Ecological Engineering 58 (2013) 84–90

Contents lists available at SciVerse ScienceDirect

Ecological Engineering

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

Short communication

# Assessment of metal(loid)s availability and their uptake by *Pinus halepensis* in a Mediterranean forest impacted by abandoned tailings

Isabel Párraga-Aguado[a], José. Álvarez-Rogel[a], María Nazaret González-Alcaraz[a], Francisco J. Jiménez-Cárceles[b], Héctor M. Conesa[a,*]

[a] *Área de Edafología y Química Agrícola, Dept. Ciencia y Tecnología Agraria, Universidad Politécnica de Cartagena, Paseo Alfonso XIII, 52–30203 Cartagena, Spain*
[b] *Biocyma, Consultora en Medio Ambiente y Calidad, S.L. C/Acisclo Díaz, N°9 4°K, 30005 Murcia, Spain*

ARTICLE INFO

*Article history:*
Received 10 December 2012
Received in revised form 15 April 2013
Accepted 8 June 2013

*Keywords:*
Mining contamination
Semiarid climate
Phytostabilisation
*Pinus halepensis*

ABSTRACT

Tailings are frequently source of pollution in mining areas due to the spread of metal(loid)s from their bare surfaces via wind, water run-off and/or leaching. For this reason, areas surrounding tailings may be affected by high concentrations of those toxic chemical elements. The aim of this study was to determine the influence of soil parameters on metal availability in a Mediterranean forest affected by mining contamination and the potential employment of *Pinus halepensis* as a suitable plant species for phytostabilising mining polluted sites under semiarid climates. Five tailing sites, including their surroundings were selected. At the same sampling area, additional soil samples were taken in less impacted zones (up to 1 km and 3 km far from tailings). The highest total concentrations occurred indistinctly at some forest samples closed to tailings (e.g. ~12,000 mg $kg^{-1}$ Pb) or tailing ones (~790 mg $kg^{-1}$ As). The alkaline soil pH and some carbonate minerals conditions low $CaCl_2$-extractable metal(loid) concentrations and therefore low risk of pollutants leaching. $CaCl_2$-extractable As and metal concentrations did not correlate with the corresponding concentrations in pine needles indicating that this procedure might not be suitable to predict metal(loid) availability in pine trees. Needles of pine trees from the less impacted areas showed lower Mn and Zn concentrations (40–100 mg $kg^{-1}$ Mn, 25–55 mg $kg^{-1}$ Zn) in relation with the ones taken from the tailings. *P. halepensis* Miller looks a suitable plant species to be employed in the phytostabilisation of tailings due to the higher root systems, which may provided a better soil retention, and its relative low metal accumulation.



## 1. Introduction

Mining contamination is considered a critical issue in many sites worldwide due to its negative effects on environment (Conesa and Schulin, 2010). Mine tailings are known to produce most of the environmental impacts in former mining sites due to the spread of metal(loid)s enriched particles from their bare surfaces by via wind, water run-off and/or leaching. In some cases, mining contamination may reach regional scales affecting urban areas, agricultural lands or ecological protected sites (García-Lorenzo et al., 2012). This may increase the risk of transferring pollutants into food chain. For this reason, it is necessary to keep the environmental risks of these areas under a safety level and to perform a periodic monitoring of the geochemistry of the pollutants, not only at the tailing sites but also at their surroundings. Soil parameters such as pH, Eh, organic compounds, mineralogy or electrical conductivity have been shown to play an important role in the metal(loid) spetiation and therefore, at their uptake by biota (María-Cervantes et al., 2010).

Phytostabilisation (using plants to immobilise metal(loid)s) have been proposed as a feasible tool to effect the surface stabilisation of mine tailings under semiarid climate (Mendez and Maier, 2008). For this purpose, suitable plant species must show good adaptation to drought, metal(loid)s soil concentrations, salinity or low metal(loid) accumulation into shoots. In order to meet these requirements, the employment of indigenous plant species seems a good alternative (Rufo and De la Fuente, 2010). The former Cartagena-La Union Mining District (Supplementary material, Fig. SM1) located at Southern Spain has been widely researched for dynamics of metal(loid) contamination (Martínez-Sánchez et al., 2008) and emerging soil remediation low cost technologies, including phytostabilisation (Conesa and Schulin, 2010). Research on plant candidates for the in situ phytostabilisation has proposed the use of grasses (e.g. *Lygeum spartum* L.,

* Corresponding author. Tel.: +34 968327034.
*E-mail address:* hector.conesa@upct.es (H.M. Conesa).

0925-8574/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.ecoleng.2013.06.013

*Piptatherum miliaceum* (L.) Cosson), halophyte (e.g. *Arthrocnemum macrostachyum* (Moric.) Moris), weed (e.g. *Zygophyllum fabago* L.) or shrubs (e.g. *Dittrichia viscosa* (L.) Greuter) (Conesa et al., 2011; Martínez-Sánchez et al., 2012). According to Jefferson (2004) the main goal of a restoration project should be to recreate sustainable plant communities which reflect the diversity and composition of the surrounding natural plant communities. For this reason, the additional employment of tree species to the already listed plants would provide a better ecological-landscape assembling. For instance, *Pinus halepensis* Miller is a woody plant species which has been widely employed on the restoration of degraded semi-arid ecosystems in the Mediterranean area (Fuentes et al., 2007). In addition, pine tree species have been proposed to be used as bioindicators of metal(loid) availability in polluted sites (Sun et al., 2009).

The aim of this study was to determine the influence of soil parameters on metal availability in a Mediterranean forest affected by mining contamination and the potential employment of *P. halepensis* for monitoring metal pollution and phytostabilising mining polluted sites under semiarid climates.

## 2. Materials and methods

Sampling was conducted at a tailing disposal area located at the Cartagena-La Union Mining District. Five tailings, where *P. halepensis* grew spontaneously, were selected (T1–T5). In addition, the spread of contamination into the surrounding areas (Supplementary material, Fig. SM2) was evaluated by performing a sampling at the tailings' surroundings (F0), 100 m far from tailings (F1), up to 1 km (F2), and up to 3 km (F3). Tailing samples (T1–T5) were waste materials, F0 and F1 were soils developed on waste materials and F2 and F3 were natural soils. All forest (F) areas had at least 90% plant cover, mainly composed of *P. halepensis* Miller and other plant species typical from Mediterranean areas (e.g. *Rosmarinus officinalis* L., *Thymus hyemalis* Lange, *Chamaerops humilis* L., etc.). At each sampling site three or four composite samples were taken by mixing sub-samples from four points randomly distributed. Each sampled point corresponded with the rhizosphere of the pine trees.

Soil samples were air dried, sieved through 2 mm grain size, homogenised and stored in plastic bags prior to lab analysis. The particle size distribution was determined using the Bouyoucos densimeter method. Equivalent calcium carbonate was determined using Bernard calcimeter. Electrical conductivity and pH in the 1:5 (soil:water) extract were determined using a Crison Basic 30 conductivity metre and a Crison Basic 20 pH metre, respectively. In the sa me 1:5 extract, dissolved organic carbon was measured using an automatic TOC analyzer (TOC-VCSH Shimadzu). Organic carbon was determined by the oxidation of organic matter using potassium dichromate and total nitrogen was determined using the Kjeldahl method. To determine the total element concentrations sub-samples were ground and analysed by X-ray fluorescence (Bruker S4 Pioneer). An aliquot of these sub-samples was used for the determination of mineralogy by X-ray diffraction (Bruker D8 Advance spectrometer), respectively.

Plant available arsenic and metal (Cd, Cu, Mn, Pb and Zn) concentrations were measured after shaking 5 g soil sample in 50 ml 0.01 M $CaCl_2$ solution for 2 h (González et al., 2011). The resulting extracts were filtered through nylon membrane 0.45 μm syringe filters (Albet-JNY) and measured by ICP-MS (Agilent 7500A, detection limit 0.002 mg $L^{-1}$)

At each sampling site pine trees of similar size (3–4 m height) were chosen. From each selected pine, three or four samples of adult needles were taken. The needles were washed with distilled water, dried at 65 °C for 72 h, and then, ground. An aliquot 0.5 g was incinerated during 5 h at 450 °C prior to a redilution using concentrated nitric acid. Arsenic and metal concentrations (Cd, Cu, Mn, Pb and Zn) were measured by ICP-MS (Agilent 7500A, detection limit 0.002 mg $L^{-1}$). Plant analyses were referenced using a CTA-VTL-2 certified material (Virginia tobacco leaves). The percentage of recoveries were 110% for As, 89% for Cd, 119% for Cu, 104% for Mn, 96% for Pb and 100% for Zn.

All the statistical analysis (ANOVA with Tukey-Test. Pearson's correlation) was carried out with SPSS 19.0.0 (SPSS, Chicago, IL, USA). The data were log-transformed when they did not meet the Levene test for homogeneity of variances. Differences at $p < 0.05$ level were considered significant. Principal component analysis (PCA) was performed using the 'CANOCO for Windows' programme v4.02 (ter Braak and Smilauer, 1999).

## 3. Results

### 3.1. Soil parameters and metal(loid) concentrations

Soil properties are shown in Fig. 1. The pH of all the samples was in the range of neutral-slightly alkaline soils (pH 7–8). The soil samples from forest zones showed lower electrical conductivity values (~0.3 dS $m^{-1}$) than the tailing ones (0.9–2.8 dS $m^{-1}$). Organic carbon (OC) total nitrogen (TN), and dissolved organic carbon (DOC) values for tailing samples were about the half of those obtained at forest samples. Tailing samples had sand percentages close to 80%, while F-samples were below 70% for F0 and F1 and of around 40% for F2 and F3. The total concentrations of the studied elements are shown in Table 1. The highest total concentrations occurred indistinctly at some forest samples (especially for F1, ~12,000 mg $kg^{-1}$ Pb and ~10,700 mg $kg^{-1}$ Zn) or tailing ones (~790 mg $kg^{-1}$ As for T2 or 115 mg $kg^{-1}$ Cu for T1). F2 and F3 showed the lowest metal(oid) concentrations specially for As, Cu, Mn and Zn ($p < 0.05$). The highest concentrations for $CaCl_2$-extractable metals occurred for Mn and Zn indistinctly at tailings (0.552 mg $kg^{-1}$ Mn for T2) or forest samples (2.506 mg $kg^{-1}$ Zn for F1).

As it is shown in Fig. 2, and according to the soil parameters measured, samples were organised into three groups: a first one, composed of tailing samples, was mainly defined by Factor 1, showing increasing sand percentages, higher electrical conductivity and metal and As concentrations (except $CaCl_2$-extractable Cu); a second one, defined by Factor 2, was formed by F0 and F1 samples (the ones from the tailings' surroundings), showing increasing $CaCl_2$-extractable metal (Cd, Cu, Pb and Zn) concentrations and organic matter content; and a third one, which included F2 and F3 samples (1–3 km from tailings), was mainly defined by Factor 1 but opposite to tailing samples, showing higher percentage of $CaCO_3$ and clay content.

### 3.2. Plant metal uptake and implications for phytostabilisation

Arsenic and metal concentrations in pine needles are shown at Fig. 3. Needles of the forest sampled trees (F0–F1) showed lower Mn and Zn concentrations (40–100 mg $kg^{-1}$ Mn, 25–55 mg $kg^{-1}$ Zn) than the ones taken from the tailings (up to 320 mg $kg^{-1}$ Mn, 80–130 mg $kg^{-1}$ Zn). For Cu, all the samples were in the same range (~2 mg $kg^{-1}$) except the ones from T5 which showed 3.5 mg $kg^{-1}$ Cu. In relation to Pb, pine needles from the forest areas corresponding to F1, F2 and F3 had concentrations of around 4 mg $kg^{-1}$, which significantly differed from the ones obtained at the tailings (from 7 to 28 mg $kg^{-1}$) and F0 (~20 mg $kg^{-1}$).