



## Chemical speciation and mobilization of copper and zinc in naturally contaminated mine soils with citric and tartaric acids

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### HIGHLIGHTS

- ▶ Effects of citric and tartaric acid on metal mobilization in contaminated mine soils.
- ▶ Metal desorption was related to the type of organic acid and its concentration.
- ▶ Decreasing pH and dissolution of oxides by organic acids determined metal desorption.
- ▶ Low concentrations of organic acids did not increase metal mobilization.
- ▶ Citric acid at high concentrations (5–10 mM) remarkably promoted Cu mobilization.

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### ABSTRACT

A one-step extraction procedure and a leaching column experiment were performed to assess the effects of citric and tartaric acids on Cu and Zn mobilization in naturally contaminated mine soils to facilitate assisted phytoextraction. A speciation modeling of the soil solution and the metal fractionation of soils were performed to elucidate the chemical processes that affected metal desorption by organic acids. Different extracting solutions were prepared, all of which contained 0.01 M KNO<sub>3</sub> and different concentrations of organic acids: control without organic acids, 0.5 mM citric, 0.5 mM tartaric, 10 mM citric, 10 mM tartaric, and 5 mM citric +5 mM tartaric. The results of the extraction procedure showed that higher concentrations of organic acids increased metal desorption, and citric acid was more effective at facilitating metal desorption than tartaric acid. Metal desorption was mainly influenced by the decreasing pH and the dissolution of Fe and Mn oxides, not by the formation of soluble metal–organic complexes as was predicted by the speciation modeling. The results of the column study reported that low concentrations of organic acids did not significantly increase metal mobilization and that higher doses were also not able to mobilize Zn. However, 5–10 mM citric acid significantly promoted Cu mobilization (from 1 mg kg<sup>-1</sup> in the control to 42 mg kg<sup>-1</sup> with 10 mM citric acid) and reduced the exchangeable (from 21 to 3 mg kg<sup>-1</sup>) and the Fe and Mn oxides (from 443 to 277 mg kg<sup>-1</sup>) fractions. Citric acid could efficiently facilitate assisted phytoextraction techniques.

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### 1. Introduction

Mining and smelting activities contribute significantly to metal contamination due to the discharge and dispersion of mine wastes into nearby agriculture soils, food crops and water ecosystems (Navarro et al., 2008). The accumulation of heavy metals in soil can negatively impact the health of humans and animals, plant growth and soil microbial activity (Vamerali et al., 2010).

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A promising strategy for remediating metal-contaminated sites involves phytoextraction, an *in situ* technique in which plants are used to remove pollutants from the environment (Vamerali et al., 2010). However, the slow desorption of metals in soils has been a major limitation for successful phytoextraction. The bioavailability of metals is affected by several soil factors, such as pH, cation exchange capacity, organic matter content, the speciation of the metal and the metal itself (Evangelou et al., 2007).

Phytoextraction can be improved by the addition of appropriate amendments or chelating agents to the soil to increase metal mobility and enhance its uptake by plants. Various synthetic chelating agents have been used in assisted phytoextraction studies. One of them is ethylenediaminetetraacetic acid (EDTA), which is

probably the most efficient chelating agent for enhancing metal uptake by plants (Blaylock et al., 1997). However, the slow degradation rate and the long persistence of EDTA in the soil could lead to an increased risk of groundwater pollution due to the leaching of metals; moreover, this compound could be toxic for plants and microorganisms (Evangelou et al., 2007).

Several compounds have been proposed as alternatives to EDTA and other synthetic chelating agents. These proposed compounds should be a compromise between their fast degradation and their ability to efficiently enhance phytoextraction. Among them, low-molecular-weight organic acids (LMWOAs) are natural compounds that originate from root exudates, microbial metabolites and the decomposition of soil organic matter (Jones, 1998). These easily biodegradable carboxylic acids, such as citric and tartaric acids, reduce soil pH and are capable of forming soluble complexes, thereby playing an important role in metal mobility and in the subsequent accumulation of metals in plants (Evangelou et al., 2007). However, several studies have observed low extraction efficiencies when these compounds have been applied at low doses because of their rapid biodegradation and their sorption onto soil particles (Evangelou et al., 2006, 2008; Liu et al., 2008). Although the effects of LMWOAs on metal desorption from soils with induced contamination have been widely studied (Qin et al., 2004; Evangelou et al., 2006, 2008; Nascimento, 2006; Schwab et al., 2008), there is limited information on the desorption behavior of metals from naturally contaminated soils with long aging times.

The aims of this study were to assess and compare through a one-step extraction procedure and a soil column experiment the effects of two natural LMWOAs, citric and tartaric acids, which are commonly present in soils, on Cu and Zn mobilization in naturally contaminated mine soils to facilitate future assisted phytoextraction techniques. This study also attempted to elucidate the main chemical processes that affect metal desorption by LMWOAs in these soils by means of speciation modeling using Visual Minteq and metal fractionation.

## 2. Material and methods

### 2.1. Soil characteristics

Two heavy metal-contaminated soils from the north of Madrid (Spain) were selected for this study. The first site was situated at the village Garganta de los Montes (G), which is close to a copper mine that was abandoned in 1965. The second site was situated in El Cuadron (C), where an old blende mine that was abandoned in 1862 is located. The soils at these site locations have been classified as humic and dystric cambisols by the FAO (Pastor et al., 2007).

Samples were collected at these sites from the top 20 cm of the soil and were air-dried and sieved to <2 mm for analysis. Soil samples were analyzed for oxidizable organic carbon (OXC) using the modified Walkley–Black procedure that was described by Nelson and Sommers (1996). The electrical conductivity (EC) and pH were analyzed in deionized water extracts (1:2.5 w/w). The cation exchange capacity (CEC) was determined using the barium chloride method adjusted to soil pH (Rhoades, 1982). Total Fe and Mn oxides were determined by performing three sequential extractions using an ascorbate-oxalate solution at 90–95 °C (Shuman, 1982). Amorphous Fe and Mn oxides were extracted using ammonium oxalate in the dark (Smith and Mitchell, 1987). The texture was determined using the Bouyoucos hydrometer method (Day, 1965). The point of zero net charge (PZNC) was measured using a KCl saturation method, which was previously described by Zelazny et al. (1996).

The total heavy metal content (Cu and Zn) in the soil samples was determined using microwave-assisted acid digestion with *aqua regia* (ISO 11466, 1995).

The metal concentrations in the soil extracts were determined by atomic absorption spectrophotometry (AAS) using a Perkin Elmer AAnalyst 400. Measurements were carried out in an air/acetylene flame (2 L min<sup>-1</sup> of acetylene and 17 L min<sup>-1</sup> of air). Single-element hollow cathode lamps were used at the corresponding wavelength (Cu: 324.8 nm; Zn: 213.9 nm; Fe: 248.3 nm; Mn: 279.5 nm) and slit width (Cu and Zn: 0.7 nm; Fe and Mn: 0.2 nm). Copper and Zn concentrations were directly measured in the extracts, whereas Fe and Mn were measured in a 0.2% calcium chloride solution to eliminate interferences. The element standard solutions used for calibration were prepared by suitable dilution of stock standard of 1000 mg L<sup>-1</sup> with the same extracting solutions used for the samples and blanks.

All analyses were performed in triplicate, and the values were adjusted for oven-dried (overnight at 105 °C) soil.

The characterization of the two types of soils is shown in Table 1. Both were slightly acidic, loamy sand and poor in organic matter. They also contained a large amount of Fe oxides and had low salinity and cation exchange capacity (CEC). Both soils possessed total concentrations of Cu that exceeded the European Union maximum permitted levels for agricultural soils that receive sewage sludge at pH 6–7 (50–140 mg kg<sup>-1</sup>; Council of the European Communities, 1986).

### 2.2. Total LMWOAs-extractable metals

To determine the total amount of metals that were extractable by LMWOAs, a one-step extraction procedure was performed on both soils as follows. First, a total of 5 g of soil samples was shaken for 48 h with 1 L of a solution that contained a background electrolyte (0.01 M KNO<sub>3</sub>) and different concentrations of citric and tartaric acids. Six different treatments were prepared for each soil, including without any organic acids (Control, pH 5.7), 0.5 mM citric acid (C0.5, pH 3.3), 0.5 mM tartaric acid (T0.5, pH 3.3), 10 mM citric acid (C10, pH 2.4), 10 mM tartaric acid (T10, pH 2.4), and 5 mM citric acid +5 mM tartaric acid (CT5, pH 2.4). Soil extracts were then filtered and analyzed for pH and metal concentrations (Cu and Zn). This experiment was performed in triplicate, and the values were adjusted for oven-dried soil.

**Table 1**  
Properties of the mine soils.

Characteristic <sup>a</sup>	G	C
Clay (%)	3.1	3.3
Silt (%)	18.8	17.3
Sand (%)	78.2	79.4
pH (1:2.5 w/w)	6.2	5.5
EC (dS m <sup>-1</sup> )	0.08	0.10
CEC (cmol <sub>c</sub> kg <sup>-1</sup> )	4.74	4.79
OXC (%)	0.74	1.37
PZNC	4.5	2.6
Total Fe oxides (g Fe kg <sup>-1</sup> )	11.9	7.31
Amorph. Fe ox. (g Fe kg <sup>-1</sup> )	2.04	1.11
Total Mn oxides (g Mn kg <sup>-1</sup> )	0.26	0.28
Amorph. Mn ox. (g Mn kg <sup>-1</sup> )	0.16	0.23
Total Cu (mg kg <sup>-1</sup> ) <sup>b</sup>	913	248
Total Zn (mg kg <sup>-1</sup> )	203	146

<sup>a</sup> Texture (Day, 1965); pH, EC: electrical conductivity (1:2.5 w/w); CEC: cation exchange capacity (Rhoades, 1982); OXC: oxidizable organic carbon (Nelson and Sommers, 1996); PZNC: point of zero net charge (Zelazny et al., 1996); Total Fe and Mn oxides (Shuman, 1982); Amorphous Fe and Mn oxides (Smith and Mitchell, 1987); Total Cu and Zn (ISO 11466, 1995).

<sup>b</sup> European Union limits (mg kg<sup>-1</sup>) for agricultural soils receiving sewage sludge (pH 6–7): Cu 50–140, Zn 150–300 (Council of the European Communities, 1986).

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