



# Changes in heavy metal extractability from contaminated soils remediated with organic waste or biochar



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## ABSTRACT

The effect of the addition of organic waste or biochar on the extractability of heavy metals (Cd, Cu, Ni, Pb and Zn) was assessed in five heavy metal-contaminated soils. The amendments studied were: municipal organic waste compost (MOW), green waste (GW), biochar derived from tree bark (BF) and biochar derived from vine shoots (BS). The amendments were added to the soil at 10% dose. A  $pH_{stat}$  leaching test was applied to the soils and soil + amendment mixtures to assess the effects of the amendments on the extractable metal concentration at the initial pH and in the 2–12 pH range. MOW increased the DOC content in the mixtures for most soils, whereas the rest of amendments only increased the DOC content for the soil with the lowest DOC value. Moreover, in the mixtures obtained from soils with a low buffering capacity, the amendments increased pH (up to 3 units) and the acid neutralization capacity, thus decreasing the extractability of heavy metals at the initial pH of the mixtures. In a few cases, the amendments further decreased the concentrations of extractable metal due to an increase in the sorption capacity of the mixture, even though the soil had high initial pH and ANC values. MOW and GW generally led to larger decreases in metal extractability in the resulting mixtures than biochar, due to their higher sorption and acid neutralization capacities.

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## 1. Introduction

Soils are one of the major sinks for heavy metals released into the environment by anthropogenic activities. Unlike other contaminants, they do not generally undergo microbial or chemical degradation, and they persist in soils for a long time after their incorporation (Adriano, 2001). Regulations regarding the management of presumably metal contaminated soils are generally based on metal total concentration, but this information is usually not sufficient to assess the derived risk. Thus, information about metal interaction in soils and related mobility is required for decision making related to the management of contaminated soils and the selection of suitable remediation strategies.

Soil remediation techniques are often aimed at decreasing the mobility and bioavailability of heavy metals in soils, by modifying their interaction mechanisms (Park et al., 2011). In this context, chemical immobilisation via the addition of amendments is an appealing option for diminishing the mobility of heavy metals in the resulting soil + amendment mixtures (Kumpiene et al., 2008). This approach is less disruptive to the soil and ecosystem than other remediation strategies and is usually less expensive when waste materials are employed (Lombi et al., 2002). The main factors governing the efficacy of the addition of an amendment to a contaminated soil are the effect on the soil

pH, given the strong dependence of metal sorption mechanisms on this parameter, and the enhancement of specific metal-amendment interactions that diminish the availability of heavy metals through sorption processes (Dijkstra et al., 2004). In this context, diverse amendments derived from biomass of natural origin (e.g. animal manure, compost and biochar) have been tested in remediation strategies, although differing conclusions about their efficiency have been reported (Clemente et al., 2007; Nwachukwu and Pulford, 2009; Beesley et al., 2010). For example, Beesley et al. (2010) assessed the effect of biochar and green-waste compost on the pore water concentration of Cd, Zn and Cu in a mildly acidic soil. The copper concentration in soil solution increased following the addition of amendments, due to an increase in the DOC content, whereas Cd and Zn concentrations decreased, due to an increase in pH of the resulting soil mixture. Clemente et al. (2007) reported that cow manure had no effect on metal extractability, while an olive husk-derived amendment increased metal availability. The authors attributed this detrimental trend to the reduction in Mn oxides due to the degradation of phenolic compounds.

The effect of the addition of amendments to contaminated soils on metal availability should be tested first at the laboratory level, in order to avoid expensive experimental work at the field level, to better monitor changes in metal availability and to control the variables affecting the efficiency of the candidate amendments. In this context, the  $pH_{stat}$  leaching test has proven to be a valuable tool in the assessment of the available fraction of heavy metals in contaminated soils and in

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soil + amendment mixtures (Van der Sloot, 1990; Van der Sloot et al., 1996; Rigol et al., 2009; González-Núñez et al., 2012). This approach is appropriate for evaluating the dependence of contaminant release as a function of pH over a broad range of pH values, providing a complete assessment of metal availability in a given pH scenario (Kosson and der Sloot, 2002; Cappuyns and Swennen, 2008).

The aim of this work was to evaluate the ability of four organic amendments to reduce heavy metal mobility, here estimated using a leaching test, in five soils contaminated with Cd, Cu, Ni, Pb and Zn. The amendments were selected based on previous complete physicochemical characterisation and sorption assays carried out at the laboratory level (Venegas et al., 2015).  $pH_{stat}$  leaching tests were applied to the soil and soil + amendment samples within a broad pH range, and the acid neutralization capacity in both untreated soils and soil + amendment mixtures was also determined to evaluate the effect of each amendment on the buffering capacity of the resulting mixtures. Comparison of the metal extractability curves obtained in the untreated soil and soil + amendment mixtures allowed assessment of the ability of the amendments to enhance heavy metal immobilisation depending on changes in pH.

## 2. Materials and methods

### 2.1. Samples

Five contaminated soils and four amendments of organic origin were used in this study. The contaminated soils were two agricultural soils originated from an area in the South of Spain affected by an accidental spill caused by a close mine exploitation (Aznalcóllar, Seville), thus being affected by pyritic sludge particles and acidic waste waters (RIB and QUE); a soil affected by mining activities (S15), also from the South of Spain; and two soils (ASCO and TENF) contaminated at laboratory level with a slightly acidic solution that contained Cd, Cu, Ni, Pb and Zn, and subsequently subjected to drying-wetting cycles to enhance the incorporation of the heavy metals and better simulate a real scenario. The drying-wetting cycles involved rewetting the samples at 100% of their field capacity and maintaining them in capped vessels at 40 °C for 24 h. Later, the samples were dried in open vessels at 40 °C for 48 h. This procedure was repeated three times.

The amendments included a compost derived from collected municipal organic waste (MOW), which was initially processed in wet treatment tanks and then anaerobically fermented generating slurry that was subjected to composting; a compost from green waste (GW) originated from vegetable and plant residues, also containing soil material; a biochar derived from tree bark (BF) and a biochar derived from vine shoots (BS), both produced by pyrolysis at 400 °C for 3 h. All samples were dried, sieved through a 2 mm mesh, homogenized and stored in bottles before analysis.

### 2.2. Soil + amendment mixtures

The soil + amendment mixtures were prepared at 10% w/w amendment dose: 30 g of amendment were homogeneously mixed with 270 g of soil. This dose represents a high application rate, probably difficult to be applied at field level, but within the dose ranges reported in previous works to test the efficacy of amendments at laboratory level (Beesley et al., 2010; Houben et al., 2013). The mixtures were subjected to three drying-wetting cycles, in order to simulate field conditions. The mixtures were subsequently mixed in an end-over-end shaker for two days and stored in bottles before analysis.

### 2.3. Soil characterisation

The amendments had previously been fully characterized in terms of physicochemical parameters such as pH, cation exchange capacity

(CEC), acid neutralization capacity (ANC), dissolved organic carbon (DOC), total organic carbon (TOC), and organic matter content in extracts obtained according to the protocols for fulvic and humic acid determination. A detailed description of the amendment characteristics is presented in Venegas et al. (2015). Regarding soil characterisation, the pH of the soil samples was measured in Milli-Q water, using a solution-to-soil ratio of 1:2.5 mL g<sup>-1</sup>. The organic matter content was determined by the loss of weight on ignition (LOI) at 450 °C for 16 h of 3 g of soil sample previously oven-dried overnight at 110 °C (Burt, 2004). CEC was determined after extraction with ammonium acetate (Bower et al., 1952) (see Supplementary material for further details). The dissolved organic carbon (DOC) in the extracts was determined using a total organic carbon analyser (TOC-50000, Shimadzu). For the determination of DOC in those extracts obtained by addition of acid, it was necessary to carry out experiments in parallel substituting HNO<sub>3</sub> with HCl. The particle size distribution was determined by the pipette method, based on the varying settling velocity in a fluid medium according to particle size (Burt, 2004). The carbonate content was determined using the calcimeter Bernard method (Mueller and Gastner, 1971). Field capacity (FC) was determined by wetting the samples until a saturated paste was obtained, and then centrifuging them at 0.33 bar (75 × g for 30 min). Later, the samples were dried at 105 °C to constant weight and FC was derived from the weight lost.

The total content of trace elements in soil samples was determined by soil digestion in a closed microwave digestion system (Milestone Ethos Touch Control) following an adaptation of the EPA3052 method (USEPA, 2008). The water-soluble metal concentrations were quantified according to DIN standard method (DIN, 1984). Trace elements were determined in the resulting solutions by ICP-OES and ICP-MS. Details can be found in the Supplementary Material.

### 2.4. Acid neutralization capacity

The neutralization capacity of the samples was examined by the CEN/TS 15364 pH titration test (CEN/TS, 2006a). To obtain the titration curve, first the initial pH of each sample was measured in a 1:100 sample mass/volume of deionized water (2 g of soil: 200 mL of water). Next, consecutive volumes of 200 µL of 0.3–1 mol L<sup>-1</sup> HNO<sub>3</sub> or 0.5–1 mol L<sup>-1</sup> NaOH were added, and the suspension was stirred. The resulting pH of the suspension was measured 30–40 min after the addition of either acid or base. The acid and base additions were repeated to achieve pH values in the range between 2 and 12. pH titration curves of soil and soil + amendment mixtures were obtained in triplicate. The titration curves permitted the quantification of the acid neutralization capacity (ANC) of the untreated soils and soil + amendment mixtures. The ANC is the quantity of acid or base (meq kg<sup>-1</sup>) required to shift the initial pH of the sample to a pH of 4. Thus, the ANC parameter permits an estimation of the buffering capacity of the soils and resulting mixtures over external acidic stresses of samples with an initial pH higher than 4.

### 2.5. $pH_{stat}$ leaching test

The  $pH_{stat}$  leaching test, based on the CEN/TS 14997 protocol (CEN/TS, 2006b), allowed the examination of metal release as a function of pH. Six grams of soil sample or soil + amendment mixtures were suspended in a given volume of deionized water to obtain a liquid–solid ratio of 10 mL g<sup>-1</sup>. Based on the information provided by the pH titration test, an appropriate amount of acid (HNO<sub>3</sub>) or base (NaOH) was added to modify the initial pH of the sample to achieve pH values between 2 and 12. A minimum of eight suspensions covering the pH range were prepared for each sample. Sample suspensions were stirred for 7 days, which is the recommended contact time for the characterisation of samples with a particle size lower than 2 mm (Kosson and der Sloot, 2002). The pH was maintained by adding small quantities of acid (0.1–1 mol L<sup>-1</sup> HNO<sub>3</sub>) or base (0.3–1 mol L<sup>-1</sup> NaOH), in order to minimise changes in the solid:liquid ratio, using an automatic pH

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