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Mobility and phytoavailability of antimony in an area impacted by a former stibnite mine exploitation

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HIGHLIGHTS

- ► Environmental assessment of an area impacted by a former stibnite mine exploitation.
- ► Severe pollution with high total and soluble Sb contents in the uppermost soil layers.
- ► Changes in environmental conditions moderately raise the current soil Sb mobility.
- ► *Daphne gnidium* L. seems a suitable species for Sb phytostabilization strategies.

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ABSTRACT

A mining area affected by the abandoned mine exploitation of a stibnite deposit was studied to establish the current and eventual environmental risks and to propose possible remediation practices. Soil and plant samples were collected at different places in this area and analyzed for their Sb content and distribution. Critical soil total concentrations of Sb were found, with values ranging from 585 to 3184 mg kg^{-1} dry weight in the uppermost soil layer, and decreasing progressively with soil depth. The readily labile Sb contents represent <2% of the total concentrations, whereas the soil Sb contents more susceptible of being mobilized under changing environmental conditions attain values of about 4–9% of the total concentrations. Remediation measures should be undertaken to limit off-site migration of Sb. Within the tolerant plant community growing in this area, the shrub *Daphne gnidium* L. stands out for its relatively high root Sb accumulation and low Sb translocation, suggesting its feasibility to be used in Sb phytostabilization strategies.

1. Introduction

Antimony is a non-essential element which exhibits a high degree of toxicity, especially to mammals (McBride, 1994). In humans it causes a great variety of adverse health effects, including carcinogenic problems (Winship, 1987; Sundar and Chakravarty, 2010). Antimony is gaining interest as a global contaminant. Antimony inputs to the environment can take place by natural sources (Reimann et al., 2010; He et al., 2012), but its release has been greatly enhanced by human activities. The main anthropogenic Sb sources include combustion of fossil fuels, waste incineration, mining operations, smelting processes, shooting practice and road traffic (Scheinost et al., 2006; Kabata-Pendias and Mukherjee, 2007; Ackermann et al., 2009; Telford et al., 2009; Reimann et al., 2010; He et al., 2012). Amongst them, mining operations are assumed to be the greatest Sb source (Takahashi et al., 2010).

Antimony is used in the manufacture of many industrial products. Thus, it is employed as flame retardant, catalyst in plastic production, pigment in paints and lacquers, additive in glassware and ceramics, and hardening agent in alloys for the production of batteries, ammunitions and brake pads (Filella et al., 2002; Oorts et al., 2008; Ackermann et al., 2009). Such diverse industrial applications result in Sb being the ninth most mined metal worldwide (Scheinost et al., 2006; Okkenhaug et al., 2011). More than 100 minerals are known to contain Sb (Kabata-Pendias and Mukherjee, 2007; Reimann et al., 2010), with stibnite (Sb_2S_3) being the main ore mineral (Alloway, 1995). The exploitation of Sb deposits has induced a wide legacy of Sb in mine wastes, especially when early mining operations were involved owing to their low efficiency. In general, these wastes have been poorly managed, promoting the Sb dispersion to the surrounding ecosystem. Antimony is readily leached form stibnite-bearing wastes (Wilson et al., 2004). Dissolution of stibnite has been shown to produce up to 55 mg l^{-1} of Sb (Ashley et al., 2003).

Antimony exists in environmental systems in predominantly two oxidation states: Sb(III) and Sb(V). Both are strongly sorbed on Fe, Al and Mn (oxyhydr)oxides (Thanabalasingham and Pickering, 1990;

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Leuz et al., 2006; Scheinost et al., 2006; Mitsunobu et al., 2010; Biver et al., 2011; Ilgen and Trainor, 2012). Antimony(III) binds to them over a wider pH range than Sb(V) for which sorption importantly decreases under neutral and alkaline conditions (Johnson et al., 2005; Leuz et al., 2006). Organic matter has been also reported to tightly bind Sb, acting as an important sink in soils, especially for Sb(III) (Buschmann and Sigg, 2004; Steely et al., 2007; Van Vleek et al., 2011; Sh et al., 2012). In any case, the sorption of Sb to organic matter strongly decreases with increasing pH from moderately acid values (Pilarski et al., 1995; Buschmann and Sigg, 2004; Tighe et al., 2005; Klitzke and Lang, 2009).

Studies performed on soils polluted with Sb using X-ray absorption spectroscopy (Mitsunobu et al., 2005, 2006; Takaoka et al., 2005; Scheinost et al., 2006; Okkenhaug et al., 2011) point out that Sb in soils exists dominantly as Sb(V), regardless of the Sb emission source and the soil redox state (Filella, 2011). The predominance of Sb(V) in soils is explained by the rapid oxidation of Sb(III) to Sb(V) by Fe and Mn (oxyhydr)oxides (Belzile et al., 2001; Leuz et al., 2006). Humic acids have been also proven to catalyze the oxidation of Sb(III) to Sb(V) (Buschmann et al., 2005; Steely et al., 2007; Ceriotti and Amarasiriwardena, 2009; Sh et al., 2012), and in some instances this oxidation process has been found to be relatively fast (Buschmann et al., 2005; Ceriotti and Amarasiriwardena, 2009). Hence, humic acids should also play an important role in the Sb(V) prevalence in soil environments. The effect of such co-oxidants could contribute to Sb mobilization and dispersion to other environmental components, especially in neutral and alkaline soils.

Concentrations of Sb are typically below 10 mg kg^{-1} in unpolluted soils (Wilson et al., 2010), but in mining-affected areas Sb concentrations can be increased up to three orders of magnitude, mainly in the close environs of mine dumps or mineral processing facilities (Okkenhaug et al., 2011; Qi et al., 2011; Hiller et al., 2012). Such huge soil Sb concentrations can pose severe hazards to the surrounding ecosystem, particularly if environmental conditions favor Sb release. Therefore, this kind of scenarios require a strict study to establish the current and eventual environmental risks and to assess the right measures to be undertaken in order to minimize such risks.

The main objectives of the present work are: a) to perform the environmental characterization of soils affected by the former mine exploitation of a stibnite deposit, and b) to study the native plants growing in this area so as to evaluate the Sb phytoavailability and the consequent environmental implications.

2. Materials and methods

2.1. Study area

The studied mining area is located 10 km southwest of Alburquerque village in the north-west of the Badajoz province (Spain) where the abandoned San Antonio mine is situated. This mine is located within the largest stibnite deposit in Spain, which was exploited extensively from 1940 to 1986. It is a hydrothermal vein deposit, with quartz–stibnite–scheelite ($CaWO_4$) mineralization hosted in limestones and calc-schists. Mining activities produced huge amounts of wastes composed of barren rocks, fine-grained ore mineral and ore weathering products.

There is a spontaneous plant colonization of the mine waste dump. Such colonization mostly occurs close to its edges (mine wastes/soil boundaries). Perennial plants (*Cistus ladanifer* L., *Daphne gnidium* L., *Quercus rotundifolia* Lam., *Retama sphaerocarpa* (L.) Boiss. and *Rubus idaeus* L.) predominate, although some annual species (*Carduus tenuiflorus* Curt., *Inula pulicaria* L. and *Kentrophyllum lanatum* (L.) DC.) are also able to grow under such adverse environmental conditions. Vegetation also grows spontaneously in the mine surrounding area. The characteristic plants present in this area include mainly annual species (*Anthemis arvensis* L., *C. tenuiflorus* Curt., *Hordeum murinum* L., *I. pulicaria* L., *K. lanatum* (L.) DC. and *Xanthium spinosum* L.).

Other study has considered this mining area before (Murciego Murciego et al., 2007). Such work investigated the sites where mine wastes and mine tailings were accumulated, assessing their total and soluble Sb contents on single superficial composite samples. The leaf Sb concentrations of two plant species growing there were also studied in such work. The present study evaluates the horizontal and vertical distribution of total, soluble and mobilizable Sb contents in soils nearby the location where mine wastes and mine tailings were deposited. This study also investigates the Sb distribution in eleven plant species characteristic of this mining area.

2.2. Sampling

Soil sampling was carried out in a neighboring area of the mine dumps. This area is affected by both the aerial dispersion and the leaching and runoff from mine wastes and tailings. Soil collection was performed at six different places in this area: A, B, C, D, E and F, the former being the closest to the mine dumps and the latter being the furthest. The distance between the successive sampling sites is 25 m, except for A and B sampling sites, which are 10 m distant from each other. Ten different samples were taken at each mentioned sampling site. A 3-cm diameter core sampler was used for the soil profile sampling in the depth up to 50 cm. Samples at the depths of 0–10, 10–20, 20–30, 30–40 and 40–50 cm were collected. Single composite samples corresponding to the different soil depths were generated for each of the indicated sampling sites. These soil samples were air-dried and sieved through a 2 mm mesh sieve prior to characterization.

Plant sampling was carried out in two locations. One of them is the neighboring area of the mine dumps where soil sampling was performed. Characteristic plants of this area were collected at the same mentioned sites (A, B, C, D, E and F). The other plant sampling location is the mine waste dump. Representative plants developed in this extreme environment were collected at seven different sites: WD-1, WD-2, WD-3, WD-4, WD-5, WD-6 and WD-7. At every one of them the substrate on which plants grew was also collected. Thus, at each site a pooled sample was obtained for a 10 cm substrate depth from a circular area of 50 cm. These samples were air-dried and sieved through a 2 mm mesh sieve prior to characterization. In both sampling locations plant collection involved the roots and the aerial parts of all the considered plants. At least ten plant specimens of the herbaceous species and three of the woody species were collected at the different sampling sites. Plant samples were separated into above-ground tissues and roots. Above-ground tissues were also separated into shoots and leaves in the case of woody species. The different plant sections were washed with tap water, then cleaned using an ultrasonic bath to remove dust contamination, and finally rinsed with deionized water. Visual inspection of cleaned plant samples was performed using a binocular magnifying glass in order to assure that the cleaning process was properly accomplished. Afterwards, these plant samples were dried at 70 °C for 48 h and powdered for analysis.

2.3. Soil physico-chemical and mineralogical characterization

Soil samples corresponding to A, D and F sampling sites and samples collected from the mine waste dump on which plants grew were subjected to physico-chemical and mineralogical characterization. Their main physico-chemical properties (Tables 1 and 2, respectively) were determined as follows: pH was analyzed potentiometrically in a soil paste saturated with water, cation exchange capacity (CEC) was obtained according to the ammonium acetate method (Tan, 1996), organic matter (OM) was calculated after dichromate oxidation using the Tiurin method (Jackson, 1960), calcium carbonate content was analyzed using the method of Bascomb (1961), total free Fe oxide content was obtained according to the method given by Jackson (1960), amorphous Fe oxide content was determined following the procedure described by McKeague and Day (1966), and particle size distribution