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Research article

# A comparative study on the influence of different organic amendments on trace element mobility and microbial functionality of a polluted mine soil

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ABSTRACT

A mine soil heavily polluted with zinc and cadmium was employed to evaluate the capacity of organic amendments of different origin to simultaneously reduce soil trace element mobility and enhance soil microbial functionality. With this aim, four organic products, namely olive processing solid waste (OPSW), municipal solid waste compost (MSWC), leonardite and peat, were applied individually at different doses (0, 1, 2 and 5%) to mine soil under controlled laboratory conditions. Extraction studies and analysis of soil microbiological parameters (basal soil respiration and dehydrogenase, β-glucosidase, urease, arylsulfatase and acid and alkaline phosphatase activities) were performed to assess the effect of such amendments on soil restoration. Their ability to decrease mine soil mobile trace element contents followed the sequence MSWC > OPSW > peat > leonardite, with the former achieving reduction levels of 78 and 73% for Zn and Cd, respectively, when applied at a dose of 5%. This amendment also showed a good performance to restore soil microbial functionality. Thus, basal soil respiration and dehydrogenase, urease and alkaline phosphatase activities experienced increases of 187, 79, 42 and 26%, respectively, when mine soil was treated with 5% MSWC. Among tested organic products, MSWC proved to be the best amendment to perform both the chemical and the microbial soil remediation.



## 1. Introduction

Soil contamination with trace elements importantly affects soil quality, and seriously threatens the whole surrounding ecosystem, as surface and groundwater resources, flora and fauna, human health and even neighboring air quality can be impacted. Soil contamination with trace elements due to anthropogenic sources provokes the major environmental concerns (Alloway, 1995). Such sources primarily involve mining, energy generation from fossil fuels, metallurgical, electronics and chemical industries, agricultural activities and waste landfilling/incineration (Alloway, 1995; Hooda, 2010). Among these activities, mining operations are a very polluting point source, releasing high levels of trace elements in soils. Under such circumstances, soils result importantly degraded, with their ecological functions (nutrient cycling, water storage, microbial habitat, plant growth support, etc.) importantly impaired.

Diverse techniques have been suggested to rehabilitate soils with hazardous levels of trace elements, comprising both engineering approaches and chemical/biological methods that seek to either soil decontamination or soil stabilization (Vangronsveld and Cunningham, 1998). In site stabilization techniques based on the application of soil amendments are regarded as the most suitable low-cost alternative to remediate soils impacted by mining activities (Vangronsveld and Cunningham, 1998; Zanuzzi et al., 2013). Numerous products of inorganic or organic nature have been studied in this regard (e.g., Pérez de Mora et al., 2007; Beesley et al., 2010; Farrell and Jones, 2010; Janoš et al., 2010; Álvarez-Ayuso et al., 2013a). Of inorganic products, alkaline materials and some clay minerals have shown the best behavior in the immobilization of cationic trace elements, whereas metal (oxyhydr)oxides are generally the most appropriate to immobilize oxyanions. Organic products add exchange capacity to soils, greatly restricting the solubility of certain trace element cations by forming strong coordination complexes with them (McBride, 1994). However, their performance highly depends on their composition and stability (Albiach et al., 2000). Thus, in some instances organic materials can incorporate soluble organic compounds to soils with the

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concomitant mobilization of trace elements (Narwal and Singh, 1998; Shuman, 1998). Anyway, the application of organic amendments can entail other benefits to soils, such as providing a carbon energy source for soil microorganisms, increasing soil nutrients, improving soil water retention capacity and promoting plant growth (Albiach et al., 2000; Caravaca et al., 2002). Additionally, this practice represents a way of valorizing organic by-products (Burgos et al., 2010; Quaye et al., 2011).

Trace elements may negatively impact soil microbial functionality by acting on microbial communities and cellular activities or by directly affecting extracellular enzymes (Lee et al., 2009). Hence, the joint assessment of both issues, i.e. soil trace element mobility and soil microbial functionality, is essential to establish the actual effectiveness of soil stabilization treatments. Several studies have been performed in this regard evaluating different inorganic materials such as clay minerals, metal (oxyhydr)oxides, phosphates, zeolites and alkaline products (Garau et al., 2007, 2011; Lee et al., 2011; Tica et al., 2011; Sun et al., 2013; Abad-Valle et al., 2015, 2016). Concerning organic materials, most of the studies have been focused on their effectiveness to reduce trace element mobility (e.g., Shuman, 1998; Walker et al., 2004; Pérez de Mora et al., 2005; Alvarenga et al., 2009a; Beesley et al., 2010; Janoš et al., 2010; Branzini and Zubillaga, 2012; Abdelhafez et al., 2014; Pérez-Esteban et al., 2014), but only a few of them have considered their ability to simultaneously recover soil microbial functionality (Pérez de Mora et al., 2005, 2006; Alvarenga et al., 2008, 2009b; Burgos et al., 2010; Pardo et al., 2014).

The main aim of this work was to evaluate the application of different organic materials to amend a mine soil heavily polluted with trace elements, studying: a) their influence on trace element mobility, and b) their effect on soil microbial functions.

## 2. Materials and methods

### 2.1. Soil

The soil (Cambisol) employed in this study was collected from the Santa Manolita mining area (40°23′52″N, 5°32′3″W), located in El Losar del Barco village (Ávila, Spain). This mine exploited during the last century, up to the 70s, a Pb-Ag-Zn sulfide deposit belonging to the Central Iberian Zone. Its metallic mineral assemblage is composed of sphalerite (ZnS), galena (PbS) and some accessory minerals (arsenopyrite (FeAsS), chalcopyrite ($CuFeS_2$), pyrrhotite ($Fe_{(1-x)}S_{(x=0-0.17)}$) and pyrite ($FeS_2$)), occurring in quartz and carbonate veins hosted in biotitic granite. Mining operations generated important quantities of wastes mainly constituted by barren rocks and sphalerite. Previous studies carried out on the environmental characterization of this mining area have revealed high soil pollution with Zn and Cd (Álvarez-Ayuso et al., 2013b).

Mine soil was sampled from the 20 cm topsoil in the vicinity of the mine dressing plant location. The collected soil was air-dried, passed through a 2-mm mesh sieve and subsequently characterized. The main soil physicochemical properties analyzed were pseudo-total trace element concentrations, pH, electrical conductivity (EC), organic matter (OM), carbonate content, texture, total nitrogen, and available calcium, potassium and phosphorus. Pseudo-total trace element concentrations were determined by microwave aqua regia digestion at a temperature of 190 °C, and further analysis by coupled plasma-atomic emission spectrometry (ICP-AES) employing a Varian 720-ES unit. Standard reference materials (SRM 2709a and SRM 2711a) were used to assess the determination method accuracy, showing analytical errors < 10%. pH and EC were determined by the saturated paste method and by potentiometric measurements in solid:water extracts (1:5), respectively. Organic matter was obtained by dichromate oxidation employing the Walkley-Black method (Walkley, 1947) after the application of the Van Bemmelen conversion factor of 1.724 to derived organic carbon. Carbonate content was analyzed by the Bernard volumetric method according to the ISO 10693 (1995) procedure. Texture analysis was performed using the pipette method (Gee and Bauder, 1986). Total N was determined according to the Kjeldahl digestion method (Bremner and Mulvaney, 1982). Available Ca and K were obtained by the ammonium acetate method (Haby et al., 1990), and available P was analyzed by the Olsen method (Olsen et al., 1954).

A non-contaminated soil (Cambisol) from a close area was sampled to be used as a control soil in the analysis of soil microbiological parameters. Its physicochemical characterization was carried out following the above-mentioned methods.

### 2.2. Amendments

Four organic materials, namely olive processing solid waste (OPSW), municipal solid waste compost (MSWC), leonardite (a soft brown coal with a high content of humic acids) and peat were used as soil amendments in this study. Such materials were analyzed for pH, EC, OM, total N, available Ca, K and P, and pseudo-total trace element concentrations as described before. The adsorption characteristics of these materials with regard Zn and Cd were also determined. With this aim, adsorption isotherms were obtained by subjecting a fixed amount of organic products to a shaking period with Zn or Cd solutions of different concentrations on a vertical rotary shaker in a climatic chamber. The following conditions were employed: solid/liquid ratio: 1 g $L^{-1}$, trace element concentration: 0.1–50 mg $L^{-1}$, solution pH: 6, shaking time: 24 h and temperature: 22 °C. After the interaction period suspensions were separated by centrifugation and trace elements were analyzed in supernatants by ICP-AES. The adsorption data were fitted to the Langmuir equation, $X/M = (KbC_e)/(1 + KC_e)$, where X/M is the amount of the trace element adsorbed per unit weight of organic material, Ce is the equilibrium trace element concentration remaining in solution, K is the equilibrium constant (affinity term) and b represents the maximum trace element amount that can be adsorbed.

### 2.3. Soil amendment treatments

Single amendments were added at increasing levels (0, 1, 2 and 5%) to a fixed (mine or control) soil amount (1 kg). All treatments were performed in triplicate. Treated samples were homogenized, put in 3 L plastic recipients, and wetted with deionized water to reach 60% of their water holding capacity (WHC). Subsequently, samples in closed recipients were subjected to an incubation period of 4 weeks at a temperature of 22 °C. During this period samples were aerated each week for some minutes. Once the incubation step has been completed, a set of sub-samples of each treatment was air-dried and used to perform trace element mobility studies, and another set was kept at 4 °C and used in the determination of soil microbiological parameters.

### 2.4. Mobility studies

Both mine and control soil samples subjected to the different amendment treatments were analyzed for their pH and EC as explained before. Mobile contents of Zn and Cd were also determined in mine soil samples following the ISO 19730 procedure (2008), and further analysis by ICP-AES. According to this procedure, water-soluble compounds, exchangeably bound ions and readily soluble trace element complexes are extracted.