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Soluble organic carbon and pH of organic amendments affect metal mobility and chemical speciation in mine soils

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HIGHLIGHTS

- Manure can reduce metal availability due to high pH and degree of maturity.
- Manure could increase soluble Cu at high pH because of higher soluble organic carbon.
- Soluble Cu and organic carbon were minimum at pH 5.8–6.3, near pH of acid mine soils.
- Manure reduced soluble Zn as it always decreased with increasing pH.
- Manure reduced the predicted proportion of free metal ions in soil solution.

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ABSTRACT

We evaluated the effects of pH and soluble organic carbon affected by organic amendments on metal mobility to find out the optimal conditions for their application in the stabilization of metals in mine soils. Soil samples (pH 5.5–6.2) were mixed with 0, 30 and 60 t ha^{-1} of sheep–horse manure (pH 9.4) and pine bark compost (pH 5.7). A single-step extraction procedure was performed using 0.005 M $CaCl_2$ adjusted to pH 4.0–7.0 and metal speciation in soil solution was simulated using NICA-Donnan model. Sheep–horse manure reduced exchangeable metal concentrations (up to 71% Cu, 75% Zn) due to its high pH and degree of maturity, whereas pine bark increased them (32% Cu, 33% Zn). However, at increasing dose and hence pH, sheep–horse manure increased soluble Cu because of higher soluble organic carbon, whereas soluble Cu and organic carbon increased at increasing dose and correspondingly decreasing pH in pine bark and non-amended treatments. Near the native pH of these soils (at pH 5.8–6.3), with small doses of amendments, there was minimum soluble Cu and organic carbon. Pine bark also increased Zn solubility, whereas sheep–horse manure reduced it as soluble Zn always decreased with increasing pH. Sheep–horse manure also reduced the proportion of free metals in soil solution (from 41% to 4% Cu, from 97% to 94% Zn), which are considered to be more bioavailable than organic species. Sheep–horse manure amendment could be efficiently used for the stabilization of metals with low risk of leaching to groundwater at low doses and at relatively low pH, such as the native pH of mine soils.

1. Introduction

Mining activities are an important source of trace metals in the environment, due to the discharge and dispersion of mine wastes into nearby soils, crops and ecosystems (Navarro et al., 2008). The accumulation of these metals in soils—especially if they predominate in the soil solution or other available fractions—can be a potential concern for human and animal health through the food chain, reduces plant growth and microorganisms diversity and increases the risk of metals leaching to groundwater (De Vries et al., 2007).

The incorporation of organic amendments can stabilize metals in soil, reducing metal availability and mobility and therefore, their toxicity and transfer to other ecosystems (Kumpiene et al., 2008;

Abbreviations: AAS, atomic absorption spectrophotometry; DTPA, diethylenetriaminepentaacetic acid; E, soil of El Cuadron; EXC, humic extractable organic carbon; E0, non-amended El Cuadron soil; E30M, El Cuadron soil mixed with 30 t ha^{-1} of sheep–horse manure; E60M, El Cuadron soil mixed with 60 t ha^{-1} of sheep–horse manure; E30P, El Cuadron soil mixed with 30 t ha^{-1} of pine bark; E60P, El Cuadron soil mixed with 60 t ha^{-1} of pine bark; FA, fulvic acids carbon; G, soil of Garganta; G0, non-amended Garganta soil; G30M, Garganta soil mixed with 30 t ha^{-1} of sheep–horse manure; G60M, Garganta soil mixed with 60 t ha^{-1} of sheep–horse manure; G30P, Garganta soil mixed with 30 t ha^{-1} of pine bark; G60P, Garganta soil mixed with 60 t ha^{-1} of pine bark; HA, humic acids carbon; IR, infrared spectroscopy; M, sheep–horse manure; NMR, nuclear magnetic resonance; P, pine bark; PZNC, point of zero net charge; TEA, triethanolamine; TOC, total organic carbon; TOM, total organic matter; WHC, water holding capacity.

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Park et al., 2011). Metal availability is reduced due to its adsorption onto solid surfaces and the formation of stable complexes with humic substances, which provide an important number of functional groups, such as carboxylic (—COOH), hydroxylic (—OH) and phenolic (aromatic ring-OH), with high affinity for metals (Park et al., 2011). These processes depend on ionic strength, redox potential, dominant cations, soil type and degree of maturity of the organic matter, but pH is the most significant factor (Park et al., 2011; Walker et al., 2004).

However, the application to soil of organic materials rich in soluble organic carbon and with a large proportion of fulvic acids could increase metal mobility through the formation of soluble metal–organic complexes, facilitating metal uptake by plants and its transport to groundwater (Ashworth and Alloway, 2008; Bolan et al., 2003; Clemente et al., 2006; Schwab et al., 2007). Moreover, the mobility of metals through the formation of these soluble complexes is strongly related to soil pH; these organic amendments should be applied cautiously, especially at relatively high pH (Temminghoff et al., 1997; Wong et al., 2007; Zhou and Wong, 2001). Many studies have evaluated the influence of varying pH and soluble organic carbon provided by organic amendments on metal mobility, but most of them applied waste materials with high levels of metals, such as sewage sludge, which induced soil contamination (Ashworth and Alloway, 2008; Wong et al., 2007; Zhou and Wong, 2001). There are fewer studies of the use of organic amendments with low or moderate concentrations of metals, such as manure or pine bark, on naturally contaminated soils and there is also limited information about the effects of these materials on chemical speciation in soil solution.

Our previous work (Pérez-Esteban et al., 2012) evaluated the use of sheep–horse manure and pine bark compost on mine soils, reporting an increase of metal availability with pine bark and a considerable reduction with sheep–horse manure due to their effect on soil pH and the nature of their organic matter. However, this study also reported that both amendments increased the concentration of soluble Cu because of a large soluble organic carbon content, which could increase the risk of metal leaching and the toxicity for plants and soil organisms and what should be studied.

In the present work we aimed to study the effects of changes in pH and soluble organic carbon caused by the sheep–horse manure and pine bark amendments on metal mobility to find out the optimal conditions for their application in the stabilization of metals in mine soils. The chemical speciation of metals was simulated to provide more information about the dynamics of metals and soluble organic carbon in the soil solution.

2. Material and methods

2.1. Soil sampling

Two metal-contaminated soils from the Lozoya Valley (north of Madrid, Spain) were selected. The first soil was collected from the village of Garganta de los Montes (G), which is in close proximity to a copper mine abandoned in 1965 (40° 55′ 04″ N, 3° 40′ 24″ W). The second soil was collected from El Cuadron (E), where there is a zinc blende mine abandoned in 1862 (40° 56′ 36″ N, 3° 39′ 31″ W). Both soils have been classified as Dystric Cambisols (Food and Agriculture Organization, 1990).

Soil samples were collected with a stainless steel scoop within the top 20 cm from three different points around the mine dumps, and were composed of natural soil and deposited mine tailings. Samples were homogenized, air-dried for 5–6 days at room temperature and sieved to <2 mm for analysis and mixing with organic amendments.

Table 1 shows the main properties of these mine soils (expressed as equivalent dry weight). Both samples were slightly acidic, loamy sand, poor in organic matter and had low electrical conductivity (EC) and cation exchange capacity (CEC); they also contained high concentrations of Fe oxides and relatively high levels of metal contamination, especially of Cu. Although both soils exhibited similar soil texture, EC and CEC, soil G had lower total organic (TOC) content and higher pH value and Fe oxides content than soil E. Soil E had lower total concentrations of metals but higher levels of exchangeable Zn (see also G0 and E0 in Table 2) and Zn extracted with DTPA/TEA, what means a higher Zn availability in this soil, probably due to its lower pH and metal oxides content. Both soils possessed mainly pH-dependent surface sorption sites due to their small clay contents and large concentrations of metal oxides (Jiang et al., 2010). Soil E also exhibited a lower PZNC—pH value at which equal number of positive and negative charges coexist—than soil G, and therefore a higher density of negative sites and a lower variability of negative charges (Jiang et al., 2010), which might affect the sorption dynamics of organic substances and metals.

2.2. Organic amendments and preparation of mixtures

Two organic amendments were added to soils G and E: mature compost made of sheep (50% v/v) and horse (50%) manure (M); mature compost made of wood fibre (30%), *Sphagnum* peat (20%) and pine bark (50%) (P).

Table 1 also shows the main properties of these organic amendments (expressed as equivalent dry weight). The sheep–horse manure amendment had higher pH values, which could lead to a lower metal availability, and exhibited higher EC and lower TOC and humic extractable carbon (EXC) contents than pine bark. Sheep–horse manure also showed a greater humification ratio (HR) and proportion of humic acids (HA) and a lower proportion of fulvic acids (FA) and C:N ratio, which indicate a greater degree of maturity and stability than the pine bark amendment (Clemente et al., 2006). Total metal concentrations were very low in the pine bark amendment, whereas sheep–horse manure had a high Zn concentration, even greater than soil E and close to soil G. Thus, the application of sheep–horse manure should not be used to reduce Zn in soils with low levels of this metal. However, sheep–horse manure exhibited a small concentration of Zn extracted with DTPA/TEA, very low in comparison with the total concentration, and therefore this amendment may not contribute to increase Zn availability in soils.

In the previous study (Pérez-Esteban et al., 2012) an incubation experiment was conducted using mixtures of these soils and organic amendments, whose data and material have been reanalyzed for the present work. In that study ten different treatments were prepared with mixtures of each soil and either one of the amendments described above. The doses applied were 0, 30, and 60 tons of dry organic matter per hectare of soil. The amount of amendment (expressed as wet weight) mixed with soil in each treatment was calculated for a soil volume of 30 cm depth from the moisture and total organic matter (TOM) content of the amendment and the soil density (soil G: 1260 kg m^{-3}; soil E: 1150 m^{-3}). Soil G was mixed with 28.4 g (30 t ha^{-1}) and 56.8 g (60 t ha^{-1}) of sheep–horse manure per kg of soil, and with 14.4 g (30 t ha^{-1}) and 28.8 g (60 t ha^{-1}) of pine bark per kg of soil; soil E was mixed with 31.1 g (30 t ha^{-1}) and 62.3 g (60 t ha^{-1}) of sheep–horse manure, and with 15.8 g (30 t ha^{-1}) and 31.5 g (60 t ha^{-1}) of pine bark per kg of soil. Thus, treatments with the soil G were non-amended soil (G0), soil with 30 t ha^{-1} of sheep–horse manure compost (G30M), soil with 60 t ha^{-1} of sheep–horse manure (G60M), soil with 30 t ha^{-1} of pine bark compost (G30P), and soil with 60 t ha^{-1} of