Antimony and arsenic uptake by vegetation growing at abandoned mines

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Abstract This paper investigates antimony (Sb) and arsenic (As) occurrence in plants (Pistacia lentiscus), an evergreen shrub, collected at abandoned mines in Sardinia. Maximum concentrations observed in plants were 22 µg/g Sb and 0.35 µg/g As, with concentrations accumulated in roots being generally higher than those in leaves. The ranges of amounts washed out from leaves were 0.003-0.088 µg/g Sb and 0.002-0.024 µg/g As. Antimony and arsenic in vegetation samples collected in the mine area were much higher than concentrations observed in plants collected on the slopes upstream of the mine, although at levels much lower than observed in plants growing at mine sites elsewhere.

Keywords Antimony, arsenic, abandoned mine, vegetation

Introduction

Antimony (Sb) and arsenic (As) are categorized as non-essential elements for plants, animals and humans, while they have been listed as priority pollutants by the US Environmental Protection Agency and the World Health Organization.

Natural concentrations of arsenic in the soil typically range from 0.5 to 80 µg/g (Kabata-Pendias and Pendias 2001), and antimony in the soil is evaluated at few µg/g (Filella *et al.* 2002), although higher concentrations are frequently found in soils and sediments that have been affected by anthropogenic activities such as mining or agriculture, or where the soils are derived from As- and Sb-rich mineralized rocks. Both elements can be readily absorbed by plant roots when occurring in soluble form. The plant uptake of As may differ with respect to plant uptake of Sb depending on their dominant species (Tschan *et al.* 2008). Arsenic concentrations in plants growing on uncontaminated soils vary from 0.01 to 1.5 µg/g (Larios *et al.* 2012), and are in the range of 0.2 to 50 µg/g for Sb (Okkenhaug *et al.* 2011). Substantially higher As concentrations (up to 1400 µg/g; Larios *et al.* 2012) and Sb concentrations (up to 1600 µg/g; Murciego *et al.* 2007) have been found in vegetation growing in mining areas.

The Sardinia Regional Government has recognized relevant antimony contamination at the Su Suergiu mining site in SE Sardinia, Italy. Studies aimed at identifying the contaminant sources, and evaluate the extent of contamination have been carried out (IGEA 2009). This study aims to investigate the plant uptake of Sb and As in soils impacted by past mining at Su Suergiu. Assessing the capacity of plants in accumulating Sb and As is fundamental for evaluating the toxicity of these elements in the food chain. Taking into account that the Sardinia Region has established the need of remediation at Su Suergiu, the information derived from this study could be relevant for planning the best actions able to mitigate contamination.

Study area

The Su Suergiu study area is shown in Fig. 1. The Sb-As deposits were mined underground since 1880, with exploitation peaks in the 1920–1930, and mine closure in 1960. Afterwards, Sb-ore coming from Turkey and China was processed, a foundry being active from

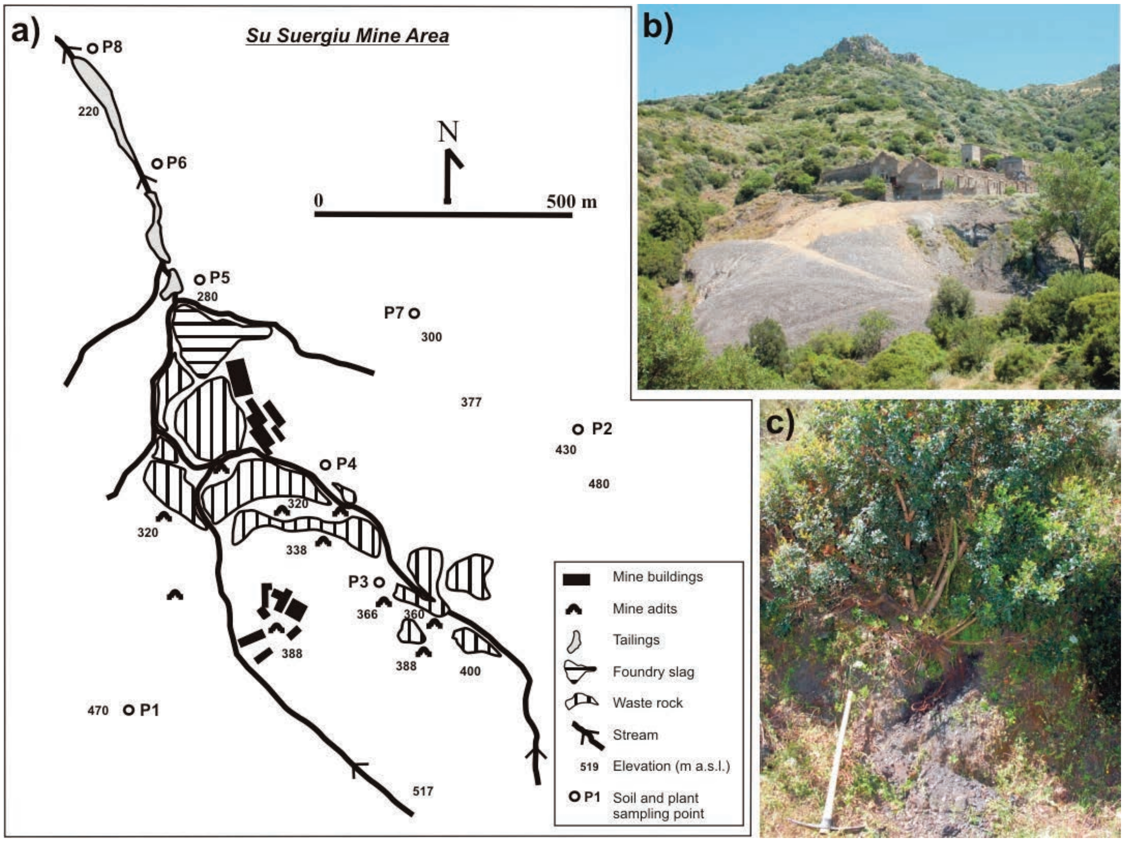

Fig. 1 *a) Schematic map of Su Suergiu and location of the vegetation samples; b) view of the slag heap and mine ruins; c) example of soil with Pistacia lentiscus.*

1882 to 1987. The mineralization is hosted in Paleozoic black schists and metalimestones, and consists of antimonite, scheelite, arsenopyrite and pyrite, with calcite and quartz in the gangue (Funedda *et al.* 2005). Slag and tailings (87 % of dumped materials), and waste rocks were left nearby the mine plant over a surface of 33,000 m^2. Mining residues are altogether estimated at about 66,000 m^3 (RAS 2003).

Climate in the study area is semi-humid, characterized by dry summer and rainfall variable from year to year, mostly occurring from October to April. Data collected from 1955 to 1992 at stations located in the area show mean annual precipitation of 670 mm and mean annual temperature of 16.2 °C (RAS 1998). Spring waters are scanty and usually have low flow (<0.1 L/s). The main river is the Flumendosa, only a few tributaries are large streams (flow > 100 L/S) while the other ones are intermittent streams. The flow of surface waters may vary dramatically depending on rainfall. The Rio Ciurixeda stream receives the untreated drainage from the Su Suergiu mine, and flows directly into the Flumendosa River, which supplies water for agricultural and domestic uses.

Methods

In June 2012, soil and vegetation samples were collected in the Su Suergiu Sb mining area and surroundings (Fig. 1). Eight soil profiles were opened down to 100 cm depth. Samples of each soil horizon were packed in polyethylene (PE) bags, air dried, hand-ground and dry-sieved with a 2 mm mesh sieve, and milled in agate vials and balls (Fritsch planetary ball milling pulverisette 5).

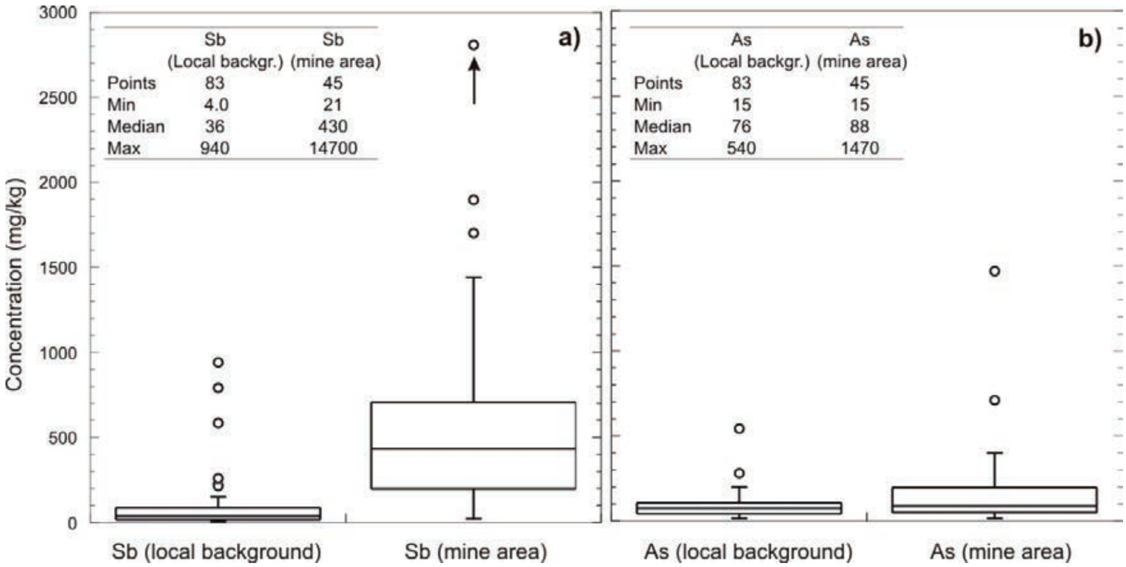

Fig. 2 *a) Antimony and arsenic concentrations in soil samples (data from IGEA 2009).*

Vegetation samples consist of Pistacia lentiscus, an ubiquitous plant in Mediterranean environments that also grows in the Su Suergiu abandoned mine area. Samples from three individual plants were collected at the same location as the soil samples. The plants were divided into roots and leaves (woody stems were not analysed), collected in separate PE bags, and stored at 4 °C until analysis. To evaluate the potential As and Sb dispersion in the atmosphere, 25 g of leaves were washed with 250 mL of 0.01 M hydrochloric acid (HCl), used as a proxy of rain water, and shaken for few minutes.

Arsenic and Sb in leaves and roots were determined by acid digestion; leaves and roots were washed with deionised water, dried at 60 °C until constant weight, and then ground to powder using a rotor mill (Retsch ZM1000). Acid digestion was carried out in a closed microwave digestion device (Milestone Ethos1) using 0.5 g of sample and 2 mL hydrogen peroxide (H_2O_2; 30 %), followed by the addition of 6 mL nitric acid (HNO_3; 67 %). Digestion of certified plant reference material was carried out for quality control (bush twigs and leaves GSV-2, and tea GSV-4; Madeddu and Rivoldini 1996).

The solutions derived from the wash of leaves, as well as those derived from acid digestion, were filtered at 0.4 µm, diluted to 50 mL with ultrapure water (>18 MΩ*cm), acidified with supra pure HNO_3 and analyzed by quadrupole inductively coupled mass spectrometry (ICP-MS) using rhodium (Rh) as the internal standard. The estimate errors of certified materials were about 9 % for As and Sb. Concentrations of As and Sb are reported in µg per g of plant dry weight.

Results and discussion

The main soils in the area are Leptosols, while Cambisols occur on slopes and colluvial deposits. Analyses on the soils samples are still in progress, but some information can be derived from previous studies at Su Suergiu (IGEA 2009). Fig. 2 shows the distribution of Sb and As in soil samples collected in the mine area and surroundings, the latter being used to estimate the local background. It can be observed that the median value of Sb in soils from the mine area is much higher than the local background median value, although a large variation in concentration occurs, *i.e.* 21 to 14700 µg/g Sb in the mine area (Fig. 2a). De-

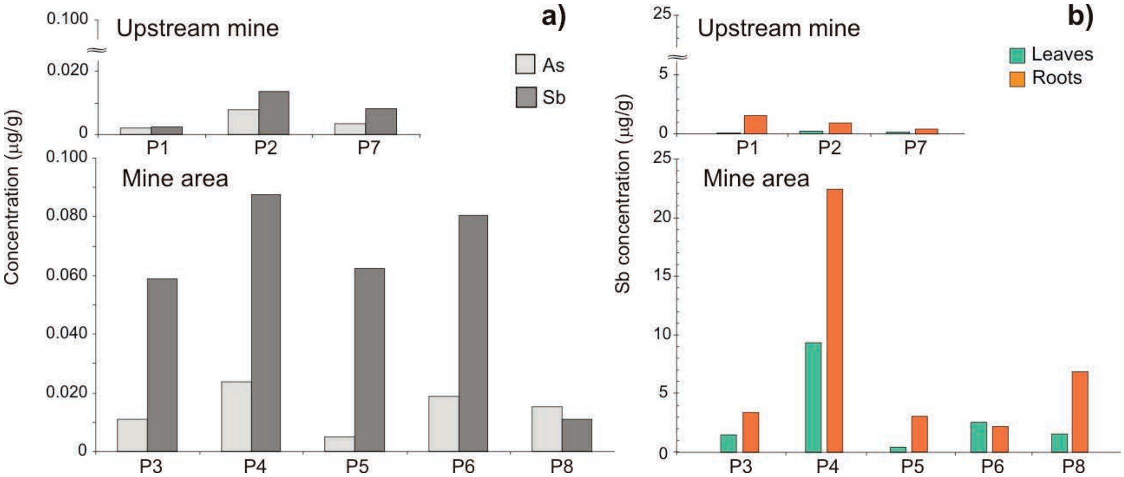

***Fig. 3** a) Sb and As concentrations leached by leaf samples. b) Sb concentrations in leaves and roots of Pistacia lentiscus*

spite the large range of As concentration too (15–1470 µg/g As), the median value of As in soils from the mine area is similar to the local background median value (Fig. 2b).

The Sb-bearing fine particles carried by the wind in the atmosphere can be deposited on vegetation, then fall again to the ground. Fig. 3a shows mean concentrations of As and Sb leached from the leaf samples collected in the study area (for sample locations see Fig. 1). Dust materials deposited on vegetation samples collected on the slopes upstream of the mine area (leaf samples P1, P2, P7) carry 0.007 µg/g Sb on average, while concentrations of Sb deposited on leaves collected in the mine area are much higher, mean 0.070 µg/g Sb (Cidu *et al.* 2013). A similar trend can be observed for arsenic with median value of 0.002 µg/g leached from samples collected on the slopes upstream of the mine area, and up to 0.024 µg/g As leached from samples collected in the mine area.

Fig. 3b shows concentrations of Sb hosted in the vegetation samples. It can be observed that the Sb uptake by the roots is higher than the leaf samples. The Pistacia lentiscus roots may accumulate up to 22 µg/g Sb. Arsenic in the Pistacia lentiscus roots was in the range of 0.08 to 0.35 µg/g, and was similar in the leaves 0.08 to 0.31 µg/g As.

In Sardinia, median concentrations in surface waters are estimated at 1 µg/L As and 0.25 Sb (Cidu and Frau 2009). Median concentrations in Sardinian groundwaters are estimated at 0.6 µg/L As and 0.5 Sb (Biddau 2012). Results on water samples at Su Suergiu show contamination peaks (up to 5900 µg/L As and 15000 µg/L Sb) in the waters flowing out of the slag heaps, clearly indicating that these materials are the main source of contamination at Su Suergiu. The contaminated water flows into the local streams. Dilution processes allow As concentrations to decrease to levels which are not of environmental concern, while the Sb contamination persists several km downstream of the mine till the Flumendosa river (Cidu 2011, Cidu *et al.* 2012, 2013).

Conclusions

Past mining at Su Suergiu affects the soil and the water system downstream of the mine. The soils may contain up to 14700 and 1470 µg/g Sb and As, respectively. Despite such high contents in the soils of the mine area, relatively low amounts of Sb and As (up to 32 and 0.5 µg/g Sb and As, respectively) are accumulated in the investigated plant Pistacia lentiscus growing nearby the mine. According to data available so far at Su Suergiu, the major effects of contamination were observed on the water bodies located downstream of the slag heap. Therefore, priorities of remediation actions should be focussed on addressing the environmental impacts of the slag heap.

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