

## **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  $\text{pH}_{\text{stat}}$  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.

**Keywords:** *immobilisation, soil, metal, organic amendments, remediation.*

## **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  $\text{pH}_{\text{stat}}$  leaching test has proven to be a valuable tool in the assessment of the available fraction of heavy metals in contaminated soils and in 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 et al., 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).  $\text{pH}_{\text{stat}}$  leaching tests were applied to the soil and soil+amendment samples within a broad pH range, and the acid neutralisation 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 characterised in terms of physicochemical parameters such as pH, cation exchange capacity (CEC), acid neutralisation 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 x 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). 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  $\mu\text{L}$  of 0.3–1 mol  $\text{L}^{-1}$   $\text{HNO}_3$  or 0.5–1 mol  $\text{L}^{-1}$   $\text{NaOH}$  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 ( $\text{meq kg}^{-1}$ ) 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. $\text{pH}_{\text{stat}}$ leaching test*

The  $\text{pH}_{\text{stat}}$  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 deionised water to obtain a liquid–solid ratio of 10 mL  $\text{g}^{-1}$ . Based on the information provided by the pH titration test, an appropriate amount of acid ( $\text{HNO}_3$ ) or base ( $\text{NaOH}$ ) 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 et al., 2002). The pH was maintained by adding small quantities of acid ( $0.1\text{--}1\text{ mol L}^{-1}\text{ HNO}_3$ ) or base ( $0.3\text{--}1\text{ mol L}^{-1}\text{ NaOH}$ ), in order to minimise changes in the solid:liquid ratio, using an automatic pH control device (Model pH-103 Adasa Sistemas). Finally, the suspensions were centrifuged and filtered through  $0.45\text{ }\mu\text{m}$  pore size nylon membranes and stored until analysis. Experiments were performed in triplicates. The concentrations of trace elements in the extracts were determined by ICP-OES, or by ICP-MS when lower detection limits were required.

### *2.6. Data treatment*

Results provided were presented as mean values of 2-3 replicates, depending of the parameters characterized and the test applied. When relevant, one standard deviation was also given. Statistical analyses to compare the average results of the different treatments (Figure 3) were performed using a multiple rank test based on Fisher's least significance differences (at  $p = 0.05$  significance). Analyses were carried out using Statgraphics software (version 16.1.11).

## **3. Results and discussion**

### *3.1. Main characteristics of untreated soils*

Table 1 summarises the main soil characteristics of the untreated soil samples, as well as the total and water-soluble concentrations of the target metals in the soils. Soils had low organic matter content, with LOI values within the 0.5–3.2% range, and a loamy texture. Field capacity values were similar in all soils tested, within the 24–35% range. The ASCO soil had neutral pH, low CEC and high carbonate content. The S15 soil had a slightly acidic pH, low CEC, and medium carbonate content. The RIB and QUE soils had a slightly acidic pH, low

CEC (6.9 and 13.3  $\text{cmol}_c \text{ kg}^{-1}$ , respectively), and a non-quantifiable carbonate content. Finally, the TENF soil had the most acidic pH and the highest CEC among the soils tested. Total metal concentrations were highest in the S15 soil, followed by the ASCO and TENF soils, whereas the QUE and RIB soils had the lowest values. Comparison of these data with the reference limits for heavy metal content for agricultural and industrial soils for two autonomous regions of Spain (see Table S1 in the Supplementary Material) showed that all soils exceeded the reference levels for agricultural use for Cd, Cu, Pb and Zn. ASCO, TENF and S15 also exceeded the maximum limits established for industrial soils for at least two metals. The water-soluble metal content was small with respect to the total content ( $<2\%$ ) in ASCO, QUE, S15 and RIB, with the exception of Ni and Zn in RIB (8% and 4%, respectively), and Cd in S15 (58%). On the contrary, water-soluble metal was proportionally higher in TENF, with yields generally over 15% for all metals. Due to the high total metal concentration, low extraction yields were not necessarily related to low extractable concentrations (expressed in  $\text{mg kg}^{-1}$ ). Therefore, the extractable concentrations were compared with the recommended limits for acceptance of waste at landfill sites according to the European Council Decision 2003/33/CE (European Council, 2003) for the management of waste (see Table S2). The water-soluble metal in ASCO, QUE and RIB exceeded the limits for inert waste for a few metals, and the soils could thus be classified as non-hazardous wastes, whereas S15 and TENF exceeded the thresholds for hazardous wastes for Cd and Zn in both soils and for Ni and Cu in TENF.

### *3.2. Effect of amendment on pH and buffering capacity of soil*

Fig. 1 shows the pH titration curves for the untreated soils and soil+amendment mixtures, which represent the changes in sample pH when adding base (negative values) or acid (positive values). Table 2 presents the initial pH in the experimental conditions of the titration test, and related ANC values of soils and mixtures. ANC and pH values for the amendments



are also included for comparison purposes (Venegas et al., 2015). Note that the added acid/base is represented in  $\text{meq g}^{-1}$  in the titration curves, while the resulting ANC values are expressed in  $\text{meq kg}^{-1}$ .

TENF and RIB showed the smallest ANC values. The low ANC for the TENF soil was consistent with its initially acidic pH (4.6). The titration curves of these soils revealed a marked decrease in pH upon addition of a small aliquot of acid, which was attributed to their low buffering capacity, and consistent with the absence of carbonate phases in these soils. In contrast, the S15 and ASCO soils showed distinctive titration curves with an inflection point at around pH 8, attributed to the neutralisation of carbonates, which were relatively abundant in these two samples (see Table 1). Consequently, these soils showed the highest ANC values among the tested soils. In fact, the ANC of the ASCO soil was as high as the highest ANC of the examined amendments (GW,  $7100 \text{ meq kg}^{-1}$ ). Therefore, a greater effect on pH and ANC could be expected following the addition of amendments to TENF, RIB and QUE than to ASCO and S15 soils.

This was confirmed when analysing the resulting mixtures, as summarized in Table 2. The largest changes were noticed for the TENF soil, with an increase in pH of around 2 units and related increases in ANC of one order of magnitude when the amendments with the highest ANC were added (mixtures containing MOW and GW). Therefore, a positive effect of the addition of the amendments can be anticipated in terms of shifting the pH of the soils with initial low ANC values (as here TENF, RIB, and QUE soils) to higher pH values in which the extractable fraction of metals could be decreased, as observed in previous works in which organic amendments were also used (Houben et al., 2013). This hypothesis will be examined in a following section.

### *3.3. Effect of amendment on DOC in the soil+amendment mixtures*

As suggested in a previous study (Clemente et al., 2007), organic matter, either in the solid phase or dissolved in the soil solution, might play a key role in the mobility of heavy metals in soils. Therefore, we tested the effect of the addition of the organic amendments on the changes in DOC content in soil+amendment mixtures. Table 2 shows the DOC values of amendments, soils and soil+amendment mixtures at the initial pH of the samples. The DOC content of the soils was low (within the 10–50 mg C L<sup>-1</sup> range), which was consistent with their low organic matter content (Rigol et al., 2009; González-Núñez et al., 2012). The DOC content in the amendments was around one order of magnitude higher than in soils, with the exception of the BF biochar. At the doses assayed, it was expected that the MOW amendment would provoke the largest increases in DOC values of the soil+amendment mixtures, as confirmed by the results presented in Table 2, especially for the soils with the lowest DOC values (S15 and ASCO). The DOC values in the mixtures were within the 10-60 mg C L<sup>-1</sup> range, with values slightly higher for the mixtures with MOW (45-95 mg C L<sup>-1</sup>), generally lower than two-fold the initial DOC content in untreated soils. Thus, the effect of the increase in DOC in the mixtures on metal extractability at the initial pH could be expected to be minor and balanced out by the increase in the sorption capacity of the resulting mixture.

Besides analysing the DOC status at initial pH, DOC was also quantified in selected extracts obtained from the application of the pH<sub>stat</sub> leaching test, thus permitting to examine changes in DOC at different pH values. DOC data within the 1.5-13 pH range for soils and amendments are shown in Fig. S1 of the Supplementary Material, whereas DOC data at the lowest and highest pH analysed for soils and mixtures are summarised in Table 3. The five studied soils followed a similar pattern with minimum DOC values around pH 6–8. Under more acidic conditions, all soils showed an increase in the DOC content in the extracts. At high pH (>10), all soils apart from S15 also exhibited an increase in DOC values in the extracts, with maximum values at around pH 12. This pattern was consistent with the pH-

dependent solubilisation of humic and fulvic acids (Van der Sloot, 2002). Regarding amendments, the DOC curves also followed a U-shaped pattern, especially in the case of the MOW and GW amendments, except for the BF biochar that showed only a slight DOC increase at high pH. The maximum DOC content was 1200 mg C L<sup>-1</sup> at pH 2 for MOW, which was 2-fold higher than at initial pH, and 1400 mg C L<sup>-1</sup> at pH 12 for GW (around a 9-fold increase with respect to the DOC content at initial pH). BS, and especially BF, showed DOC values similar to those obtained in soils (always lower than 300 mg C L<sup>-1</sup> for BF). As observed in Table 3, DOC concentrations for soil+amendment mixtures at strong alkaline and acidic pH values were systematically higher than at the initial pH (4- and 7-fold higher at acid and basic pH on average, respectively), with DOC contents up to 20 times higher than at the initial pH, due to the simultaneous increase in DOC in soils and amendments. However, the direct comparison between the DOC content of soils and soil+amendment mixtures showed that addition of amendments resulted in more than a 2-fold rise in DOC concentrations in the mixtures with respect to the soils only for the S15 and for most soils when using the MOW material, under acidic conditions. At basic pH, the increase was only relevant for the S15 soil. As changes in DOC concentrations in the mixtures with respect to the untreated soils were only significant in a few cases (mainly for the S15 soil, which had the lowest DOC among the soils tested), it thus could be anticipated that DOC is not having a major effect on the extractable concentrations of heavy metals following the addition of amendments.

### *3.4 Extractability pattern of heavy metals*

Fig. 2 shows the pH-dependent extractability curves of heavy metals (Cd, Cu, Ni, Pb and Zn) for untreated soils and soil+amendment mixtures. The extractability curves of the untreated soils were rescaled with a factor of 0.9 to correct for the dilution effect due to amendment addition at 10% dose, thus allowing a direct discussion of the effect of the addition of the

amendment without taking into consideration the dilution effect on extractable metal concentration.

A strong dependence of the extractable metal concentrations with respect to pH was noticed in all cases. Curve patterns were similar for all metals in the RIB, QUE and TENF soils, in which larger extraction yields were generally observed at strongly acidic pH values, with much lower extractability at neutral and alkaline pH (generally lower than 2%). This pattern was consistent with the competitive effect of protons at acidic pH for the sorption sites, as well as with the positively charged surfaces at acidic pH, the slight increase in DOC and the partial dissolution of the mineral phases in soils (Dijkstra et al., 2004; Sastre et al., 2004). In the case of RIB soil, the curves also showed a significant increase in metal extractability at strongly alkaline pH, except for Ni. This increase was also observed for Pb and Zn in a few soils, probably due to the formation of soluble hydroxyl carbonate complexes, especially for those soils with a significant carbonate content (ASCO and S15), or of hydroxyl complexes (Dijkstra et al., 2006).

The addition of amendments did not generally alter the curve patterns in the mixtures with respect to those of the untreated soils, as already reported for similar amendments (Houben et al., 2013). However, minor changes were noticed in a few cases, probably explained by an increase in the sorption sites following the addition of the amendments (e.g., see ASCO and S15 mixtures with MOW and GW for Cd and Zn in the acidic pH range, and for Pb at high pH). As previously reported (Venegas et al., 2015), MOW showed high sorption capacity for Cd, GW for Pb and Zn, and BS for Cu, Zn and Pb, which partially explains minor changes observed in a few cases in the leaching pattern of the metals in the mixtures with respect to untreated soils.

### *3.5 Extractability of heavy metals at initial pH*

Besides examining the role of the amendments across the entire pH range, we also assessed the effect of the addition of the amendments at the initial pH of the mixtures. Fig. 3 displays the extractable metal concentrations at initial pH for soil and soil+amendment mixtures. European Council Decision threshold limits for “inert waste” (black line), “non-hazardous waste” (cyan dotted line) and “hazardous waste” (red dashed line) are also indicated.

Regardless of the total and extractable metal concentrations, which were higher or lower depending on the particular soil and metal, extraction yields (%) were generally low (<2%) at the initial pH, with the exception of Cd, Cu, Ni and Zn in TENF, Ni and Zn in RIB and Cd in S15. However, for those cases in which total metal concentration was high, even low extraction yields could lead to extractable metal concentrations that exceed the recommended limits for the acceptance of inert or non-hazardous wastes (even the hazardous waste threshold for the TENF soil).

In general, amendments reduced the extractable metal concentration at the initial pH of the resulting mixtures. The efficacy of the amendments varied according to the initial soil ANC and pH, metal extraction yield and sorption capacity of the materials (quantified through the solid-liquid distribution coefficient,  $K_d$  (Venegas et al., 2015)). In this sense, our observations consistently differed from those of previous studies that reported an increase in heavy metal extractability in soils upon addition of organic amendments, partially attributable to an increase in the DOC content, which formed soluble chelates with heavy metals in solution, competing with the binding sites in the solid phase (Schwab et al., 2007; van Herwijnen et al., 2007). As the amendments examined here had a minor effect on the DOC, this detrimental effect of metal extractability could be disregarded.

Although the ASCO soil already had a high buffer capacity and pH, the addition of GW, BF and BS led to a large reduction in the extractable Cu concentrations, which could be explained by a

significant increase in specific sorption sites in the resulting mixtures, consistent with the relatively high  $K_d$  values quantified for these amendments for Cu (Venegas et al., 2015). Significant reductions were also observed for extractable Cd, Pb and Zn concentrations in this soil (from 0.4 to 0.13 mg kg<sup>-1</sup> for Cd, 9 to 2 mg kg<sup>-1</sup> for Pb and 7.3 to 1.6 mg kg<sup>-1</sup> for Zn) following addition of the MOW amendment, also consistent with the  $K_d$  values of this amendment (over 103 L kg<sup>-1</sup> in all cases (Venegas et al., 2015)). These results are consistent with reductions in extractable Cd and Zn concentrations observed when adding compost to contaminated soils (Beesley et al., 2010). The positive effect of the addition of MOW in terms of reducing the extractable metal concentration was also observed in S15 soil for Cd (5950 mg kg<sup>-1</sup> to 1900 mg kg<sup>-1</sup>) and Zn (6650 mg kg<sup>-1</sup> to 1910 mg kg<sup>-1</sup>), although this soil also had high initial ANC and pH values. However, the addition of the amendments did not change the ASCO and S15 waste categories. RIB soil showed a significant reduction in Ni (from 1.9 mg kg<sup>-1</sup> to 0.02 mg kg<sup>-1</sup>), Zn (13.5 mg kg<sup>-1</sup> to 1 mg kg<sup>-1</sup>) and Cd (0.1 mg kg<sup>-1</sup> to 0.007 mg kg<sup>-1</sup>) extractability, likely because of the combination of an increase in pH and an increase in specific sorption due to the addition of amendment, although the pH effect is expected to be dominant (Sauvé et al., 1997). For this soil, the addition of the amendments would generally lead to extractable concentrations lower than the thresholds for inert waste. A similar pattern was also observed for Ni and Zn in the case of the QUE soil.

TENF soil was originally over the threshold concentrations for hazardous wastes for all metals. Addition of the amendments significantly reduced the metal concentrations, often by almost two orders of magnitude depending on the amendment. These large reductions in metal extractability could be related to the large effect on pH caused by the addition of the amendments, and additionally to the high  $K_d$  of the MOW and GW amendments (Venegas et al., 2015). The observed pattern is consistent with previous studies that observed similar reductions in metal extractable concentrations following the addition of organic amendments to an acidic soil (Pardo

et al., 2014). These significant reductions in metal extractable concentrations modified the waste classification of the TENF soil, which subsequently fell below the hazardous waste threshold, and also under the non-hazardous waste threshold for all metals when using MOW and GW amendments.

#### **4. Conclusions**

Laboratory experiments identified the organic amendments that were most effective in reducing the extractable concentrations of heavy metals in contaminated soils. Besides an increase in the metal sorption capacity in the resulting mixtures, a beneficial effect that might be minor given the low doses at which the amendments are added to contaminated soils (and given that  $K_d$  values over  $10^4$  L kg<sup>-1</sup> would be required to observe consistent effects), key aspects are how the DOC, ANC and pH status may vary in the resulting soil+amendment mixtures. Amendments can increase the pH and ANC values of acid soils and/or soils with low initial buffering capacity, whereas the effect in soils with high buffering capacity is smaller. The effect of pH and ANC modifications upon amendment was clearly observed here for the RIB and especially TENF soils, which had an acidic initial pH that was raised by 2–3 pH units following amendment addition in all cases, and resulted in a general lowering of extractable heavy metal concentrations. Thus, the use of organic amendments in the remediation of soils is especially recommended for acid soils, but only after confirming that their addition would not increase the DOC in the resulting mixtures. However, as the increase in pH and ANC were the main driving mechanisms leading to the decrease in metal extractability, attention should be paid when applying these materials at field level to ensure that the increases in pH, which may be reversible, are maintained over time.

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**Table 1**

## Soil characteristics

| Soil | pH  | Moisture (%) | FC (%) | LOI (%) | CaCO <sub>3</sub> (%) | CEC (cmolc kg <sup>-1</sup> ) | Sand (%) | Clay (%) | Texture    |    | Cd (mg/kg) | Cu (mg/kg) | Ni (mg/kg) | Pb (mg/kg) | Zn (mg/kg) |
|------|-----|--------------|--------|---------|-----------------------|-------------------------------|----------|----------|------------|----|------------|------------|------------|------------|------------|
| ASCO | 7.0 | 2.1          | 24     | 0.5     | 36                    | 4.1                           | 28.5     | 8.2      | Silty loam | TC | 30         | 11040      | 230        | 5375       | 1835       |
|      |     |              |        |         |                       |                               |          |          |            | WS | 0.4        | 37         | 1.0        | 8.9        | 7.3        |
| QUE  | 6.2 | 3.4          | 32     | 3.2     | <1.q                  | 13.3                          | 51.2     | 5.6      | Sandy loam | TC | 12         | 380        | 20         | 1580       | 2150       |
|      |     |              |        |         |                       |                               |          |          |            | WS | 0.1        | 0.9        | 0.7        | 0.01       | 33.5       |
| RIB  | 6.2 | 1.1          | 29     | 1.0     | <1.q                  | 6.9                           | 76.5     | 7.2      | Sandy loam | TC | 4          | 120        | 25         | 265        | 350        |
|      |     |              |        |         |                       |                               |          |          |            | WS | 0.1        | 0.4        | 1.9        | 0.1        | 13.5       |
| S15  | 6.4 | 7.9          | 34     | 0.9     | 16                    | 13.1                          | 63.9     | 9.5      | Sandy loam | TC | 10200      | 16430      | 150        | 91520      | 275500     |
|      |     |              |        |         |                       |                               |          |          |            | WS | 5950       | 6.0        | 5.6        | 36         | 6650       |
| TENF | 4.6 | 4.3          | 35     | 1.8     | <1.q                  | 48.3                          | 38.3     | 25.1     | Loam       | TC | 30         | 2105       | 225        | 5360       | 1810       |
|      |     |              |        |         |                       |                               |          |          |            | WS | 7.8        | 316        | 95         | 16         | 697        |

TC: metal total content; WS: water-soluble metal content.

**Table 2**

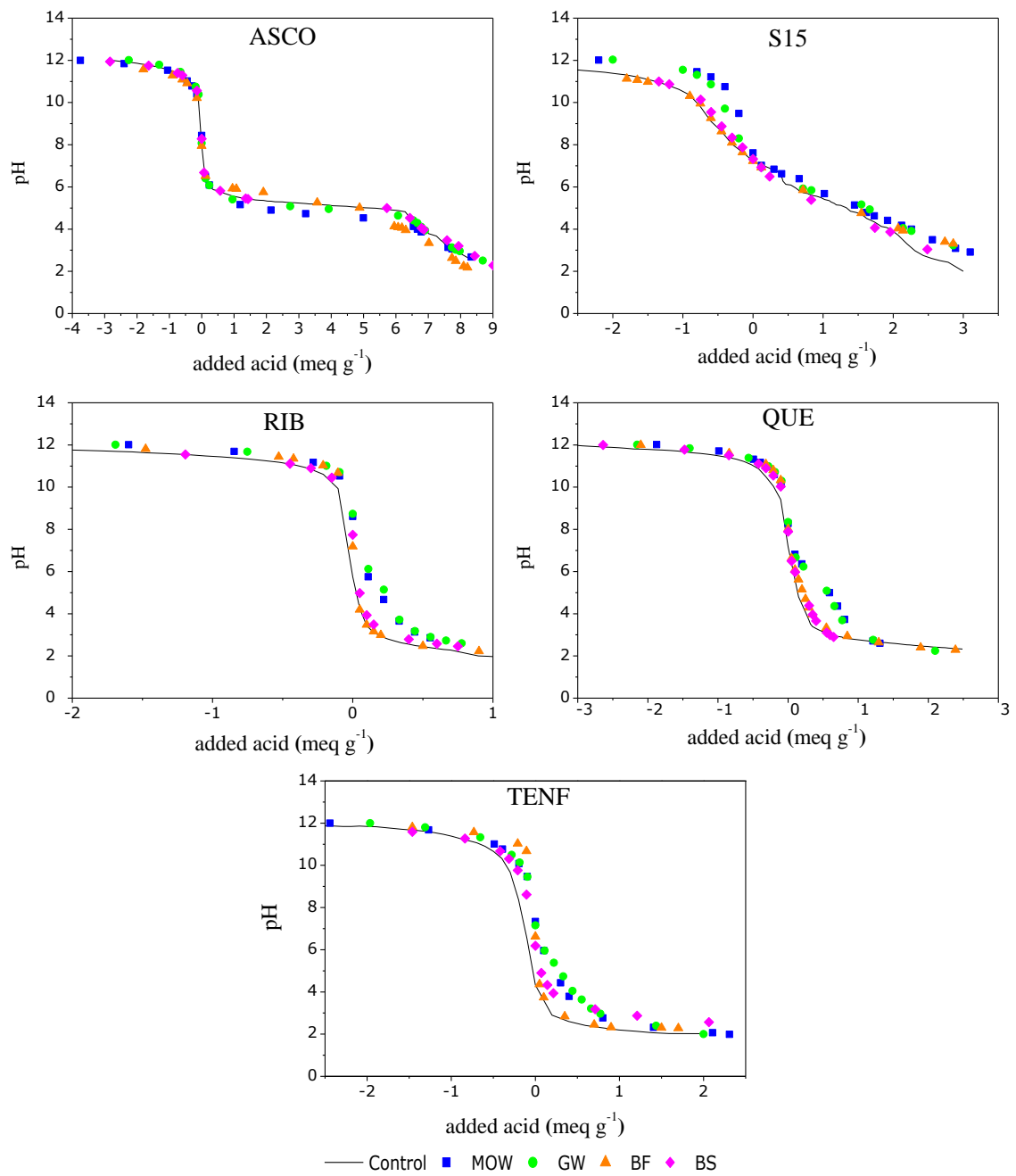
pH, ANC and DOC (at initial pH) of the amendments, soils and mixtures

|          | pH   | ANC (meq kg <sup>-1</sup> ) | DOC (mg C L <sup>-1</sup> ) |
|----------|------|-----------------------------|-----------------------------|
| MOW      | 8.3  | 4280 (150)                  | 530                         |
| GW       | 8.4  | 7100 (190)                  | 160                         |
| BF       | 8.9  | 420 (10)                    | 10                          |
| BS       | 10.0 | 725 (9)                     | 220                         |
| ASCO     | 7.7  | 6950 (300)                  | 15                          |
| ASCO+MOW | 7.8  | 6665 (150)                  | 50                          |
| ASCO+GW  | 7.7  | 6840 (170)                  | 35                          |
| ASCO+BF  | 7.8  | 6190 (200)                  | 10                          |
| ASCO+BS  | 7.8  | 6790 (120)                  | 35                          |
| QUE      | 6.9  | 300 (50)                    | 30                          |
| QUE+MOW  | 7.3  | 755 (30)                    | 65                          |
| QUE+GW   | 7.5  | 720 (15)                    | 40                          |
| QUE+BF   | 7.5  | 340 (8)                     | 25                          |
| QUE+BS   | 7.6  | 340(3)                      | 35                          |
| RIB      | 6.3  | 60 (17)                     | 25                          |
| RIB+MOW  | 7.7  | 290 (6)                     | 55                          |
| RIB+GW   | 7.8  | 305 (10)                    | 40                          |
| RIB+BF   | 7.6  | 90 (4)                      | 20                          |
| RIB+BS   | 7.7  | 95 (5)                      | 25                          |
| S15      | 6.8  | 1960 (150)                  | 10                          |
| S15+MOW  | 7.1  | 2260 (130)                  | 45                          |
| S15+GW   | 6.9  | 2140 (95)                   | 20                          |
| S15+BF   | 6.7  | 2070 (100)                  | 5                           |
| S15+BS   | 6.9  | 1740 (150)                  | 30                          |
| TENF     | 4.6  | 40 (3)                      | 50                          |
| TENF+MOW | 7.0  | 365 (7)                     | 95                          |
| TENF+GW  | 7.6  | 440 (8)                     | 60                          |
| TENF+BF  | 7.4  | 75 (2)                      | 50                          |
| TENF+BS  | 6.3  | 195 (10)                    | 55                          |

**Table 3**

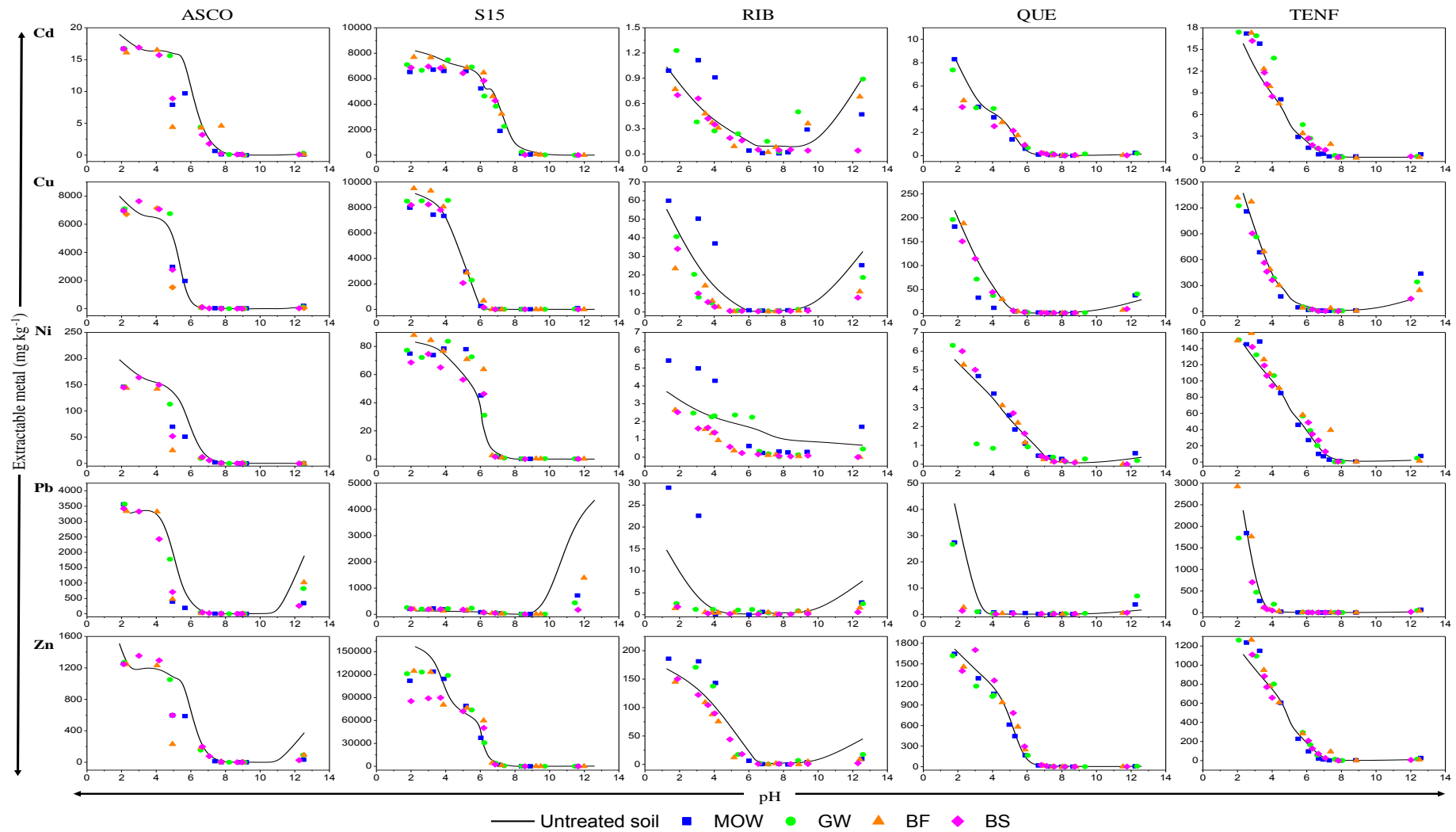
DOC content of the soils and mixtures at acidic and alkaline pH

| Soil/mixtures | pH   | DOC | Soil/mixtures | pH   | DOC |
|---------------|------|-----|---------------|------|-----|
| ASCO          | 3.2  | 110 | S15           | 1.5  | 45  |
|               | 12.4 | 105 |               | 12.1 | 10  |
| ASCO+MOW      | 3.0  | 290 | S15+MOW       | 2.0  | 150 |
|               | 12.0 | 115 |               | 11.6 | 85  |
| ASCO+GW       | 4.9  | 225 | S15+GW        | 2.0  | 110 |
|               | 12.0 | 240 |               | 11.4 | 150 |
| ASCO+BF       | 3.7  | 105 | S15+BF        | 2.0  | 45  |
|               | 12.5 | 120 |               | 12.0 | 30  |
| ASCO+BS       | 2.7  | 140 | S15+BS        | 2.0  | 120 |
|               | 12.0 | 180 |               | 11.6 | 95  |
| QUE           | 1.6  | 155 | TENF          | 1.8  | 160 |
|               | 12.1 | 145 |               | 12.0 | 360 |
| QUE+MOW       | 2.0  | 255 | TENF+MOW      | 2.3  | 265 |
|               | 12.2 | 195 |               | 12.0 | 370 |
| QUE+GW        | 1.7  | 180 | TENF+GW       | 2.6  | 210 |
|               | 12.0 | 140 |               | 12.0 | 470 |
| QUE+BF        | 1.6  | 140 | TENF+BF       | 4.5  | 90  |
|               | 11.5 | 160 |               | 12.0 | 440 |
| QUE+BS        | 4.0  | 60  | TENF+BS       | 2.7  | 140 |
|               | 11.8 | 225 |               | 12.0 | 465 |
| RIB           | 1.6  | 50  |               |      |     |
|               | 12.8 | 250 |               |      |     |
| RIB+MOW       | 2.0  | 85  |               |      |     |
|               | 12.5 | 315 |               |      |     |
| RIB+GW        | 3.2  | 75  |               |      |     |
|               | 12.6 | 370 |               |      |     |
| RIB+BF        | 2.0  | 30  |               |      |     |
|               | 12.4 | 385 |               |      |     |
| RIB+BS        | 2.1  | 135 |               |      |     |
|               | 12.3 | 310 |               |      |     |

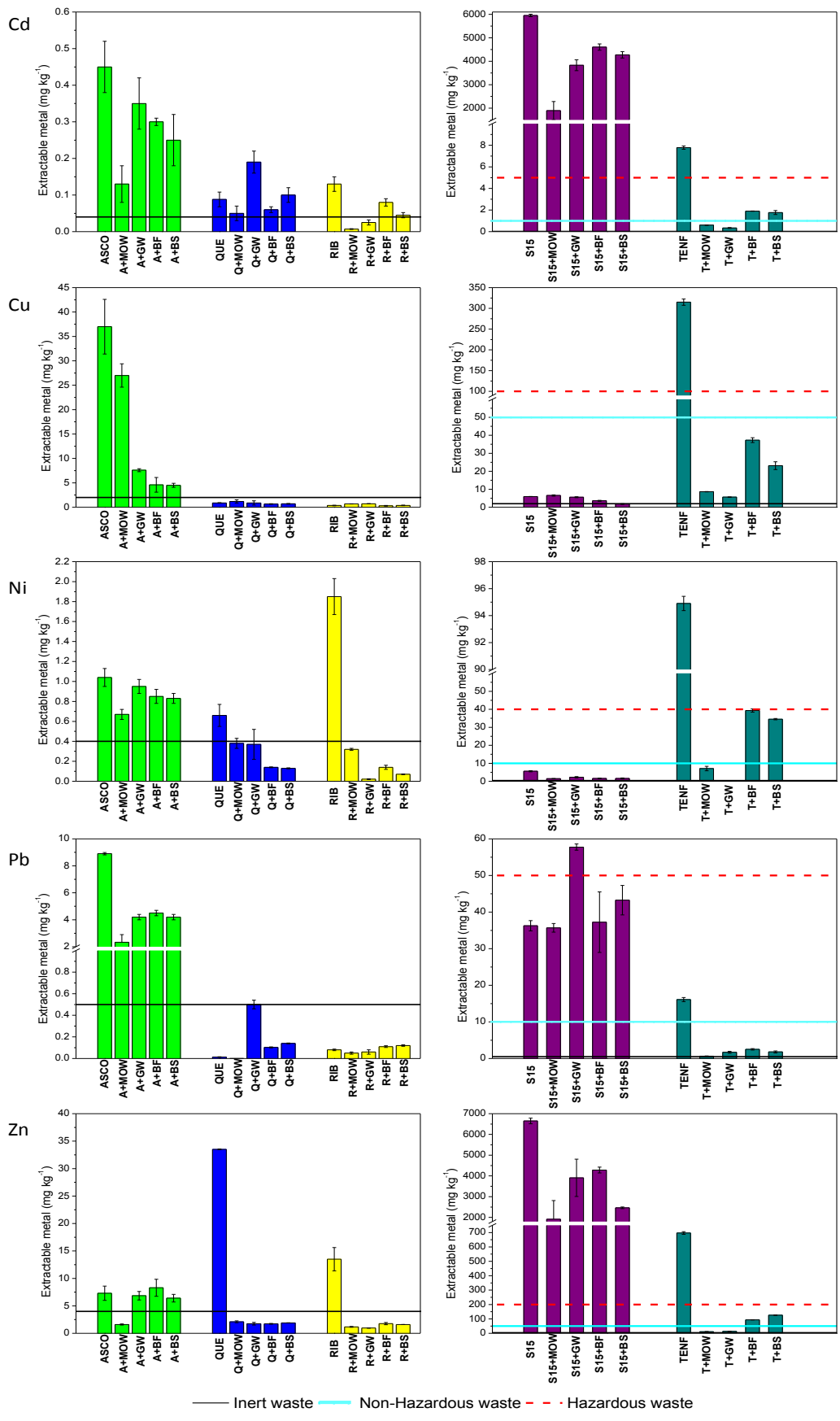


**Fig. 1.** pH titration curves of soil and soil+amendments mixtures.





**Fig. 2.** Metal extractability ~~leaching~~ curves (extractable metal ( $\text{mg kg}^{-1}$ ) vs. pH) of soil and soil+amendment mixtures.



**Fig. 3.** Extractable metals in soils and soil+amendment mixtures at initial pH. Error bars indicate the standard deviation.

# **Supplementary material**

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

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### *Soil characterization*

CEC was determined after extraction with ammonium acetate (Bower et al., 1952). In short, 5 g of the material was added to 30 mL of 95% ethanol, and the resulting suspension was stirred for 5 min and centrifuged. Then, the supernatant was discarded. This procedure was repeated three times to remove the soluble salts. Next, 30 mL of 1 mol L<sup>-1</sup> ammonium acetate was added to the remaining solid, and the suspension was stirred for 5 min and centrifuged. Then, the supernatant was collected in a volumetric flask. The extraction with ammonium acetate was repeated three times, and the supernatants were collected in the same flask. The flask was filled to the reference volume with 1 mol L<sup>-1</sup> ammonium acetate. The exchangeable cations were determined in the supernatant by ICP-OES, and the CEC was calculated as the sum of the exchangeable cations.

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). In brief, 0.3 g of sample was weighed in a PTFE vessel and 6 mL 69% HNO<sub>3</sub>, 3 mL 40% HF and 2 mL 30% H<sub>2</sub>O<sub>2</sub> were added. The temperature was gradually increased from 25°C to 190°C over 15 min followed by a dwell time of 30 min. After a cooling time of 10 min, 16 mL 5% H<sub>3</sub>BO<sub>3</sub> was added to mask the free fluoride ions present in the solution and dissolve fluoride precipitates. The resulting suspension was submitted to the same digestion procedure as in the first stage. After cooling the extracts at room temperature, they were diluted with Milli-Q water to a final volume of 50 mL and stored in polyethylene bottles at 4°C until analysis. The water-soluble metal concentrations were quantified by obtaining water extracts after equilibrating a known amount of the soil or amendment with Milli-Q water in a 1:10 solid:liquid ratio for 48 h at room temperature (DIN, 1984). Finally, the

samples were centrifuged, and the water extracts were filtered through a 0.45  $\mu\text{m}$  filter and stored at 4°C before analysis. Trace elements were determined in the solutions by ICP-OES using a Perkin-Elmer Model OPTIMA 3200RL ICP-OES. The emission lines employed for ICP-OES (Perkin-Elmer Model OPTIMA 3200RL) were (nm) Cd: 214.440 and 228.802; Cu: 324.752 and 327.393; Pb: 220.353; Zn: 206.200 and 213.857; Ca: 315.887 and 317.933; Mg: 279.077 and 285.213; K: 766.490; Na: 330.237 and Ni: 231.604. The detection limits using this technique were 0.01  $\text{mg L}^{-1}$  Cd; 0.01  $\text{mg L}^{-1}$  for Cu; 0.1  $\text{mg L}^{-1}$  for Ni; 0.2  $\text{mg L}^{-1}$  for Pb and 0.025  $\text{mg L}^{-1}$  for Zn. For samples with lower metal concentrations, a Perkin-Elmer ELAN 6000 inductively coupled plasma mass spectrometer was used (ICP-MS). The detection limits of the ICP-MS measurements were 0.02  $\mu\text{g L}^{-1}$  for Cd; 0.1  $\mu\text{g L}^{-1}$  for Cu; 0.2  $\mu\text{g L}^{-1}$  for Ni; 0.05  $\mu\text{g L}^{-1}$  for Pb and 0.2  $\mu\text{g L}^{-1}$  for Zn.

**Table S1**

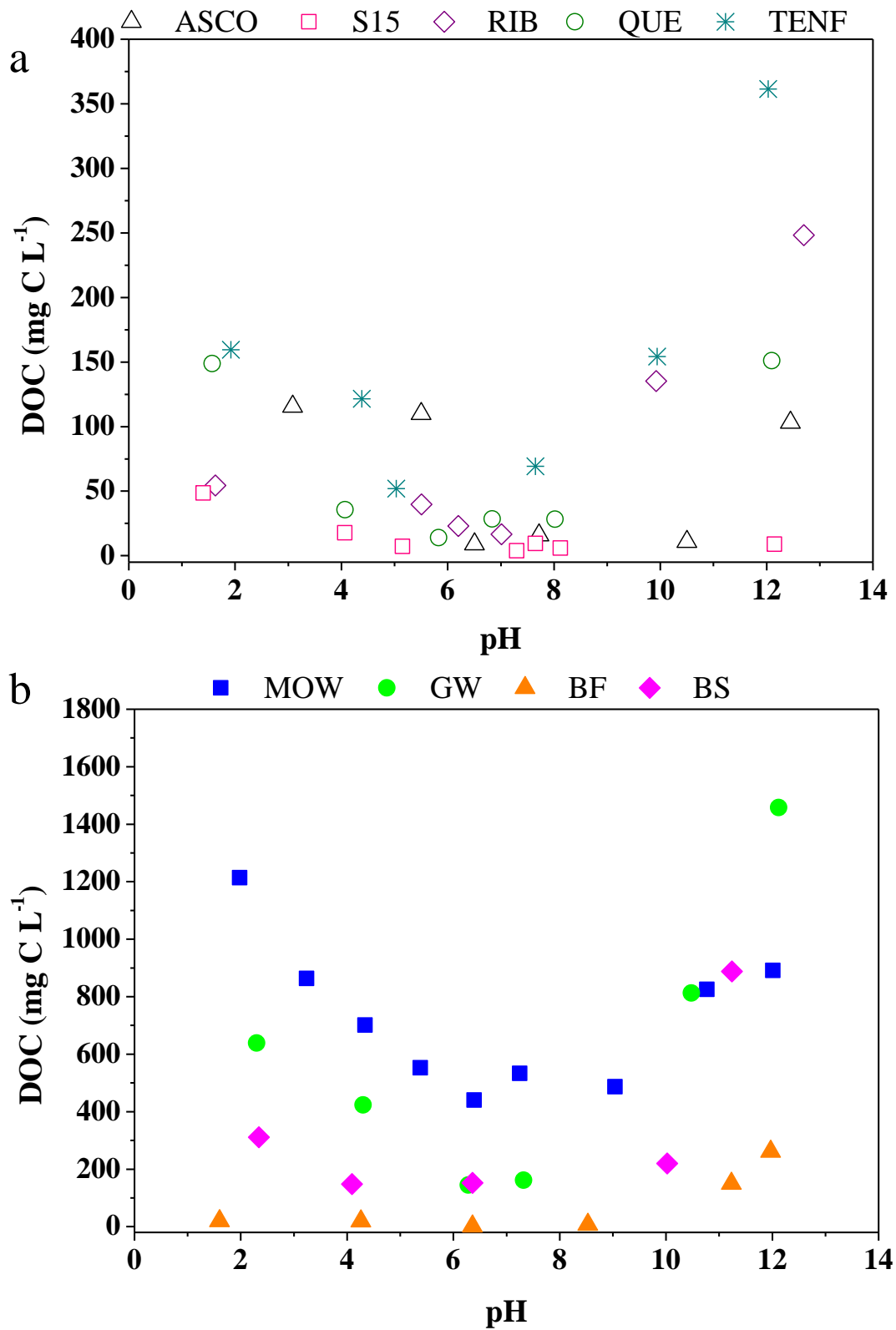
Reference limits ( $\text{mg kg}^{-1}$ ) of metal total concentration in soils (data gathered from regulations of Catalunya and Andalucía autonomous regions in Spain)

| Metal | Agricultural use | Industrial use |
|-------|------------------|----------------|
| Cd    | 2-3              | 55             |
| Cu    | 50-100           | 1000           |
| Ni    | 40-50            | 1000           |
| Pb    | 60-200           | 550            |
| Zn    | 170-300          | 1000           |

**Table S2**

Threshold limits (mg kg<sup>-1</sup>) of water soluble metal concentrations (European Council, 2003)

| Metal | Inert waste | Non-hazardous waste | Hazardous waste |
|-------|-------------|---------------------|-----------------|
| Cd    | 0.04        | 1                   | 5               |
| Cu    | 2           | 50                  | 100             |
| Ni    | 0.4         | 10                  | 40              |
| Pb    | 0.5         | 10                  | 50              |
| Zn    | 4           | 50                  | 200             |



**Fig. S1.** pH<sub>stat</sub> curves of DOC in a) untreated soils and b) amendments.