



Arsenic speciation in soils and *Erica andevalensis* Cabezudo & Rivera and *Erica australis* L. from São Domingos Mine area, Portugal

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ABSTRACT

Arsenic is very abundant in the Iberian Pyrite Belt (IPB) and it might have hazardous consequences for plants. The chemical speciation is an important factor to take into account in toxicity evaluations. Arsenate is analogous to phosphate and it can seriously interfere with cellular processes. In the present study we have analysed by high performance liquid chromatography-inductively coupled plasma-mass spectrometry (HPLC-ICP-MS) the arsenic speciation in soils from São Domingos mine area (IPB) and arsenate resulted to be the major species. The arsenic content and speciation analysis have been carried out also in two metal tolerant species from that area: *Erica andevalensis*, endemic heather from the mining areas of the Southwest Iberian Peninsula, and *Erica australis*, a widely distributed species. The total content of arsenic ranged in soils from 194 to 7924 mg kg⁻¹ (dry mass), and from 1 to 24.4 mg kg⁻¹ in *E. andevalensis* and from 2.7 to 11.6 mg kg⁻¹ in *E. australis*. The organic forms of arsenic were almost absent, with only dimethylarsinate (DMA) found in some samples of *E. andevalensis*. These plant species must possess different tolerance mechanisms, as *E. australis* accumulates mainly arsenite, while in *E. andevalensis* arsenate is the most abundant species in some cases.

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1. Introduction

The Iberian Pyrite Belt (IPB; SW Iberian Peninsula, from Portugal to Spain) is one of the most outstanding massive sulfide provinces in the world since it contains more than 80 deposits and about 1700 Mt of reserves (Sáez et al., 1999). The long-term mining activity in the region started in the Third Millennium B.C. (Nocete et al., 2005). The intense exploitation has produced a large amount of sulfide-rich wastes that, in contact with precipitation water, are oxidized generating highly pollutant acid mine drainage (AMD). This phenomenon is responsible for the presence of acidity and metal(loid)s in the soils and superficial water of the area.

São Domingos mine is an abandoned copper mine located on the IPB, in the South-East of Portugal. In this area, several plant species have been described as tolerant to metals, which are present in

local soils in some cases with high levels because of past mining activities, with special relevance in the case of heathers, *Erica andevalensis* Cabezudo & Rivera and *Erica australis* L. (Abreu et al., 2008). *E. andevalensis* is an endemic species of the IPB, which was described by the first time growing within the mining districts of the Spanish segment, in the area crossed by the Odiel and Tinto rivers by Cabezudo and Rivera (1980), and lately within the São Domingos mine area in the Portuguese segment (Capelo et al., 1998). *E. australis* is a species with a wide distribution in the Iberian Peninsula growing both in natural soils and in areas under the influence of the mines.

Arsenic is a widely distributed trace element in soils and it is abundant in the IPB due to the oxidation of arsenical pyrite (Sarmiento et al., 2009). Arsenic in soils might have hazardous consequences, since its role is unclear in plant metabolism and might yield toxic effects on them (Zhao et al., 2009). The effects of arsenic on plants depend on several factors such as concentration in soil, arsenic species, and soil properties like redox potential (Mascher et al., 2010). The inorganic forms are arsenate (As(V)) and arsenite (As(III)); As(V) is analogous to phosphate what makes it able to interfere with the essential cellular processes (Tripathi et al., 2007). These forms are interconvertible depending on the redox status of the environment (Tripathi et al., 2007).

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Extraction of arsenic species is a critical step on speciation studies of environmental samples, and there is not a lot of agreement between authors about the best extraction conditions. On the extraction of arsenic species from plants different methods have been described, such as mixtures of methanol/water (Bohari et al., 2002; Quaghebeur and Rengel, 2005; Zheng and Hintelmann, 2009), mixtures of sucrose, 2-(*N*-morpholino)ethanesulfonic acid (MES), ethylenediaminetetraacetic acid (EDTA) and ascorbic acid (Quaghebeur and Rengel, 2003), potassium hydroxide, phosphate buffers, ammonium dihydrogenphosphate, chloroform/methanol among others (Zheng and Hintelmann, 2009). For the arsenic speciation in soils, different extractants have also been used, including water, ammonium oxalate or phosphoric acid solutions (Bissen and Frimmel, 2000; Koellensperger et al., 2002; Ruiz-Chancho et al., 2005). By far, high performance liquid chromatography (HPLC) coupled to inductively coupled plasma mass spectrometry (ICP-MS) is the most used technique for the determination of arsenic species on the extracts (Francesconi and Kuehnelt, 2004).

The aim of the present study was to analyse the arsenic levels and its speciation in soils and leaves of *E. andevalensis* and *E. australis* growing in different emplacements in São Domingos area, to deepen the knowledge about the behaviour of this toxic element in mine regions. As stated before, both *E. andevalensis* and *E. australis* are able to survive in soils with low pH and high metal concentrations; such soil conditions that make it difficult for other plant species to survive.

2. Materials and methods

2.1. Site description and sampling

The area of study was selected following the water course (Ribeira de São Domingos) that crosses the São Domingos mine area, in a sparsely-vegetated area affected by extreme acid waters, in gossan, leaching tanks and at the foot of the road (Fig. 1), taking samples from soils developed on different materials and therefore different chemical and mineral composition (Pérez-López et al., 2008). São Domingos mine is a massive sulfide mine located in Mértola (Beja District, South of Portugal). The orebody, exploited in open pit and underground, was a single subvertical body of sulfides, whose main features were: (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 sulfosalts; and (iii) reserves of 27 Mt 1.25% Cu, 1% Pb, 2% Zn and 45–48% S (Leistel et al., 1998). The mining area includes an open pit mine originally capped by an extensive gossan formed *in situ* by weathering of the sulfide mineralization. The beginning of mining has been dated back to pre-Roman times, and remained active until 1966 when the exploitation ceased. Nowadays the contamination of the ecosystem is still important due to the continuous leaching of the mine residues that are spread out near the mine complex. According to a set of leaching experiments reported by Pérez-López et al. (2010), minesoils and wastes are capable of producing solutions with average As concentrations of 210 $\mu\text{g kg}^{-1}$. The mining wastes in the area are highly heterogeneous, and two main groups can be recognized: mine wastes heaped as dumps, including gossanized coarse blocks, host rocks (volcanic rocks and shales); and industrial wastes derived from ore processing operations, including Roman and modern slags, processed gossan materials, roasted pyrite piles, smelting ashes and leaching tank refuses. The provenance of each waste can be found in Pérez-López et al. (2008, 2010).

A total of 14 sampling points were selected (Fig. 1). Samples were collected in April 2009, and for each sample point, five plants were selected and the aerial parts were collected. The soil samples were collected close to the roots of the sampled plants (also five different samples in each sampling point). The samples were transported to the laboratory in plastic bags and the soils were dried at 50 °C and sieved at 2 mm. The plant samples were washed three times with tap water and two times with distilled water, then they were dried at 45 °C and afterwards the stems were discarded and only the leaves were ground.

2.2. Reagents, standards and reference materials

Deionised water with a resistivity of 18.2 M Ω cm was used to prepare all the solutions. For the standards of arsenic compounds, stock solutions (1000 mg L⁻¹ as As) were prepared as follows: (1) arsenite (As(III)) from As₂O₃ (NIST oxidimetric primary standard 83d, 99.99%) dissolved in 4 g L⁻¹ NaOH (Suprapure, Merck, Darmstadt, Germany); (2) arsenate (As(V)) from Na₂HAsO₄·7H₂O (Carlo Erba) dissolved in water; (3) dimethylarsinate (DMA) from (CH₃)₂AsNaO₂·3H₂O (Fluka) dissolved in water; (4) methylarsonate (MA) from (CH₃)AsO(ONa)₂·6H₂O (Carlo Erba) dissolved in water; (5) arsenocholine (AC, (CH₃)₃As⁺CH₂CH₂OH) standard was supplied by the "Service Central d'Analyse" (CNRS Vernaison, France); (6) arsenobetaine (AB, (CH₃)₃As⁺CH₂COOH) was obtained as a Certified Reference Material (BCR CRM 626) with a concentration of 508 ± 1 mg As L⁻¹; and (7) trimethylarsine oxide (TMAO) from Argus Chemicals srl dissolved in water.

For the preparation of the mobile phase solutions of the HPLC, methanol (HPLC gradient), formic acid (98%, p.a.), ammonium dihydrogen phosphate (p.a.) and aqueous ammonia solution (25%, p.a.) were purchased from Panreac, and pyridine (p.a.) from Scharlau.

For the extraction of arsenic species from soils a solution of 1 mol L⁻¹ *o*-phosphoric acid (85% H₃PO₄, Merck, pro analysis) with 0.5 mol L⁻¹ L(+)-ascorbic acid was used. This solution was purged with an argon stream for about 15 min before the microwave extraction. A solution 0.3 mol L⁻¹ *o*-phosphoric acid was used for the extraction of arsenic species from plants.

An aliquot freeze-dried extract of *Fucus serratus* L. containing the four most common arsenosugars; phosphate-sugar (PO₄-sug), sulfate-sugar (SO₃-sug), sulfonate-sugar (SO₄-sug) and glycerol-sugar (Gly-sugar) was used to assign the arsenosugar peaks in the chromatograms from the sample extracts (Madsen et al., 2000).

2.3. pH, electric conductivity determination and sample moisture

The pH and the conductivity of soil samples were determined by shaking aliquots of each sample in triplicate with deionised water in a weight ratio of 1 g of solid and 2.5 g of water for 1 h and, after centrifugation, measuring both parameters in the supernatant solution (Abreu et al., 2008).

The moisture was determined gravimetrically, in duplicate, by drying 1 g of sample at 105 °C until the weight remained constant. All results in the present study are referred to dry mass.

2.4. Total arsenic determination

Arsenic contents in soils and plants (leaves) were carried out 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 (HNO₃-HClO₄-HF-HCl) and

Fig. 1. Location map of São Domingos Mine, indicating the sampling points: (i) mining wastes ⇒ E1 – modern slag, E2 – Roman slag, E3 – smelting ashes, E4 – Gossan coarse blocks, E5 – Gossan, E7 – Gossanized volcanic rocks, E8 – host volcanic rocks + shales, E9 – shales, E11 – roasted pyrite, E12 – pyrite orebody, A1 – leaching tanks; (ii) minesoils (S) ⇒ F – leached materials in seasonal flooded areas, L – mine landfill, UL – urban contaminated landfills, AW – sparsely-vegetated area affected by extreme acid waters and (iii) acid mine drainage (AMD). Adapted from Matos (2004).

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