Science of the Total Environment 439 (2012) 35–43

Contents lists available at SciVerse ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Antimony, arsenic and lead distribution in soils and plants of an agricultural area impacted by former mining activities

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HIGHLIGHTS

- Environmental assessment of an agricultural area impacted by former mining activities.
- Soil Sb, As and Pb contents exceed the maximum tolerable levels in agricultural soils.
- Wheat grain Pb contents (up to 1.36 mg kg^{-1}) exceed the prescribed health standard.
- High risk of As and Pb mobilization under reducing conditions (up to 38 and 71%).
- The species *Dactylis glomerata* L. seems suitable for Pb phytostabilization strategies.

ARTICLE INFO

Article history:
Received 17 July 2012
Received in revised form 3 September 2012
Accepted 4 September 2012
Available online 9 October 2012

Keywords:
Toxic elements
Agricultural soil pollution
Mobilization
Phytoavailability
Environmental and health risks

ABSTRACT

An agricultural area impacted by the former exploitation of an arsenical lead-antimony deposit was studied in order to assess the current and eventual environmental and health impacts. Samples of soils and cultivated (wheat) and spontaneously growing plants were collected at different distances from the mine pits and analyzed for the toxic element content and distribution. The soil total concentrations of Sb, As and Pb found in the uppermost soil layer (14.1–324, 246–758 and 757–10,660 mg kg^{-1}, respectively) greatly surpass their maximum tolerable levels in agricultural soils. Wheat grain Pb concentrations (0.068–1.36 mg kg^{-1}) exceed the prescribed health standard, whereas Sb (<0.05–0.103 mg kg^{-1}) and As (<0.05–0.126 mg kg^{-1}) concentrations are below the permissible limits fixed for cereals. Of the spontaneously growing plants, *Dactylis glomerata* L. shows a relatively high root Pb accumulation and a very low Pb translocation, suggesting its feasibility to be used in Pb phytostabilization strategies.

1. Introduction

Contamination of soils with toxic elements represents a serious threat to environmental quality and human health. Although toxic elements can be incorporated into soils from natural sources (weathering of parent materials, emissions from volcanoes, forest fires, etc.), most of their inputs have an anthropogenic origin (Alloway, 1995). In this regard, mining activities are recognized as one of the most highly polluting sources, being responsible for really elevated toxic element discharges in some settings. Furthermore, pollution that occurs as a consequence of hard rock mining persists for hundreds of years after the cessation of mining operations (Nagajyoti et al., 2010). Hence, areas impacted by former mining activities could remain nowadays severely polluted even if vestiges of such operations are not really apparent.

Among the most toxic elements emitted by mining activities are antimony, arsenic and lead. These elements are frequently present together in ore minerals or in mineral associations. The exploitation of such deposits for the economic ore minerals provokes a simultaneous release of such toxic elements into the environment. None of them has a known biological function in animals or plants, being highly toxic, especially to mammals. In humans Sb and As cause a great variety of adverse health effects, including mutagenetic and carcinogenic effects, whereas Pb mainly causes hematological, gastrointestinal and neurological dysfunctions, with children being particularly sensible (Winship, 1987; Lockitch, 1993; Mandal and Suzuki, 2002; Sundar and Chakravarty, 2010).

Concentrations of Sb and As in non-contaminated soils are typically below 10 mg kg^{-1} (Adriano, 1986; Fitz and Wenzel, 2002; Wilson et al., 2010). Lead is present at concentrations less than 20 mg kg^{-1} in soils of remote or recently settled areas, but elsewhere a general low-level contamination has raised concentrations overall to 30–100 mg kg^{-1} (Alloway, 1995). In mining-affected areas the soil concentrations of these toxic elements can be increased up to three orders of magnitude, mainly in the close environs of mine dumps or mineral processing facilities (Alloway, 1995; Okkenhaug et al., 2011; Hiller et al., 2012). Places impacted by the exploitation of deposits containing

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http://dx.doi.org/10.1016/j.scitotenv.2012.09.023

such elements constitute very hazardous settings, especially when located in agricultural areas. Except for occupational exposure, dietary intake of contaminated food has become the main route for human intake of toxic elements (Sharma et al., 2007). The study of the environmental status of this kind of scenarios is, therefore, crucial to establish the current and eventual environmental and health impacts and to assess the right measures to be undertaken in order to minimize such impacts.

The main objectives of this work are: a) to perform the environmental characterization of agricultural soils impacted by the former exploitation of an arsenical lead-antimony deposit, and b) to study the cultivated and spontaneously growing plants of this area so as to evaluate the toxic element phytoavailability and the consequent environmental and health implications.

2. Materials and methods

2.1. Study area

The studied mining area is located 1 km west of Losacio village in the north-west of the Zamora province (Spain) where the former Clara mine is situated. This mine belongs to the Losacio vein field and corresponds to a hydrothermal Pb–Sb–Ag-rich deposit worked intermittently from the thirties of the XIX century until about the middle of the XX century. Mineralization is present in quartz veins hosted in leucogranites and andalusite schists. The mineral association is mainly composed of galena (PbS), stibnite (Sb_2S_3), sphalerite (ZnS), cerusite ($PbCO_3$), pyromorphite ($Pb_5(PO_4)_3Cl$), mimetite ($Pb_5(AsO_4)_3Cl$), pyrolusite (MnO_2) and tourmaline ($NaAl_9(BO_3)_3Si_6O_{21}(OH)$). This mine exploitation generated a volume of wastes of about 1000 m^3. Nowadays, in this area there are hardly visible vestiges of the past mining activities; the mine pits have been covered and only some mineral wastes appear disseminated on the land.

2.2. Sampling

Soil and plant sampling was carried out in an agricultural field located near the covered mine pits. Wheat (*Triticum aestivum* L.) is the crop cultivated in this area. Plant species growing spontaneously are also present in this field. These plants include mainly perennial species (*Andryala ragusina* L., *Campanula rapunculus* L., *Carduus tenuiflorus* Boiss. et Reut, *Centaurea paniculata* Lam., *Dactylis glomerata* L., *Lavandula stoechas* L., *Santolina rosmarinifolia* L., *Thymus mastichina* L. and *Thymus zygis* L.), and also some annual species (*Echium plantagineum* L., *Eryngium campestre* L., *Lolium strictum* C. Presl. and *Papaver rhoeas* L.).

Soil collection was carried out at 0, 10, 25, 50 and 75 m from the mine pits. Ten different samples were taken at each mentioned sampling distance. A 3-cm diameter core sampler was used for the soil profile sampling in the depth up to 60 cm. Samples at the depths of 0–10, 10–20, 20–30, 30–40, 40–50 and 50–60 cm were collected. Single composite samples corresponding to the different soil depths were generated for each of the indicated distances. These soil samples were air-dried and sieved through a 2-mm screen prior to subsequent characterization.

Plant sampling was performed at the same mentioned distances from the mine pits and involved collecting the roots and the aerial parts of the cultivated and spontaneously growing plants. At least ten plant specimens of the herbaceous species and three of the woody species were collected at the different sampling distances. Plant samples were separated into above-ground tissues and roots. Above-ground tissues were also separated into shoots and grains in the case of wheat, and 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 distances from the mine pits of 0, 25 and 75 m were subjected to physico-chemical and mineralogical characterization. The main physico-chemical soil properties (Table 1) 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 derived by 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), available P was derived following the method of Olsen et al. (1954), and particle size distribution was analyzed by the pipette method (Tan, 1996). The mineralogical composition of powder soil samples was determined by X-ray diffraction (XRD) using a Philips 1710 diffractometer with the Cu Kα radiation.

2.4. Soil total and soluble contents of Sb, As and Pb

All the collected soil samples were analyzed for the total and soluble contents of Sb, As and Pb. For the determination of the total element concentrations finely ground soil samples were digested in triplicate with aqua regia, using a Milestone Ethos Plus microwave oven working

Table 1
Soil physico-chemical characteristics. (Concentration values are reported in a dry weight (DW) basis.)

Distance (m)	Depth (cm)	pH	OM (%)	Total free Fe_2O_3 (%)	$CaCO_3$ (%)	Clay (%)	Silt (%)	Sand (%)	CEC (cmol(+) kg^{-1})	Available P (mg kg^{-1})
0	0–10	7.6	2.6	2.6	3.4	16.3	20.7	63.0	8.6	18.7
0	10–20	7.8	1.8	3.7	4.0	16.8	21.5	61.7	8.5	19.2
0	20–30	7.8	1.6	3.8	4.5	16.7	21.8	61.5	8.5	28.1
0	30–40	7.9	1.5	3.7	4.5	15.4	18.9	65.7	8.0	13.3
0	40–50	8.0	0.62	2.3	2.4	13.4	15.5	71.1	6.8	10.6
0	50–60	8.0	0.40	1.6	1.7	13.2	15.8	71.1	7.1	13.8
25	0–10	6.6	1.3	2.0	n.d.	12.8	16.1	71.1	8.0	29.1
25	10–20	6.8	1.1	2.8	n.d.	12.3	15.3	72.4	8.9	23.1
25	20–30	7.2	1.0	3.0	0.60	13.0	15.9	71.1	8.4	18.6
25	30–40	7.5	1.0	2.9	1.1	12.2	15.1	72.6	7.1	19.0
25	40–50	7.8	0.52	2.5	1.4	9.8	14.1	76.0	6.2	11.9
25	50–60	7.7	0.71	2.9	1.1	9.9	15.0	75.0	8.2	15.0
75	0–10	7.1	0.97	1.8	n.d.	10.6	15.7	73.7	6.8	12.7
75	10–20	7.3	0.91	2.6	n.d.	10.5	17.0	72.5	6.9	12.2
75	20–30	7.4	0.73	2.8	n.d.	12.0	21.5	66.5	6.4	6.0
75	30–40	7.4	0.35	3.6	n.d.	13.0	21.6	65.4	5.6	8.4
75	40–50	7.5	0.32	3.6	n.d.	14.3	25.0	60.7	5.8	4.2