Journal of Geochemical Exploration 123 (2012) 109–113

Contents lists available at SciVerse ScienceDirect

Journal of Geochemical Exploration

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

Accumulation of Pb and Zn in *Bidens triplinervia* and *Senecio* sp. spontaneous species from mine spoils in Peru and their potential use in phytoremediation

Jaume Bech [a], Paola Duran [a,b], Núria Roca [a,c,*], Wilfredo Poma [d], Isidoro Sánchez [d], Luis Roca-Pérez [e], Rafael Boluda [e], Juan Barceló [f], Charlotte Poschenrieder [f]

[a] Soil Science Laboratory, Faculty of Biology, Universitat de Barcelona, Avda Diagonal 645, 08028 Barcelona, Spain
[b] Center of Plant, Soil Interaction and Natural Resources Biotechnology, Scientific and Technological Bioresource Nucleus, Universidad de la Frontera, Avda. Francisco Salazar 01145, Temuco, Chile
[c] Faculty of Agronomy, Universidad Nacional del Centro de la Provincia de Buenos Aires, CC 47, 7300 Azul, Argentina
[d] Universidad Nacional de Cajamarca, Perú. Av. Atahualpa Nº 1050, Cajamarca, Peru
[e] Plant Biology Department, University of Valencia Spain, Av. Vicent Andrés Estellés, s/n, 46100 Burjassot, Valencia, Spain
[f] Plant Physiology Laboratory, Bioscience Faculty, Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain

ARTICLE INFO

Article history:
Received 5 December 2011
Accepted 22 June 2012
Available online 29 June 2012

Keywords:
Soil heavy metals
Metal mine tailing
Phytoextraction
Phytoimmobilisation
Hyperaccumulator plants

ABSTRACT

Heavy metal toxicity has become a global concern due to the ever-increasing contamination of soil, water and crops. Until recent decades little has been known about the remediation of mining sites using spontaneous plants in Latin America. Soil and plant samples were taken in Peru, at a polymetallic mine (mainly silver, lead and copper) in Cajamarca Province, Hualgayoc district. Top soils (0–20 cm) were analyzed for physical and chemical properties by standard methods. Total Pb and Zn concentrations in top soils were determined by ICP-OES. Similar metals in plants were analyzed separately (aerial and root system). Ti content was used as an indicator for contamination of plant samples with soil particles. Translocation Factor (TF) and Shoot Accumulation Factor (SAF) were determined to assess the tolerance strategies developed by these species and to evaluate their potential for phytoremediation purposes. The non polluted soils had near neutral pH (6.8 ± 0.1), a great content of organic carbon (42 ± 4.0 g kg^{-1}) and a silt loamy texture. According to the total metal concentrations, the polluted soils exceeded toxicity thresholds; large Pb ($13{,}105 \pm 3147$ mg Pb kg^{-1}) and Zn ($28{,}393 \pm 3458$ mg Zn kg^{-1}) concentrations were detected. Unusually elevated concentrations of these metals were detected in roots of *Bidens triplinervia* L. (e.g. up to 5180 mg Pb kg^{-1} and 9900 mg Zn kg^{-1}) while *Senecio* sp. accumulated more heavy metals in shoots (e.g. up to 4250 mg Pb kg^{-1} and 3870 mg Zn kg^{-1}). The TF values were <1 in *B. triplinervia* and >1 in *Senecio* sp., while the SAF were <1 in both species collected in contaminated soils. *B. triplinervia* can be considered potentially useful for phytostabilization due to its capacity to restrict the accumulation of elevated amounts of Pb and Zn to the roots, while *Senecio* sp. could be utilized for phytoextraction technologies. Moreover, these plants showed an elevated transfer factor and grew in the presence of other toxic metals. The present study, to the best of our knowledge, is the first report on the metal accumulation in roots of *B. triplinervia* and provides a pioneer contribution to the very small volume of data available on the potential use of native plant species from contaminated sites in phytostabilization and phytoremediation technologies.

1. Introduction

Soil pollution by trace elements due to mining and smelting activities is a worldwide problem. This large legacy of polluted and degraded soils requires reclamation in order to prevent the entrance of potentially toxic trace elements into the food chain. Conventional techniques that are used for remediation for contaminated soil are costly, disruptive and labor intensive (Raskin and Ensley, 2000). Recently there is considerable interest in developing sustainable, cost-effective phytotechnologies for remediation of heavy metal-contaminated soils and water (Sainger et al., 2011). Metal mine tailings are usually covered by poorly structured soils, have deficient availability of essential nutrients, and contain potentially toxic levels of several trace elements. These mine tailings are potential sources of pollution due to wind and water erosion. Efforts to restore a vegetation cover can benefit stabilization and pollution control, and improve aesthetical aspects (Deng et al., 2006; Wong, 2003; Wong and Bradshaw, 2002). Therefore, the use of plants to remediate hazardous soils is considered as a highly promising approach for improving the environmental quality of the site (Mench

* Corresponding author.
E-mail addresses: jaumebechborras@gmail.com (J. Bech), paoladurancuevas@gmail.com (P. Duran), nroca@ub.edu, nuria@faa.unicen.edu.ar (N. Roca), wilfredopomarojas@yahoo.es (W. Poma), svisidoro@yahoo.com (I. Sánchez), luis.roca@uv.es (L. Roca-Pérez), rafael.boluda@uv.es (R. Boluda), juan.barcelo@uab.es (J. Barceló), Charlotte.poschenrieder@uab.es (C. Poschenrieder).

0375-6742/$ – see front matter
doi:10.1016/j.gexplo.2012.06.021

et al., 2009). Two major options can be envisaged, phytoextraction and phytostabilization.

Efficient phytoextraction requires plant species combining both high metal tolerance and elevated capacity for metal uptake and metal translocation to easily harvestable plant organs (e.g. shoots). Among plant species, there are large differences in the capacity to translocate and tolerate high concentrations of trace elements in the shoots. Most extreme behavior is displayed by metal hyperaccumulator plants. Hyperaccumulators are plant species able to concentrate and tolerate extremely high metal concentrations in their shoots; e.g. more than 1% of Zn or Ni or 0.1% of Pb or Cd (Baker et al., 2000). Moreover, hyperaccumulators are characterized by: a) a shoot to root metal concentration ratio (i.e., the translocation factor, TF) of more than one (Sun et al., 2008) and b) a shoot to soil metal concentration ratio (i.e., the shoot accumulation factor, SAF) of more than one (Vyslouzilova et al., 2003). Over 500 plant species comprising of 101 families have been reported as hyperaccumulators, including members of the Asteraceae, Brassicaceae, Caryophyllaceae, Cyperaceae, Cumouniaceae, Fabaceae, Flacourtiaceae, Lamiaceae, Poaceae, Violaceae and Euphobiaceae (Sarma, 2011). Metal hyperaccumlating plant species have attracted considerable research interest during the last years because of their evident interest for cleaning contaminated soils (Rascio and Navari-Izzo, 2011).

Plants growing on naturally metal-enriched soils are of particular interest in this perspective, since they are genetically tolerant to high metal concentrations and efficient excluders (Bech et al., 2012). These species store the excessive levels of trace elements that may enter in their roots, thereby protecting the more sensitive photosynthetic tissues from toxicity. Low levels for both shoot to root and shoot to soil element ratios are the consequence of this behavior (Caille et al., 2005). Excluders may become useful for phytostabilization purpose. This technique does not remove the excess of trace elements, but by fixing the elements in the roots, the rhizosphere soil pollution spread is limited. Phytostabilisation requires metal tolerant species that are efficient in both rapid coverage of the polluted soil and exclusion of metals from plant parts that are consumed by herbivores (Mench et al., 2009; Vangronsveld et al., 2009).

All phytoremediation techniques to be efficient in practice require plant species that are not only tolerant to the target soil's ionic environment but are also adapted to the prevailing local climate conditions. The use of native plants for phytoremediation can be a useful option because these plants are better adapted to the environmental conditions of the region than plants introduced from other environments (Antonsiewicz et al., 2008; Frerot et al., 2006). Therefore, plants that spontaneously grow on mine spoils are potential sources of germplasm for phytoremediation purposes (Bech et al., 2002). The Peruvian Andes are very rich in ore deposits (Cardozo and Cedillo, 1990) and an important mining activity has developed there. Plant screening in South American mining areas has already identified some potentially useful species (Orchard et al., 2009). Nonetheless, the metallophyte flora most of the mining areas in this region are still poorly explored.

Hualgayoc is a complex mining district in the Central Andes characterized by the influence of many superimposed geologic events and ore-forming processes, removed by early mining (Canchaya, 1990). Nowadays, many polymetallic (i.e. Zn, Pb and Cu) mines are currently being operated by individual small companies. Therefore, public concern over soil and water contamination by heavy metals around the mining district complex has been growing (Arana, 2005). Based on a first study, *Plantago orbignyana* Steinheil from this site has been suggested as Pb hyperaccumulator due to its ability to accumulate more than 1000 mg Pb kg^{-1} in the shoots with TF and BF values greater than one (Bech et al., 2012). Several factors make field work in this zone extremely difficult. Among those, the difficult accessibility to the mine, remotely located at an altitude of 3677 m in the Andes, deserves special mention. Due to this difficult accessibility only few metal-tolerant plants with potential application to this mining area have been sampled and analyzed. A more detailed study of plant species with the potential for phytoremediation is necessary to better characterize metal-tolerant species from this site with potential application in phytoremediation of this mining area. The purpose of the present study was to identify metal accumulation patterns in native species in the Hualgayoc mining area in order to make a first evaluation of their potential usefulness in phytoremediation.

2. Materials and methods

2.1. Site description and collection of samples

The polymetallic Carolina mine is located in the Hualgayoc district of the Cajamarca region in the Peruvian Andes (latitude 6°45′57″ S, longitude 78°37′08″ W and altitude of 3853 m above sea level). The Hualgayoc district is characterized by the predominance of calcareous sediments from lower Albian to Turonian. However, almost all of the mantos in Hualgayoc are hosted by Albian sediments. All of these sedimentary sequences were folded into a series of anticlines and synclines during tertiary orogenesis. The folding of the area was accompanied by faulting and fracturing. Volcanic rocks of the Upper Cretaceous and Tertiary age also crop out, especially on the west side of the district. The area has a number of stocks, sills, and dikes of basic to intermediate composition (Canchaya, 1990). On the basis of geometric and mineralogical characteristics, the manto of the Carolina mine is characterized by ores in the form of massive bodies, lenses, concordant accumulations, and short veinlets. These mantos are composed essentially of pyrite, sphalerite, and galena. Additionally, the mine was rich in silver at the intersection of cross-cutting veins (Canchaya, 1990). However, the hydrothermal alteration of host rocks was very weak or absent.

The climate is cold and wet, which is typical for equatorial orobiomes (Walter and Breckle, 1984). The average annual temperature is 7.4 °C; in fact, the monthly mean temperature is almost constant. The daily temperature difference is about 10 °C. Average annual rainfall is 1448 mm in the region, distributed mainly from January to April, whereas a drought period typically occurs from June to August.

The studied area is predominately populated by *Stipa ichu* Ruiz & Pavon (i.e., "ichu") and other grasses, such as *Plantago* spp., *Senecio* spp., *Bidens* spp., *Sonchus oleraceus* L. and *Lepidium bipinnatifidum* Desv. Endemic Andean shrubs, such as *Polylepis racemosa* Ruiz & Pavon (i.e., "quinoa") and *Baccharis latifolia* Ruiz & Pav Pers., were observed.

The impact of the mining activity is indicated by the changes in species composition and the density of the vegetation cover around the mine. Two sampling sites, reference site and polluted site, as assessed by their visual aspect, were chosen according to the following selection criteria: vegetation cover, distance to the mine and predominant direction of wind. At each site, a representative unique volume per soil samples (0–20 cm depth) was taken and 2 kg sub-sample of sample was taken back to laboratory for sample preparation and analysis. Plant samples were collected from the same sites as the soil samples. Two Asteraceae species were selected: *Bidens triplinervia* L. and *Senecio* sp. Three individual plants of each species were taken at reference site and four individual plants of each species were taken at polluted site.

2.2. Soil and plants analysis

The collected samples were transferred at ambient temperature to the laboratory, air dried for a week and then sieved through a 2 mm screen. After that, the 2 mm fraction of the soil samples was stored in paper bags, in dark, dry conditions, at room temperature, for subsequent analysis. Air dried and sieved soil samples were analyzed for pH, organic matter and calcium carbonate contents, electrical conductivity, and particle size fractions (Burt, 2004). The organic carbon content was determined by Walkley and Black's (1934) titration method. Calcium carbonate content was measured by treating the samples with hydrochloric acid and then measuring the evolved CO_2 manometrically. Soil acidity (pH) was measured using a suspension of soil in