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Erica andevalensis and *Erica australis* growing in the same extreme environments: Phytostabilization potential of mining areas

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ABSTRACT

Mining activities in the abandoned São Domingos mine (Portugal, Iberian Pyrite Belt, IPB) generated a large amount of sulphide-rich waste rocks and tailings. *Erica andevalensis* Cabezudo and Rivera and *Erica australis* L. plants grow spontaneously in contaminated sites that have high concentrations of potentially hazardous elements, high acidity and nutrient deficiency. The aim of this paper was to analyse the behaviour of monospecific and mixed communities of both *Erica* species in these extreme environments in order to evaluate their potential for phytostabilization of soils and mining wastes. Metal and metalloids were analysed in the soils (total and available fraction) and in the roots and above-ground biomass of the plants, and these values were then used to estimate uptake, tolerance, translocation and accumulation in the plants. The plants showed a high content of trace elements in the roots and above-ground biomass. In fact, the content of chemical elements in the aerial parts was higher than the range considered as normal for Al and Fe, and exceeded the toxic values for As, Mn and Pb. These values were superior to those found in the available soil fraction for these elements, and even superior to the soil total content for Mn. The lack of phytotoxicity symptoms suggests that *Erica* plants can be considered as a Mn-accumulator and acid-, Al-, As-, Fe- and Mn-tolerant. Furthermore, both *E. andevalensis* and *E. australis* were found to form a large biomass in monospecific and mixed communities on both wet acid sulphate soils/sediments in riverbanks and dry mine tailings and contaminated soils. Hence, both *Erica* species can be considered suitable for phytostabilization of metal(loid)-polluted sites in abandoned mining districts of the IPB.

1. Introduction

Trace element contamination of soils affected by acid mine drainage (AMD) from the mining of sulphide-bearing ore deposits is a main cause of environmental contamination throughout the world. Trace elements are not subject to chemical or biochemical decomposition and remain active for a long time in the environment. This is a serious problem due to the high ability of contaminants to accumulate in the biota and cause significant toxicity in microorganisms, plants, animals and humans. The tolerance of some plant species to the accumulation of hazardous chemical elements is proposed as an in situ low-cost technology for remediation of contaminated soils, and has received considerable attention in recent years (Ma et al., 2011; Moreno-Jiménez et al., 2011; Sun et al., 2011). In particular, phytostabilization is a phytoremediation strategy that consists of immobilising metals in soil or roots, thus reducing their mobility and bioavailability in the environment (Abreu and Magalhães, 2009; Pivetz, 2001).

The Iberian Pyrite Belt (IPB; SW Iberian Peninsula, Spain and Portugal) has been acknowledged as a world-class massive sulphide province. The IPB holds over one hundred deposits and 1700 Tg of reserves (Sáez et al., 1999). Mining activity dates back to 5000 years ago and has generated a large volume of AMD by oxidation of sulphide-rich mining wastes, which is drained by the Tinto and Odiel river basins in the Spanish sector and the Guadiana river basin between the Spanish and Portuguese sectors. The production of AMD has strongly impacted on the quality of these watercourses (Abreu et al., 2010; Delgado et al., 2009; Nieto et al., 2007) as well as on the sediments and soils of the region (Abreu and Magalhães, 2009; Fernández-Caliani et al., 2009).

In the IPB, two heather species of the genera *Erica* (Ericaceae family) have been described as tolerant to metals: *Erica australis* L. and *Erica andevalensis* Cabezudo and Rivera (Abreu et al., 2008; Monaci et al., 2011). *Erica andevalensis* is an endemic heather that grows only in mining areas of the IPB (Cabezudo and Rivera, 1980). Both *Erica* species can survive in hostile soils with high concentrations of hazardous elements,

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such as As, Cu, Pb and Sb, which are developed on materials (wastes, sediments) from sulphide mining operations. *Erica australis* can also grow in the remaining Iberian Peninsula and NW Africa on non-contaminated soils (Valdés et al., 1987).

Previous studies have proposed the use of both *Erica* species as a tool to phytostabilize hazardous trace elements in sulphide mining districts of the IPB. In several mine areas within the Spanish sector, *E. andevalensis* can grow to form monospecific or mixed communities with *E. australis* both on the banks of AMD-affected rivers and on the dry mine spoil heaps (Márquez-García and Córdoba, 2009, 2010; Monaci et al., 2011). The extraordinary capacity to adapt to these extreme habitats has made both *Erica* species potentially useful plants in promoting the phytostabilization and the development of a self-sustaining vegetative cover on mine tailings and contaminated riverbank sediments. In fact, the singularity of *E. andevalensis* and the restricted flowering territory has informed its inclusion in the list of protected species agreed by the Andalusian Government (Southern Spain) (Aparicio, 1999).

The distribution of both species seems to be, however, different in the abandoned mines of the Portuguese sector when compared to those of the Spanish sector. Until the present, *E. andevalensis* was only found in the abandoned São Domingos mine area within the Portuguese sector (Abreu et al., 2008). According to that study, at the time of sample collection (2001–2003) these two *Erica* species did not coexist together in the same area and their habitats were different; while monospecific populations of *E. andevalensis* only grew on the banks of AMD-affected rivers in areas that were periodically flooded and with a pH between 3.0 and 4.0, monospecific populations of *E. australis* grew in soils unaffected by AMD and with a pH always above 3.5 (Abreu et al., 2008).

Nevertheless, field observations in the São Domingos mine following the above-mentioned study (Abreu et al., 2008) identified young populations of *E. andevalensis* also growing in soils located far from riverbanks, and even sharing habitat with *E. australis*. At the same time, populations of *E. australis* were also identified growing together with *E. andevalensis*, sharing the same riverbanks. Our working hypothesis is that there may be a change in the territoriality of both *Erica* species in the Portuguese sector. This fact has aroused an interest in re-evaluating the potential use of both species of *Erica* in phytostabilization programmes of the IPB mining districts of the Portuguese sector. Thus, the main objectives of this study, which are new insights regarding the study performed by Abreu et al. (2008), were to: (1) describe and compare monospecific and mixed populations of *E. andevalensis* and *E. australis*, both on riverbanks periodically flooded by AMD, or even channel margins affected by AMD, and on non-flooded soils developed on mining tailings; (2) determine the concentrations of major and trace elements in different parts of *Erica* plants (aerial parts and roots); (3) establish possible relationships between some physicochemical parameters of soils and content of chemical elements in plants; and (4) compare plants from São Domingos with similar communities found in mining areas of the IPB Spanish sector.

2. Materials and methods

2.1. Site description

São Domingos mine is a massive sulphide mine located near Mértola (Beja District, South Portugal). The geographical coordinates of the study site are approximately 37°40′–37°37′N and 7°30′–7°29′W. The orebody, exploited in open pit and underground, was a single subvertical body of sulphides located at the top of a volcano-sedimentary sequence, represented by black shales, felsic, basic and intermediate-basic volcanic rocks (Matos et al., 2006). The main features of the orebody are: (i) lens-shaped — 537 m in length and 45 to 70 m in thickness; (ii) mineral assemblage composed of pyrite, sphalerite, chalcopyrite, galena, arsenopyrite and sulphosalts; and (iii) reserves of 27 Tg with 12.5 g Cu/kg, 10 g Pb/kg, 450–480 g S/kg and 20–30 g Zn/kg (Leistel et al., 1998; Matos, 2004). The mining area includes an open pit mine originally capped by an extensive gossan formed in situ by weathering of the sulphide mineralization. The beginning of the mining activity has been dated back to pre-Roman times, and remained active until 1966 when the exploitation ceased.

During the operational period, mine wastes were spread in the field forming tailing piles and slopes in the São Domingos river valley. Several facilities were built during the mine operations: a mine village, water reservoirs, cementation tanks, sulphur factories, network channels for acid water evaporation, and a railway and harbour (Pomarão) for ore transportation and exportation, respectively (Quental et al., 2002). The mining wastes in the area are highly heterogeneous, and two main groups can be recognised: mine wastes heaped as dumps, including gossanized coarse blocks and host rocks (volcanic rocks and shale); and industrial wastes derived from ore processing operations, including Roman and modern slags, processed gossan materials, roasted pyrite piles, smelting ashes and leaching tank refuse. The provenance of each waste can be found in Pérez-López et al. (2008, 2010). In the mining area, *E. andevalensis* and *E. australis* was associated with *Cistus monspeliensis* L., *Cistus ladanifer* L. and *Juncus conglomeratus* L. In general, coverage of species is sparse (some very few plants in an area of approx. 5 m^2), but it can be slightly to moderately dense depending on the growing areas.

2.2. Soil sampling and characterisation

A total of 26 composite samples of soils were taken in the São Domingos mine area in March 2009 (Fig. 1). Soil samples were collected (≈2 kg at 0–15 cm depth) from a restricted area around the plant root system of each species (*E. andevalensis* and *E. australis*) and consisted of a homogenate of five subsamples, considered as representative of the plant population in each collection site. Immediately after sampling, an aliquot of soil samples (approx. 1 g, in duplicate) was dried at 105 °C until constant weight for gravimetric determination of soil moisture. The remaining samples were dried at room temperature, mixed, homogenised and sieved through a 2 mm net. The fine fraction of the soil samples was characterised as follows (Póvoas and Barral, 1992): pH in water suspension (1:2.5 soil/solution), extractable aluminium by 1 mol/L KCl, and exchangeable cations and cation exchange capacity (CEC) by 1 mol/L ammonium acetate at pH 7. Iron content in both non- or poorly crystalline oxides and total oxides (i.e. poorly crystalline and crystalline phases) was extracted and determined by a single step extraction using Tamm reagent (0.1 mol/L oxalic acid and 0.175 mol/L ammonium oxalate at pH 3.2) in dark conditions (Schwertmann, 1964) and under UV radiation (De Endredy, 1963), respectively. Total organic carbon (TOC) was also determined using a LECO analyser (SC-144DR model) after sample combustion at 550 °C.

Metal content in the soils was determined by Acme Analytical Laboratories Ltd. (Vancouver, Canada), accredited under ISO 9002, through its Italian affiliate (ERS Srl, Napoli). The soil samples were subjected to a four-acid mixture digestion (HNO_3–$HClO_4$–HF–HCl) and analysed by inductively coupled plasma–mass spectrometry (ICP–MS). Further details of analytical procedures can be found on the website www.acmelab.com. The available soil fraction for plant uptake was extracted with an AB-DTPA solution (Hanlon et al., 1999) and analysed for specific elements (Al, As, Cd, Cu, Fe, Mn, Pb and Zn) by inductively coupled plasma–atomic emission spectrometry (ICP–AES). This fraction corresponds to the weakly adsorbed trace elements on soil particles and to those present in the soil solution (exchangeable + soluble forms).

2.3. Plant sampling and analysis

In the same period and soil sampling area, 34 composite samples of plants were collected (five subsamples per species and collection site), comprising the roots and aerial parts (stems, branches, leaves and flowers). The plant sampling involved the collection of 23 samples of *E. andevalensis* (15 samples from monospecific communities and eight samples from mixed communities) and 11 samples of *E. australis*