluded for the high plasticity of this plant to colonize sulphur mining soils with different biogeochemical characteristics. Despite *E. australis* was widespread in those mining environments most authors, except Soldevilla et al. (1992), did not present any data for this species. Other studies carried out by Garcia et al. (2005) and Garcia (2006) on both *E. andevalensis* and *E. australis* were focused on the antioxidant mechanisms for stress induced by soil trace metals contamination.

E. andevalensis belong to the *Ericetum australi–andevalensis* plant community and, although it can grow as a monospecific population, it is frequently found in heathlands associated with other plants, such as *E. australis* and *Cistus ladanifer* in the Andévalo region (Spain) (Rivas-Martínez et al., 2001). In the São Domingos mining area, *E. andevalensis* has not been found growing side by side with *E. australis*, being however in some few places associated with *Cistus monspeliensis*, *C. ladanifer* and *Juncus conglomeratus*.

The aim of this study was to evaluate the potential of *E. andevalensis* and *E. australis* for phytostabilisation of mining areas with acid mining generation, as the low substrate pH (often <4) of these environments usually inhibit or affect the growth of a great number of other plant species. In this context, it was evaluated, apart from biological parameters, the soil characteristics that justify the different spatial distribution of both *Erica* species in the São Domingos mining area.

2. Site description

São Domingos copper mine, located in SE Portugal (Fig. 1), is one of a number of volcanogenic massive sulphide deposits within the Iberian Pyrite Belt (IPB), which extends from Spain along the south region of Portugal, in Baixo Alentejo Province. The IPB hosted in Late Devonian to Middle Carboniferous ages a huge quantity of volcanic-hosted massive sulphide mineralization (1700 Mt of sulphides, totalling 14.6 Mt Cu; 13.0 Mt Pb; 34.9 Mt Zn, 46,100 t Ag and 880 t Au), distributed for more than 80 known deposits. The most important deposits in the Portuguese IPB include some not exploited (Lagoa Salgada), some presently exploited (Neves Corvo) or to be exploited again (Aljustrel), and some in an abandoned state (São Domingos, Chança, Lousal and Caveira, Cercal, Gavião, Montinho, Salgadinho) (Leistel et al., 1998).

The large area covered by the São Domingos mine, with more than 25 Mt of ore extracted, is one of the most interesting abandoned mines in Portugal from the historical mining view point (Gaspar, 1998). The general geology of the mining area consists of the Volcano-Sedimentary Complex with acid and basic rocks from Tournaisian age (Webb, 1958). The area was described as being underlain by Palaeozoic sediments. In the northern mine area, Palaeozoic sediments consist of Gafo Formation with schists, silts, greywackes, acid and basic volcanism, and Represa Formation composed of schists, silts, greywackes and quartzwackes from the Upper Devonian age. In the south of the area occurs the Phylito–Quartzitic Formation of phyllites, silts, quartzites and quartzwackes and Barrranco do Homem Formation of phyllites, silts and greywackes of the same age (Oliveira and Silva, 1990). With the Hercynian compression the sedimentary assemblage was intensely folded and the more incompetent beds marked with a strong flow cleavage, dip at steep angles to the NNE.

Along the regional strike, sediments are intruded by dykes ranging from acid (porphyries) to basic (diabases) composing the Volcano-Sedimentary Complex of Lower Carboniferous age (Oliveira and Silva, 1990). To the south a large area covered by the Mértola Formation of Lower Carboniferous age consists of a turbiditic sequence of pelites and greywackes. The Volcano-Sedimentary Complex, orientated WNW–ESE, is represented by the alignment of the São Domingos and Pomarão anticline. In the flanks of this structure representative IPB rocks are exposed and marked by three volcanic acid episodes, separated by sedimentary episodes.

Associated with the mining works several facilities were developed, including a railway and harbour for ore transportation, two pyrite burning factories, water reservoirs, cementation tanks, network channels for acid water evaporation, and the mining village. These factories, one for copper concentration and another for sulphur extraction, were built in the beginning of the 20th century as a consequence of the lower Cu prices attained in the international market. Mine waste materials in the area were estimated as several hundred thousand tons. The open pit covers 6.2 ha and is 120 m deep; it is now partially filled with acid, brown to reddish coloured water (Custódio, 1996).

In the surrounding area of the open pit and downstream to Telheiro area (Fig. 1) were deposited different type of materials, such as metallurgical slags, sub-grade ore, pyrite ash, weathered host rock, and materials from gossan. The environmental problems associated with waste materials are still visible within an area around 30 km^2. In the area between Achada do Gamo and the Chança river confluence (Fig. 1) the slopes of the stream valley, where acid mine drainage flows, are bleached due to ancient acid leaching by mine waters (Quental et al., 2002).

The climate, according to the Thornthwaite classification, is semiarid mesothermic with no excess water and small thermal efficiency in the hot season, and it can be divided in two distinct periods, a wet period from November to March and a dry period from May to September. The annual average air temperature is 17.6 °C, and annual precipitation is 559 mm. Most of the area is covered by thin soils and natural rock outcrops are abundant.

3. Materials and methods

3.1. Waste dump materials leachates

Fourteen samples of waste dump materials were collected from the open pit to Achada do Gamo where the two pyrite burning factories were built (Fig. 1). After milling, 100 g of this material was shaken in 1 L of distilled water, for 24 h, filtered with a 0.45 μm filter and the solution leachate was analysed for several elements and for the anions Cl^-, SO_4^{2-}, S^{2-}, NO_2^-, NO_3 by AAS and Ion Chromatography respectively.

3.2. Superficial and seepage water

Conductivity, pH and Eh were measured *in situ* in superficial water (24 samples; Fig. 1), including open pit water and seepage water (12 samples; Fig. 1), using a field pH meter, a conductivity meter and a potentiometer. Seepage water that flows in the main river system draining the mining area, results from the underflow of the

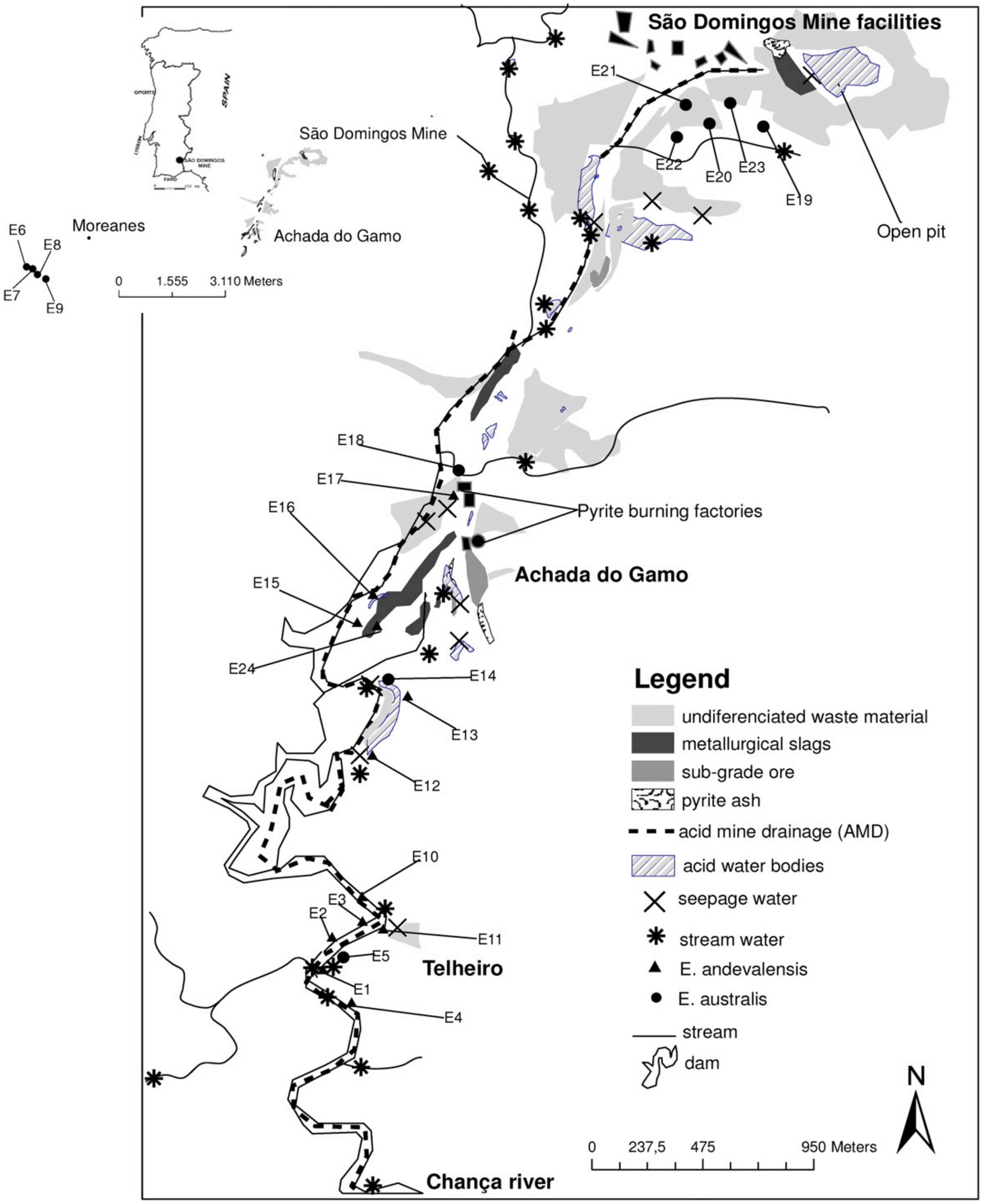

Fig. 1. Map of the São Domingos mining area with location of sample sites (soil, plant and water).

infiltrated water in the waste materials, between consolidated bedrock and unconsolidated weathered material.

3.3. Soils and plants

Soil samples, developed on waste materials, weathered rocks mixed with waste materials with different composition and river bank sediments, were collected in the São Domingos mining area (20 samples; Fig. 1) and are representative, in the area, of the different soil environments where *Erica* plants grow. Aerial parts (stems, branches and flowers) of *E. andevalensis* and *E. australis* plants were also sampled in the same places; the roots were not included in the samples. Near the contaminated area, a non-contaminated site (Moreanes, Fig. 1) where *E. australis* grows was sampled for soils and plant composition reference (four samples).

Soils developed on coluvio-alluvial materials (river bank areas) were collected along São Domingos water stream (12 samples; Fig. 1) and *E. andevalensis* was sampled in the same areas as it corresponds to the spatial distribution of the plant. Soils from Moreanes were developed on schists and greywackes. Soils, where *E. australis* grows at São Domingos, were mainly developed on different waste materials (mostly of gossanous nature, but also slags and pyrite ash) and some on mixtures of weathered rocks, with a Moreanes similar lithology, and waste materials (eight samples; Fig. 1).

Soil samples were collected (0–15 cm depth) in a restricted circle about 60 cm around the *Erica* plants and consisted of a homogeneous sample (around 4 kg) of four subsample points. After sampling, the soils were dried at room temperature, mixed, homogenized and sieved through a 2 mm screen.

Soil samples (fraction <2 mm) were characterised as follows: pH in a water suspension (1:2.5 soil/water), organic carbon by Walkley-Black method (1934), and iron oxides (Mehra and Jackson, 1960). The same soil fraction (<2 mm) of each sample was analysed for total chemical content by ICP and INAA after four acid (HF 50%, $HClO_4$ 60%, HNO_3 70% and HCl 37%) digestion in Activation Laboratories Ltd. (Canada). Soil bioavailable fraction of the chemical elements was extracted with AB-DTPA (Hanlon et al., 1999) and analysed by AAS and ICP.

For plant samples, representative quantities of the aerial part of the plant (stems, branches and flowers) were collected in the same soil sampling places and, as soon as possible (within one or two days), were washed in abundant freshwater and rinsed with deionised water, dried at 30 °C, homogenized and finely ground. Plants were analysed for total chemical content by ICP/MS also in Activation Laboratories, after ashing (480 °C) and acid digestion.

3.4. Data analysis

Data analysis was carried out by univariate statistic using central tendency measures of the Gauss curve, such as mean and geometric mean, in the case of waste materials, median and dispersion measures, such as standard deviation and extreme measures (minimum and maximum values). Bivariate analyses were also performed using the relation between soil pH, AB-DTPA extractable fraction of As, Cu, Mn, Pb, Sb and Zn, and the same elements in plants. Absorption coefficients (soil-plant coefficient transfer and bioconcentration coefficient; adapted after Nagaraju and Karimulla, 2002; Anawar et al., 2006) were estimated from the soil-plant relationship. The soil-plant coefficient transfer (TC) evaluates the transference of an element from soil to plant and represents the capacity of a species to accumulate the element ($TC = [\text{plant element}]/[\text{total soil element}]$). Most plants have a $TC < 1$ for trace elements (heavy metals and metalloids). However, there are some few plant species that can be considered accumulators when $TC > 1$. This coefficient can also be an indirect indicator of the soil bioavailable fraction of the element. The bioconcentration coefficient (BC) reflects the plant capacity to absorb the element from the soil when it occurs in an available form (water soluble or water soluble plus exchangeable) determined after soil chemical extraction using an appropriated solution ($BC = [\text{plant element}]/[\text{element bioavailable soil fraction, extracted by AB-DTPA}]$). Therefore, when trace elements are considered, and in lack of phytotoxicity signs, BC represents the level of plant tolerance for a potential toxic element, the plant being tolerant when $BC > 1$.

4. Results and discussion

4.1. Waste dump leachates, seepage and superficial water

Table 1 shows the results of Al, Fe, Pb, Cu, As, Zn and SO_4^{2-} concentrations in the waste leachates. All leachate solutions presented very high concentrations of Fe (median 3.4 g L^{-1}), sulphur (median 7 g L^{-1}) and Al (median 0.97 g L^{-1}) and relatively low concentrations of all other determined elements. However, water leachates from gossanous materials and metallurgic slags showed high Pb and high Zn and Cu concentrations, respectively. The high Pb found in gossanous material is considered a relative Pb increase as the result of ore weathering processes, while other elements are easily remobilised from the ore materials. The Zn concentration in the metallurgical slags is expected as the element exists in the mineralization but was not recovered in the treatment process. The Cu concentration can also be justified by the inefficient metallurgical treatment of Cu extraction process.

Seepage water that flows into the São Domingos stream, in Achada do Gamo and São Domingos sites (Fig. 1) showed the lowest values of pH (mean 2.6), and the highest values of Eh and conductivity, respectively, (mean 481 mV) and (mean 4337 µS cm^{-1}). The main stream, beginning at São Domingos mine buildings and extending to the Chança river confluence (Fig. 1), constitutes the acid mine drainage (AMD) as indicated by low pH and high Eh (Fig. 2) and conductivity, ranging from 162 µS cm^{-1} to 19 999 µS cm^{-1} (median value 580 µS cm^{-1}). This acidic water shows a dark red colour due to high concentrations of Fe. The low pH–high Eh range lies in the mine water stability field for the oxidised water (mining water) according to Garrels and Christ (1965) pH–Eh diagram and represents the seepage and São Domingos stream water (Fig. 2).

By contrast, the superficial water outside the direct influence of the mining area presented low Eh and conductivity values and high pH. The stability of these water samples shown in the pH–Eh diagram (Fig. 2) is within the transition zone.

4.2. Soils and plants

Soil characteristics (pH, organic carbon and iron oxides) are presented in Table 2. Comparing both contaminated and non-contaminated (Moreanes reference site) soils, the organic carbon content was similar, being low to very low, in agreement with the climatic conditions of the region. In the contaminated soils, iron oxides presented the highest values, and the pH ranged between 3 and 4.5, while in the reference soils pH was above 4.6. The enrichment of São Domingos soils on iron oxides is related to acid weathering of solid phases and to mining water characteristics (Fig. 2).

Table 1
Statistics of concentrations of Al, Fe, Pb, Zn, Cu, As and SO_4^{2-} measured in leachates of 14 samples of mining waste (g L^{-1})

Statistics	Al	Fe	Pb	Zn	Cu	SO_4^{2-}	As
Mean	1.48	4.21	0.0300	2448.07	0.100	7.70	0.0062
Median	0.97	3.45	0.0070	50.00	0.016	7.10	0.0009
Geom. Mean	0.80	3.99	0.0095	173.45	0.022	7.50	0.0019
Minimum	0.05	2.95	0.0012	20.00	0.002	5.60	0.0003
Maximum	3.94	7.02	0.1400	15052.00	1.100	11.60	0.0298

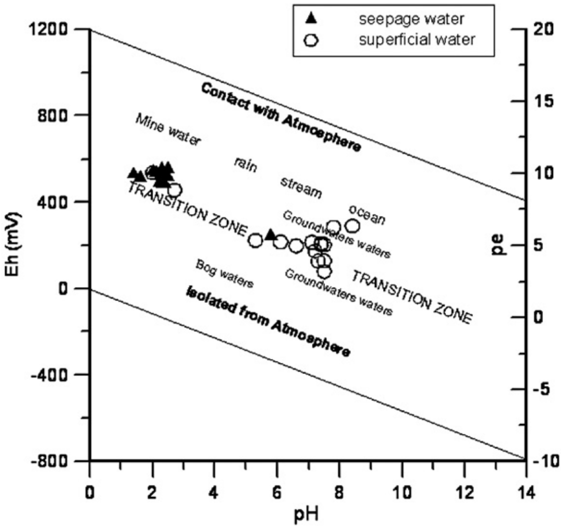

Fig. 2. Representation, in the diagram of stability limits for natural waters at the Earth surface, of the São Domingos waters (seepage and superficial), in terms of Eh and pH at 25 °C, after Garrels and Christ (1965).

The organic carbon and the iron oxides concentrations were also similar for both contaminated soils (Table 2), but *E. australis* soils presented the minimum values of iron oxides lower than those of *E. andevalensis*. This is a consequence of the Fe concentration in the AMD, which enriched soils where *E. andevalensis* grows. The pH values were considerably lower in the *E. andevalensis* soils due to its location near the AMD. In the São Domingos area, *E. australis* was not found in soils with pH values below 3.5, while *E. andevalensis* grows in soils with pH between 3 and 4 (Table 2). A study *in vitro* carried out by Garcia et al. (2005) showed that *E. andevalensis* does not need acid soils to survive, but its prevalence in such hostile environments should be due to mechanisms which allow a competitive advantage in extreme conditions. This mechanism seems to be related to the synthesis or activation of enzymes with peroxidase activity (Garcia, 2006).

Buján et al. (2006) found *E. andevalensis* plants growing in soils (Andalusia, Spanish IPB) with pH values between 3.3 and 6.2, which do not agree with the results obtained for São Domingos soils (Table 2). The pH differences observed between the two sites (Spain and Portugal) may be related to biological characteristics of *E. andevalensis* growing in the different mining areas. At São Domingos *E. andevalensis* may correspond to a different plant phenotype not adapted to soil pH values higher than 4, and probably related to recent colonization of mining sulphide sites in Portugal. In

Table 2
Descriptive statistics of soil chemical properties (pH, Fe oxides — Fe ox and organic carbon — OC) and elements concentrations of AB-DTPA extractable fraction of soil samples collected in three areas with *Erica* growth

Statistics	pH	Fe ox	OC	AB-DTPA extractable fraction							
				Fe	Mn	Al	Cu	Zn	Pb	As	Sb
E. australis — non contaminated soil (n=4)											
Mean	4.8	10.04	32.91	305.8	55.42	45.83	<dl	5.00	12.57	<dl	0.36
Min.	4.6	6.82	12.71	106.7	14.67	6.67	<dl	1.00	1.60	<dl	0.14
Max.	5.0	12.00	55.73	480.0	122.67	86.67	<dl	8.67	30.00	<dl	0.84
Median	4.8	10.67	31.60	318.3	42.17	45.00	<dl	5.17	9.33	<dl	0.23
Stand. Dev.	0.2	2.38	18.88	184.0	48.81	32.93	<dl	4.06	13.57	<dl	0.33
E.australis — contaminated soil (n=8)											
Mean	4.0	29.25	27.13	211.3	35.79	55.83	34.04	6.33	79.6	5.08	0.59
Min.	3.5	4.78	3.41	66.7	1.67	10.00	1.33	1.33	1.67	0.67	0.28
Max.	4.5	56.95	137.40	600.0	144.33	126.67	102.00	13.33	223.3	20.00	0.91
Median	4.0	28.56	8.30	156.7	3.50	35.00	22.83	5.83	28.17	1.33	0.58
Stand. Dev.	0.3	18.09	45.35	175.3	53.31	49.11	34.60	4.05	95.72	7.21	0.23
E.andevalensis — contaminated soil (n=12)											
Mean	3.5	34.39	11.08	460.3	30.47	30.00	39.03	29.17	236.7	32.31	0.97
Min.	3.0	18.49	2.95	110.0	2. 67	3.33	2.67	2.00	3.00	1.00	0.28
Max.	4.1	58.49	32.14	790.0	109.00	80.00	137.67	83.33	1163.3	165.7	2.92
Median	3.5	30.89	9.08	483.3	17.50	20.00	20.00	16.00	41.67	5.83	0.79
Stand. Dev.	0.3	13.39	8.58	242.8	35.47	25.23	38.88	27.83	408.6	58.48	0.70

dl: detection limit.
(Fe ox and OC in g kg^{-1}, AB-DTPA extractable fraction in mg kg^{-1}, Hg <dl for all soil samples).

fact, *E. andevalensis* was identified more recently in Portugal than in Spain and, at our knowledge, in the Portuguese IPB *E. andevalensis* grows exclusively in the São Domingos mining area (river bank of AMD).

The total concentration of trace elements in the soil samples (Table 3) is high and within the same range as that given for contaminated soils from the Spanish Pyrite Belt studied by Buján et al. (2006) but higher than those referred by Garcia (2006), both for *E. andevalensis* soils. The AB-DTAP extractable fraction (Table 2) of all trace elements was higher in the contaminated than in the non-contaminated soils,

Table 3
Descriptive statistics of total elements concentrations in the soils collected in three areas with *Erica* growth (mg kg^{-1} except Al, Fe and S in g kg^{-1})

Statistics	As	Al	Cu	Fe	Mn	Pb	S	Sb	Zn	Hg
E.australis — non contaminated soil (n=4)										
Mean	15.03	40.36	21.49	24.63	280.6	23.71	0.20	3.30	26.41	<dl
Min.	12.60	31.52	15.14	19.80	64.8	18.41	0.12	1.50	19.50	<dl
Max.	18.90	48.15	31.47	29.00	853.7	26.76	0.23	8.20	38.62	<dl
Median	14.30	40.89	19.66	24.85	102.0	24.83	0.20	1.75	23.75	<dl
Stand. Dev.	2.74	7.45	6.99	3.90	383.5	3.81	0.08	3.27	8.44	–
E. australis — contaminated soil (n=8)										
Mean	2123.8	44.88	266.8	91.49	120.7	5108.7	7.60	437.9	99.40	5.3
Min.	175.0	22.65	25.2	18.30	18.65	255.6	2.67	19.2	36.41	<dl
Max.	11600.0	68.70	988.8	313.0	255.0	24930.0	20.99	2150.0	215.56	17.0
Median	759.5	45.41	193.3	62.75	109.3	2429.7	6.96	199.0	85.35	3.0
Stand. Dev.	3864.9	16.36	312.1	95.00	82.13	8240.9	5.85	707.4	63.71	6.0
E.andevalensis — contaminated soil (n=12)										
Mean	1590.1	58.55	228.5	79.91	262.7	2318.0	10.59	237.0	245.9	6.5
Min.	332.0	41.20	28.0	40.10	47.9	217.8	2.12	67.6	37.2	<dl
Max.	3640.0	74.28	646.4	207.00	655.2	7168.7	25.31	550.0	1368.7	32.0
Median	1580.0	57.54	214.7	71.45	186.6	1505.6	10.12	179.0	109.4	5.0
Stand. Dev.	1001.4	13.34	166.9	43.33	173.4	2128.7	6.85	160.6	371.0	8.6
MAV	12**	–	50*	–	–	50*	–	20**	150*	1*

MAV: maximum allowed values for soils with pH ≤5 (*) according to the Portuguese legislation (Portaria 176/96) or CCME (1997) (**).

Table 4
Descriptive statistics of trace elements concentrations (mg kg^{-1}, except for Hg in μg kg^{-1}) in the aerial tissues of the plants (dry weight) collected in the same areas of the soils

Statistics	Al	Mn	Cu	Fe	Zn	As	Sb	Pb	Hg
E.australis — non contaminated soil (n=4)									
Mean	331.3	304.0	4.36	234.6	12.28	0.77	0.022	0.92	0.49
Min.	294.8	203.6	3.48	210.6	10.15	0.57	0.010	0.62	0.36
Max.	382.3	460.3	5.12	260.2	13.63	0.99	0.040	1.15	0.59
Median	324.1	276.1	4.43	233.7	12.68	0.76	0.018	0.96	0.50
Stand. Dev.	37.07	111.8	0.76	21.11	1.54	0.17	0.014	0.22	0.10
E. australis — contaminated soil (n=8)									
Mean	346.3	264.8	6.66	381.1	26.01	4.94	0.077	13.58	4.37
Min.	181.7	82.40	3.01	206.9	9.93	1.58	0.028	2.40	1.27
Max.	494.2	455.8	12.77	679.8	64.41	12.47	0.177	59.13	14.20
Median	314.8	259.6	5,70	380.7	18.41	3,56	0.061	8.04	2.90
Stand. Dev.	115.5	133.2	3.59	150.0	17.41	4.11	0.051	18.89	4.17
E. andevalensis — contaminated soil (n=12)									
Mean	535.8	597.1	10.42	1281.6	23.97	13.13	0.279	35.13	13.15
Min.	182.2	256.6	4.05	268.5	11.23	3.01	0.053	3.05	2.81
Max.	2314.2	1129.7	38.30	5639.2	43.45	42.99	1.027	262.81	44.39
Median	425.4	591.3	8.11	708.3	23.28	7.75	0.18	10.88	7.00
Stand. Dev.	573.5	271.1	9.25	1538.3	9.75	11.89	0.276	72.62	12.16
Mature leaves tissues for plants in general[a]									
Normal	50–200[b]	30–300	5–30	–	27–150	1–1.7	7–50	5–10	–
Toxic	–	400–1000	20–100	–	100–400	5–20	150	30–300	0.001–0.003

[a] Kabata Pendias and Pendias (2001).

[b] Srivastava and Gupta (1996).

mainly for As, Pb and Cu, which may be due to low soil pH, AMD or soil mineralogy.

Mercury, in contaminated soils, presented concentration values from 32 mg kg^{-1} to values lower than the detection limit (1 mg kg^{-1}), being the majority above 3 mg kg^{-1} (Table 2). These concentrations exceeded the maximum allowed value for soils according to the Portuguese legislation (1.0 mg kg^{-1}, Portaria 176/96); however, the available fraction for this element was below the detection limit. In both *Erica* species, the Hg concentration was also very low (<0.04 mg kg^{-1} dry weight; Table 4).

Comparing the contaminated soils where *E. andevalensis* or *E. australis* grow, Al, S, Mn and Zn total concentrations are greater for *E. andevalensis* soils, while Cu, Hg, Pb, Sb and As were within the same magnitude in both soils (Table 3). However, the available fraction of Zn, Pb, As and Sb reached highest levels in the *E. andevalensis* soils (Table 2).

The chemical analysis of the aerial parts of both *Erica* species growing at São Domingos and Moreanes are presented in Table 4. Concentrations of elements in the *E. australis* aerial tissues were below the toxicity levels referred by Kabata Pendias and Pendias (2001) for most studied elements. However, some plant samples presented Mn, Pb and As within the excessive or toxic limits (Table 4). Concentrations of most trace elements in the *E. andevalensis* species were also below the toxicity levels, except for As, Mn (75% of the samples) and Pb (three samples) which were above the toxic limit for plants. Also, Al concentration (for 92% of both *Erica* samples) was higher than the maximum value considered normal for plants in general (200 mg kg^{-1}; Srivastava and Gupta, 1996).

Erica species growing in the São Domingos mining site showed similar Cu, Al and Zn concentrations, but Fe, As, Sb, Pb and Hg were higher in *E. andevalensis* (Table 4), which may be due to its soils location near the AMD. The Mn content in *E. andevalensis* was higher than in *E. australis* in contaminated soils, presenting *E. australis* similar amounts of Mn when growing either in contaminated or non-contaminated soils (Table 4; Fig. 3). Both species are Mn accumulators as demonstrated by the soil-plant transfer coefficient (TC) > 1, for most of the samples (only three plant samples showed TC between 0.43 and 0.59) (Table 5). This capacity for Mn accumulation was also reported for *E. andevalensis* by Soldevilla et al. (1992) and Buján et al. (2006). As expected, the lowest values of most trace elements were found in *E. australis* growing in the non-contaminated site (Table 4).

Both *Erica* species, even in the non-contaminated soils, were able to transport relatively high amounts of Al when compared with most other plants (Table 4), indicating a plant tolerance to this element, which according to Kabata Pendias and Pendias (2001) is not necessarily associated with Al retention in roots. In fact, the bioconcentraction factor (BC) for Al ranged from 2.38 to 277.65, whereas the calculated Al soil–plant transfer coefficient (CT) was <0.03 (Table 5). The bioconcentraction coefficient reflects more accurately the capacity of the element to be assimilated by plant than the soil–plant transfer coefficient, as only a fraction of the element total soil content is readily available to be uptake. Therefore, to assess plant tolerance to trace elements the soil available fraction rather than soil total trace elements concentration must be considered. Consequently, based on the calculated BC, both *Erica* species can be considered as Al tolerant plants. The Al tolerance can be a valuable characteristic of these plants as potential colonizing species for high acidic soils, as sulphide mining soils, where Al in cationic forms is readily available associated with trace elements and low nutrients content. Although for a great number of plant species these conditions induce Al toxicity markedly depressing plant growth, this behaviour was not observed in the studied *Erica* species.

Concerning As, a severe contaminant in São Domingos mining area, the high levels in the aerial parts of the plants (Table 4) may indicate, as for Al, tolerance for this element (65% of the samples with BC ranging from 2.26 to 43; Table 5). In most plants, As is passively absorbed staying in the roots (Srivastava and Gupta, 1996). This effect was confirmed by Buján et al. (2006) for *E. andevalensis*. However, in this study, plant roots were not analysed, but the aerial part of the plants contained between 3 and 43 mg As kg^{-1} (Table 4), which are above the normal range for plants (1–1.7 mg kg^{-1}), according to Kabata Pendias and Pendias (2001). Although *E. andevalensis* presented higher concentrations of As than *E. australis*, the relationship between As extractable by AB-DTPA (soil bioavailable fraction) and As concentration in the plant follows a similar pattern, that is, the bioavailable fraction concentration increase corresponds to a plant concentration increase (Fig. 3).

Despite the generally high total and available Pb concentrations in soils (Tables 2 and 3), this element was not highly transported to the aerial parts of the plants (BC<1 in 70% of the plants in contaminated soils and TC ranging between 0.002 and 0.224; Table 5), which may suggest that Pb is retained in the roots. These results seem to be consistent with those obtained in Spain for *E. andevalensis*: 437 mg Pb kg^{-1} in roots (Buján et al., 2006) and 2.8–21 mg Pb kg^{-1} in shoots (Garcia, 2006). Although the Pb amounts was higher than 10 mg kg^{-1} (maximum normal value for most other plants, Table 4) in some *Erica* plants on the contaminated soils (six samples of *E. andevalensis* and two samples of *E. australis*, in the range of 13–263 mg kg^{-1}), the transport to shoots seems to be independent of Pb available fraction in the soils (Fig. 3).

Despite Cu was the main exploited element in São Domingos, the mean concentration of this element in soils where *E. andevalensis* and *E. australis* grow (mean of total and available fraction, 229–267 and 39–34 mg kg^{-1}; respectively; Tables 2 and 3) was lower than those reported by Asensi et al. (1999) (mean of soil total Cu — 942 mg kg^{-1}), similar to those found by Soldevilla et al. (1992) (mean of total and available fraction, respectively 205 and 36 mg kg^{-1}) and higher than those presented by Garcia (2006) (mean of soil total Cu — 66 mg kg^{-1}) concerning soils from the Spanish Pyrite Belt where copper was also exploited. These differences are related to the irregular Cu recovery by the metallurgical processes in different mines of the IPB.

Copper concentrations observed for *E. andevalensis* plants at São Domingos are of the same order of magnitude of the results reported in literature. The estimated bioaccumulation coefficient lies between 0.072 and 0.861 for 11 samples (Table 5), which is in disagreement with Asensi et al. (1999) conclusion. The studies carried out by Asensi et al. (1999) on *E. andevalensis*, growing in a pot experience using a mixture of commercial potting substrate and Cu ore, concluded by its high Cu-tolerance, despite similar copper concentrations found in the plant. However, the relationship between Cu available fraction in the São Domingos soils and *E. andevalensis* Cu concentrations (Fig. 3) follows the same pattern of that obtained by Asensi et al. (1999). Increasing levels of soil bioavailable Cu did not correspond to high Cu concentration in the plant. A similar behaviour was also observed for *E. australis* (Fig. 3). The TC <1 (Table 5) for both *Erica* species shows that are not Cu-accumulators, which is in opposition with Soldevilla et al. (1992) conclusions.

Iron concentration was relatively high in *E. andevalensis* (269–5639 mg kg^{-1}) (Table 4) when compared with the amounts (185 and 409–744 mg kg^{-1}) reported by Soldevilla et al. (1992) and Garcia (2006), respectively, reflecting the soil Fe available fraction enrichment (Table 2) by the AMD, although no visual morphological symptoms of Fe toxicity disorders were observed. The BC factors estimated for both *Erica* species (Table 5) may suggest a Fe-tolerance.

Zinc concentration in *Erica* plants was, in general, below the normal range for most plants (Table 4) and even, in some samples, within the deficiency range (10–

20 mg kg^{-1}; Kabata Pendias and Pendias, 2001), despite the concentrations of bioavailable Zn fraction (percentage from total soil concentration ranging between 1.1 and 63.1, median=9.3%). The low Zn concentration in *Erica* plant tissues could not imply deficiency as no visual morphological symptoms of Zn deficiency were

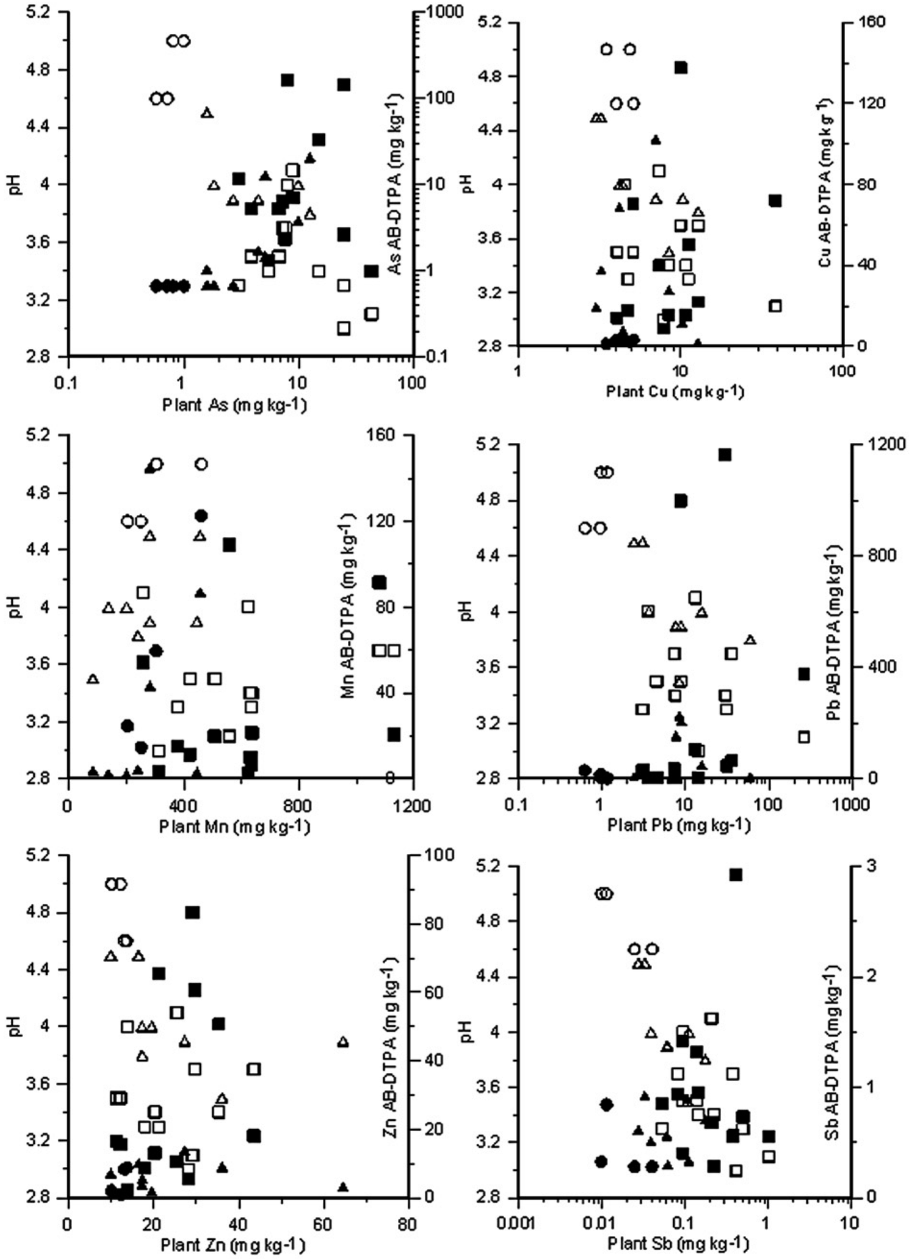

Fig. 3. Scatter plot diagrams representing the relation between As, Cu, Mn, Pb, Zn and Sb concentrations in *Erica australis* and *Erica andevalensis* (mg kg^{-1}) and pH and AB-DTPA extractable fraction in soils (mg kg^{-1}) where these plants grow.

Table 5
Soil-plant transfer coefficients — TC ([plant]/[total soil]) and bioconcentration coefficients — BC ([plant]/[bioavailable soil fraction, extracted by AB-DTPA]) for *E. australis* growing in non-contaminated soils (NCEa), *E. australis* growing in contaminated soils (Ea) and *E. andevalensis* growing in contaminated soils (Eand), of Al, As, Cu, Mn, Fe, Pb, Sb and Zn

Sample	Al		As		Cu		Mn		Fe		Pb		Sb		Zn	
	TC	BC	TC	BC	TC	BC	TC	BC	TC	BC	TC	BC	TC	BC	TC	BC
NCEa6	0.007	6.61	0.039	–	0.338	–	3.14	8.25	0.010	0.533	0.036	0.114	0.005	–	0.583	1.58
NCEa7	0.007	47.63	0.043	–	0.110	–	0.54	3.75	0.007	1.99	0.043	0.576	0.006	–	0.263	5.07
NCEa8	0.009	3.40	0.052	–	0.203	–	3.76	17.02	0.011	0.48	0.027	0.072	0.016	–	0.547	1.57
NCaE9	0.010	9.56	0.079	–	0.248	–	2.20	5.07	0.011	1.35	0.053	0.972	0.007	–	0.625	12.20
Ea5	0.003	6.06	0.009	0.624	0.507	9.58	5.10	65.24	0.009	1.95	0.224	25.34	0.002	0.254	0.415	3.46
Ea14	0.004	6.33	0.003	0.414	0.029	0.313	0.43	24.72	0.008	1.13	0.002	0.038	<0.001	0.121	0.276	4.16
Ea18	0.008	3.81	0.008	8.00	0.094	0.935	1.74	190.54	0.005	3.97	0.009	0.044	0.001	0.218	0.855	24.15
Ea19	0.020	5.70	0.001	2.69	0.015	0.599	3.11	119.47	0.001	2.41	0.001	0.353	<0.001	0.343	0.433	14.63
Ea20	0.007	24.24	0.003	1.58	0.012	0.087	2.67	5.28	0.005	2.42	0.003	0.246	<0.001	0.036	0.076	1.70
Ea21	0.013	55.59	0.004	2.66	0.007	0.069	1.96	6.59	0.004	1.37	0.002	0.051	<0.001	0.110	0.286	2.04
Ea22	0.006	27.80	0.009	4.74	0.032	0.161	3.71	1.94	0.006	1.55	0.009	0.801	0.001	0.046	0.064	1.49
Ea23	0.014	2.42	0.005	5.44	0.081	0.061	7.30	68.06	0.015	4.06	0.001	2.15	<0.001	0.079	0.472	5.16
Eand1	0.010	50.94	0.009	0.169	0.031	0.861	1.61	94.12	0.013	1.02	0.004	8.58	<0.001	0.142	0.060	5.29
Eand2	0.006	10.87	0.004	0.048	0.161	1.69	13.02	234.01	0.008	0.948	0.016	1.19	<0.001	0.067	0.372	6.92
Eand3	0.004	2.38	0.002	0.258	0.023	0.263	3.54	100.05	0.003	0.624	0.002	0.094	<0.001	0.063	0.178	2.08
Eand4	0.010	47.27	0.008	0.452	0.063	0.541	0.964	63.18	0.026	3.54	0.009	1.26	<0.001	0.150	0.189	1.56
Eand10	0.006	8.65	0.027	1.27	0.062	0.184	0.587	4.72	0.017	1.30	0.019	0.122	<0.001	0.306	0.222	2.38
Eand11	0.004	2.74	0.002	1.26	0.061	0.282	4.45	37.04	0.005	0.879	0.011	2.68	<0.001	0.231	0.129	0.688
Eand12	0.009	20.34	0.012	9.20	0.050	0.222	2.21	25.06	0.025	3.07	0.011	0.667	<0.001	0.677	0.189	0.323
Eand13	0.003	24.47	0.003	0.720	0.022	0.072	2.92	25.32	0.004	0.582	0.002	0.009	<0.001	0.104	0.118	0.775
Eand15	0.009	248.22	0.004	4.08	0.017	0.686	2.54	29.31	0.003	6.48	0.004	0.026	<0.001	1.60	0.026	0.696
Eand16	0.006	25.57	0.013	1.14	0.036	0.072	6.16	11.83	0.015	1.15	0.012	0.198	<0.001	0.088	0.307	0.486
Eand17	0.031	277.65	0.050	43.00	0.093	0.530	1.64	5.13	0.072	45.72	0.061	0.698	<0.001	1.84	0.128	0.350
Eand24	0.008	24.72	0.016	3.25	0.087	0.584	2.60	54.66	0.013	6.04	0.031	0.545	<0.001	0.666	0.349	2.41

observed, which may suggest that *Erica* species show low Zn requirement when compared with most plants. Moreover, the deficiency content of Zn in plants may vary considerably, being related to each genotype and the interaction of Zn with other elements within the plant tissues (Kabata Pendias and Pendias, 2001). The uptake of this micronutrient, considering the soil available fraction concentrations (AB-DTPA extracted), seems to be efficient, as BC >1 for most of the *Erica* plants (ranging between 0.35 and 24.2; median of 3.81 for *E. australis* and 1.16 for *E. andevalensis*; Table 5). In addition, the transport of Zn to shoots is independent of Zn available fraction in the soils (Fig. 3).

In the contaminated soils of São Domingos Sb attained high concentrations (Table 3), exceeding 20 mg kg^{-1}, the maximum allowable value for soils (CCME, 1997). However, the bioavailable Sb soil fraction concentrations lie between 0.28 and 0.97 mg kg^{-1} (one *E. andevalensis* soil sample exception with 2.92 mg kg^{-1}), which directly influence the low Sb plant content (Table 4 and Fig. 3).

The relation between soil pH, AB-DTPA extractable fraction of As, Cu, Mn, Pb, Sb and Zn, and the same elements in plants (Fig. 3) established a clear difference between contaminated and non-contaminated soils and the respective plants collected in the same sites. At São Domingos, the two *Erica* species were never found cohabiting in the same areas, a peculiar characteristic of this zone in opposition to the soils of the Spanish IPB (Garcia et al., 2005; Buján et al., 2006). In the São Domingos contaminated soils the relation between the elements concentrations in plants and soil bioavailable fraction is not a unifying criterion to evaluate the difference observed between *E. andevalensis* and *E. australis* field implantation, as illustrated by Sb, As, Pb and Cu irregular distribution (Fig. 3). Soil pH is then the characteristic which divides the growth areas of both *Erica* species, as *E. australis* was found in soils with pH ranging between 3.5 and 4.5 while *E. andevalensis* grows in soils with pH between 3 and 4 (Fig. 3).

Considering the size of São Domingos area (30 km^2) affected by the old mining processes, the use of high cost remediation technologies is not realistic. Therefore, the phytostabilisation technique, by using specific tolerant plants with or without the application of soil amendments, could be a promising strategy for this abandoned mining area. The objective of phytostabilisation, a non-expensive and non-disruptive technique to the landscape, is not to remove contaminant elements from a site but rather to stabilise them and reduce the risk to human health and the environment (Wong, 2003; Rittmann, 2004; Adriano et al., 2004; Clemente et al., 2006), hence the importance of appropriate vegetation. The acidic soils of São Domingos ($\text{pH} \leq 4.5$), highly contaminated by trace elements, began to be colonized by some plants species that seem to be adapted to such extreme environmental conditions. This is the case of *E. andevalensis* and *E. australis* plants according to the results discussed above. As both species are Mn-accumulators and tolerants to low pH and high Al, Pb and As concentrations, chemical stabilisation of soils and waste materials of mining sulphide areas can be achieved. *Erica* species can also contribute to increase weathering and pedogenic processes of the waste materials and river bank sediments improving its physical and chemical characteristics by organic matter addition as a result of plant development. This will increase the substratum fertility making possible its colonisation by other plant species more nutrient exigent.

In addition, *E. andevalensis* by growing in the river banks may partially decrease the negative impact of current velocity and high water discharge in spring and winter periods, decreasing river bank erosion. *E. australis*, which colonise mainly waste dump materials of gossanous nature, may contribute to mitigate wind and water erosion of these hazardous materials. Moreover, *E. andevalensis*, an endemic plant restricted to the Iberian Pyrite Belt, is classified as endangered species growing in extreme ecological conditions as the sulphide mining environments, so its habitat preservation is essential in conservation of this species. These two ornamental species can then attenuate the visual impact of degraded mining areas promoting and preserving the mining patrimony.

5. Conclusions

The different types of waste materials deposited in the São Domingos mining area has high acid generating potential, as it can release enormous quantities of Al, Fe, SO_4^{2-} and in some extend Pb and Cu, which contaminate the river bank soils and stream system. Also, seepage water showed high redox potential, high conductivity and low pH values, being classified as oxidised water (mining water).

Soils in the mining area, especially those located in the vicinity of waste materials and acid mine drainage, are highly contaminated in trace elements, mainly Pb, As, Sb, and to some extent Cu and Zn. Soil bioavailable fraction (AB-DTPA extracted) for most of the elements showed relatively high values when compared with the soil total concentration.

E. andevalensis and *E. australis* do not cohabit in the same area at São Domingos; on the contrary, their habitats are clearly distinct in this zone. Unlike the Andévalo region, at São Domingos *E. andevalensis* was not found outside the river bank areas periodically flooded. The most interesting feature of *E. andevalensis* is the ability to grow in very hostile conditions for life, such as soils with pH values between 3 and 4 and high contents of toxic elements such as Al, Pb, Fe, As and Sb. Also, *E. australis* grows in highly contaminated soils but, in this study, was not found in soils with pH values below 3.5.

Most of trace elements concentrations in *E. andevalensis* and *E. australis* growing in the contaminated soils ranged the normal levels, however some plant samples presented Mn, Pb and As within the excessive or toxic limits for plants. Both *Erica* species, even in the non-contaminated soils are Al-tolerant and Mn-accumulators. In contaminated soils these species are also As-tolerant.

For all the exposed reasons, *E. andevalensis* and *E. australis* may be considered of great importance for the recovery of the sulphide mining areas in regions with climate conditions compatible with breeding and growing of these plant species.

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