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Assessment of metal availability to vegetation (*Betula pendula*) in Pb-Zn ore concentrate residues with different features

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Physicochemical characteristics and mineralogy of mining tailings determine metal availability to vegetation in abandoned mining sites.

Abstract

In this work, characterisation of several ore concentrate remains from an abandoned Pb-Zn mining factory was performed determining chemical and physical properties such as pH, organic carbon content, particle size distribution, total heavy metal content (Pb, Zn, Cu, As and Cd) as well as mineralogical composition which showed, in most cases, the oxidization of the parent ore material (mostly galena: PbS and sphalerite: ZnS) to more mobile fractions as anglesite ($PbSO_4$) and goslarite ($ZnSO_4$). Moreover, two operational defined extraction procedures commonly used in soil and sediment studies (first and second steps of BCR procedure and DTPA extraction protocol) were applied in the different mining wastes in order to study Pb and Zn mobility and likely bioavailability to *Betula pendula* growing on the same mining spoils, which presents lead and zinc contents in leaves over ten times background values.

Keywords: Heavy metals; Mining tailings; Availability; Mobility; *Betula pendula*

1. Introduction

Abandoned mining sites contain large quantities of mineral processing wastes stored in dumps that are characterised by high concentrations of heavy metals. These pollutants could be mobilised from spoil piles by weathering and leaching, but their release is exacerbated when mineralogical, physical and chemical changes in the ore material occurs (Ye et al., 2002; Álvarez et al., 2003; Marguí et al., 2004).

Besides knowledge of the total heavy-metal content as well as the main chemical, physical and mineralogical characteristics of the mining tailings, it is essential to have information on the mobility and bioavailability of the heavy metals in order to estimate the impact to the environment arising from these sources (Gäbler, 1997). Different approaches have been used to describe the mobility of heavy metals in soils and sediments but the easiest and most often used to assess heavy-metal mobility in soils and sediments are laboratory extraction experiments, both single and sequential extraction procedures (Quevauviller, 1998).

In sequential extraction procedures (EES) various extractants are applied successively (each extractant is chemically more active than the previous one) for selective fractionation of metals associated with the different constituents of the solid sample. Commonly, the first one or two extracted fractions are taken to be the labile pool of the metal that is potentially mobile and therefore bioavailable. Among EES procedures, one of the most widely used procedures is the three-step extraction proposed by the European Community Bureau of Reference (BCR), now the Standard Measurements and Testing Programme of the European Community,

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which has been successfully applied to a large variety of matrices (Sahuquillo et al., 2003; Mossop and Davidson, 2003).

Otherwise, single extraction procedures using chelating agents (usually EDTA or DTPA) are also used at present for determining plant-available trace elements in soils and sediments (Ye et al., 2002; Stephens et al., 2001).

Because of their capacity to act as efficient interceptors and accumulators of chemicals, plants are widely employed as passive monitors in areas contaminated by heavy metals (Álvarez et al., 2003; Fernández and Cerballeria, 2002; Sánchez et al., 1998). Thus, combination of data from extraction procedures and analysis of plants growing on metal contaminated sites provides a good basis for identifying the input of metals into the environment.

In the present work, chemical and physical properties including pH, organic carbon content, particle size distribution, total heavy metal concentrations (Pb, Zn, Cu, As and Cd) and mineralogical composition were determined in several mine tailing samples from an old Pb-Zn treatment factory, to study the potential mobility of the metals. The presence of chemicals and residues from the ore processing operations, as well as weathering, can change the parent ore material composition and therefore the mobility and availability of the metals.

Statistical analysis of the collected data, carried out with principal component analysis and cluster analysis methods, revealed existing similarities or differences among the different mining tailings of concern.

On the other hand, the possibility of using two operationally defined procedures commonly used to assess metal mobility and availability in soils and sediments (the first two extractions of the BCR protocol and the DTPA procedure) was also investigated by correlating extracted metals using these procedures and accumulated metals in a plant species (*Betula pendula*) grown in the same mining spoils. In previous works, *Betula pendula* has been often found on soils contaminated with metals and has shown tolerance to zinc and lead (Kopponen et al., 2001). Accordingly, the usefulness of this birch as Pb and Zn bio-indicator has also been tested.

The aim of the present work is to investigate, under field conditions, the effect of the form in which metals are present in the mine spoils on their mobility and bioavailability to vegetation specimens.

2. Experimental

2.1. Area of study and sampling

The study was performed in an abandoned Pb-Zn mining area located in the northern part of Spain (Pyrenean Range, Aran Valley) where important lead-zinc ore dumps are found (Fig. 1).

The extraction work from the mines (Victoria Mine and Liat Mine) was carried out underground, and the mineral was transported by overhead cables and trucks to a treatment factory placed close to the village of Les (Pontaut factory). The "tout-venant" (mostly composed by galena, PbS and sphaleryte, ZnS) was treated by flotation techniques in order to obtain an enrichment of lead and zinc (Marques et al., 2003). Exploitation ended in the 1950's and ever since, mines and the areas affected by mining operations have not been reclaimed.

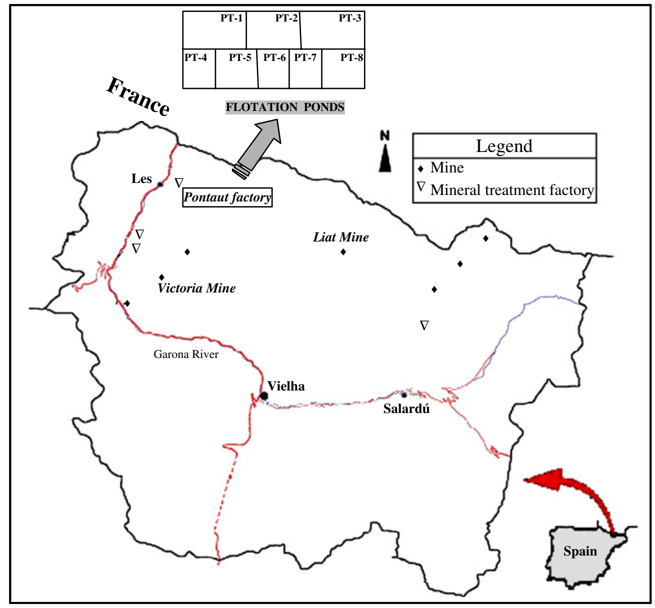

Fig. 1. Main mining sites at the Aran Valley Region. Location of the ore treatment factory and sampling sites (flotation ponds) related with the present work.

At present, at the Pontaut treatment factory, the remains of eight flotation ponds (approximately 15 m^2 each one) are still full of the ore concentrate residues. Some spontaneous vegetation (such as *Betula pendula* species) has started the reforestation of the mining landfills placed in the area.

Sampling of the mining wastes was carried out specifically in each of these eight flotation ponds (from PT-1 to PT-8). A typical feature of these kinds of spoils is the high heavy metal content, mostly Pb and Zn, and also the presence of chemicals and residues from the ore processing operations which can produce possible changes in the parent ore material. Flotation tailings were collected using a polypropylene shovel, and subsequently transferred to clean polypropylene bags.

Sampling of vegetation specimens was carried out in early autumm (just before shedding) to assure maximum metal accumulation. Vegetation was very scarce on the dump, so only *Betula pendula* species were sampled at each pond. Leaves were sampled from the upper third of 1 to 5 plants and a composite sample was prepared for analysis. For comparison purposes, a sample of the same species was also collected in the surroundings, but far from the contaminated mining areas (blank sample).

All the vegetation specimens were stored in a clean, labelled, polyethylene bags, closed tightly, and kept in a plastic container to avoid contamination during transportation.

2.2. Materials and methods

2.2.1. Vegetation specimens

Once at the laboratory, the mixed leaf samples were washed thoroughly with deionised water to remove superficial dust and oven-dried at 55 ± 5 °C for 24 h. To reduce particle size they were ground in an agate ball mixer mill using a grinding time in the range 2–5 min. Once plants were powdered and dried, they were kept in labelled capped polypropylene flasks until analysis.

Atomic absorption (FAAS, ETAAS) and atomic emission (ICP-OES, ICP-MS) techniques combined with wet or dry ashing procedures are commonly used to determine various metal concentrations in vegetation specimens. However, energy-dispersive X-ray techniques (EDXRF) have been proven useful for metal determinations in environmental samples such as plants (Potts et al., 2002; Anjos et al., 2002). In this work, a procedure using EDXRF is