

# **Effect of ageing on the availability of heavy metals in soils amended with compost and biochar: evaluation of changes in soil and amendment properties**

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## **Abstract**

Remediation strategies using soil amendments should consider the time-dependence of metal availability to identify amendments that can sustainably reduce available pollutant concentrations over time. Drying-wetting cycles were applied on amendments, soils and soil+amendment mixtures, to mimic ageing at field level and investigate its effect on extractable Cd, Cu, Ni, Pb and Zn concentrations from three contaminated soils. The amendments investigated were municipal waste organic compost and biochars. The amendments, soils and mixtures were characterised by their physicochemical properties at different ageing times. The amendments were also characterised in terms of sorption capacity for Cd and Cu. The sorption capacity and the physicochemical properties of the amendments remained constant over the period examined. When mixed with the soils, amendments, especially the compost, immediately reduced the extractable metals in the soils with low pH and acid neutralisation capacity, due to the increase in pH and buffering capacity of the mixtures. The amendments had a relatively minor impact on the metal availability concentrations for the soil with substantially high acid neutralisation capacity. The most important changes in extractable metal concentrations were observed at the beginning of the experiments, ageing having a minor effect on metal concentrations when compared with the initial effect of amendments.

*Keywords:* metal availability, organic amendments, biochar, remediation, drying-wetting cycles.

## **1. Introduction**

The accumulation of heavy metals in soils is a worldwide problem because these pollutants can have a large impact on the environment and human health. Total metal concentration is a value often used to establish the degree of contamination of a soil. However, reliance solely on this term impedes the accurate assessment of risk, particularly if no further knowledge on the contaminant's availability exists (Adriano 2001).

Heavy metal availability depends on sorption reactions with mineral and organic soil phases, which are controlled by pH, ionic strength, surface area and the concentration of complexing ligands, among other factors (Hooda 2010; Kabata-Pendias 2011). Understanding the key interaction mechanisms that govern metal mobility in soils has allowed researchers to focus on soil remediation approaches that reduce metal availability in soils (Khan et al. 2004). In situ chemical stabilisation through the addition of amendments has relatively low costs and facilitates the treatment of large polluted areas (Kumpiene et al. 2008). Organic wastes generated from biomass are promising candidate amendments for this remediation approach, as they can regulate soil pH and provide specific sorption sites for heavy metal binding (Lee et al., 2004). However, organic amendments may also remobilize metals if they have high dissolved organic matter contents able to form soluble complexes with metals in the soil solution (Khokhotva and Waara 2010). Furthermore, chemical processes such as oxidation, hydrolysis, depolymerisation and microbial degradation of the organic amendment may modify the availability of heavy metals (Martínez et al. 2003; Nwachukwu and Pulford 2008). Experiments investigating the effects of mineral additions and organic amendments on Cd, Zn and Pb leaching in contaminated soils showed a decrease in Cd and Zn leaching when the pH of the applied mixtures increased, a result that remained over time (Houben et al. 2012). In contrast, those amendments with a high dissolved organic carbon (DOC) content provoked an increase in Pb leaching at the initial time; at later times, changes in Pb leaching corresponded with changes in the DOC content. Beesley et al. (2010) investigated the initial effects of

biochar and greenwaste compost on the pore water concentrations of Cd, Zn and Cu in a mildly acidic soil, as well as the impacts of ageing experiments over time. In that experiment, Cu concentrations in soil solution increased with the addition of amendments as a result of an increase in the DOC content, but the initial remobilisation had decreased by the end of the ageing period. On the other hand, an increase in the pH of the soil mixtures at the initial time resulted in a decrease in the leachable concentrations of Cd and Zn, which remained until the end of the experiment.

The effects of ageing on organic amendments added to contaminated soils over time appear to be dependent on the amendment and metal considered. This work examines the stability over time of organic amendment-treated soils more deeply. Specifically, our study evaluated the effect of three organic wastes (a municipal compost and two biochar materials) on Cd, Cu, Ni, Pb and Zn availability in three contaminated soils with contrasting characteristics. We also analysed the effects of ageing on metal leachability in soils, amendments and soil+amendment mixtures by applying drying-wetting cycles to simulate the field conditions. An evaluation of the changes in metal interaction in the target samples over time was carried out using sorption and leaching tests to elucidate whether the ageing process could significantly affect the efficiency of organic amendments in mediating metal availability over time.

## **2. Materials and methods**

### **2.1. Samples**

Three amendments and three contaminated soils were used in this study. The amendments were a biochar derived from tree barks (BF) and a biochar derived from vine shoots (BS), both of which were produced by pyrolysis at 400°C, as well as a compost derived from municipal organic waste (MOW2).

Of the three soils, one was contaminated with pyritic sludge particles and acidic wastewater (RIB), and two were contaminated by continuous exposure to mining activities (S15 and ALJ). All soils originated from the Andalusia autonomous region in the southwest of Spain.

All samples were dried, sieved through a 2 mm mesh, homogenised and stored in bottles before analysis. The methods used for sample characterisation are described in the Supplementary Material.

## **2.2. Preparation of soil+amendment mixtures: ageing experiment**

The soil+amendment mixtures were prepared with a 10% dose of the amendment. 40 g of amendment were homogeneously mixed with 360 g of soil. The mixtures were placed in plastic pots and subjected to a maximum of ten drying-wetting cycles (DW) to simulate a natural ageing process that might occur in the field. This was done to examine the effect of soil ageing on metal extractability. Samples of amendments and soils were also submitted to DW cycles to better understand the ageing process and its effect on metal extractability in the mixtures.

Every DW cycle consisted of wetting the sample to its respective field capacity (FC), maintaining the samples in closed vessels at room temperature for 72 h and later drying them at 40°C for 48 h. In the case of the soil+amendment mixtures, the FC was estimated by averaging the FC of the soil and the amendment, taking into account the amendment dose. Samples were collected after 0, 5 and 10 DW cycles (thus defining the T0, T1 and T2 samples, respectively). Two replicates were conducted for each experiment. Cation exchange capacity (CEC) was determined at T0 and T2 in the amendments, whereas pH, acid neutralisation capacity (ANC) and DOC were determined in all samples at T0 and T2. The extractable metal contents were determined in soils, amendments and mixtures at T0, T1 and T2.

## 2.3. Sorption tests

### 2.3.1. Quantification of $K_d$

Sorption experiments for Cd and Cu, representatives of the examined heavy metals, were conducted on amendments at T0, T1 and T2, according to recommended protocols (OECD 2000; Sastre et al. 2006). The amendment samples (2 g) were pre-equilibrated with 50 mL of a 0.01 mol L<sup>-1</sup> CaCl<sub>2</sub> solution for 16 h using an end-over-end shaker. After the pre-equilibration time, known volumes of the metal solution (Cd and Cu) were added to create at least four different initial metal concentrations up to 0.8 meq L<sup>-1</sup>. These represented the concentrations observed in different environmental contamination episodes (Nwachukwu and Pulford 2008). The volume of the metal solutions added to the batches was kept below 1% of the total volume of the suspension to avoid significant changes in the solid-liquid ratio. The resulting suspensions were shaken end over end for 24 h. Subsequently, suspensions were centrifuged, the supernatants were filtered through a 0.45- $\mu$ m filter and the metal concentrations were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) as described in the Supplementary Material. The sorbed metal concentrations were calculated by quantifying the metal concentration in the initial solution ( $C_i$ ) and in the equilibrium solution ( $C_{eq}$ ), as follows:

$$C_{sorb} = \frac{(C_i - C_{eq}) V}{m} \quad (1)$$

where  $C_{sorb}$  is the sorbed concentration of metal (meq kg<sup>-1</sup>),  $m$  is the mass of the amendment (kg) and  $V$  is the volume of the contact solution (L). The solid-liquid distribution coefficient,  $K_d$  (L kg<sup>-1</sup>), was calculated for each initial concentration as the ratio between the amount of the target metal sorbed onto the amendment,  $C_{sorb}$  (meq kg<sup>-1</sup>), and the amount of metal at equilibrium in the final contact solution,  $C_{eq}$  (meq L<sup>-1</sup>), using the following equation:

$$K_d = \frac{C_{sorb}}{C_{eq}} \quad (2)$$

### 2.3.2. Fitting of sorption isotherms

The experimental sorption isotherms were fitted to Freundlich and linear models. The Freundlich model is represented by the following equation:

$$C_{sorb} = K_f C_{eq}^N \quad (3)$$

where the  $K_f$  and  $N$  parameters were obtained by fitting  $C_{sorb}$  vs.  $C_{eq}$ . The  $K_f$  parameter describes the partitioning of the metal between the solid phase and the liquid phase; and  $N$  relates to the heterogeneity of the sorption sites and is indicative of the non-linearity of the sorption isotherm. When  $N=1$ , the Freundlich equation approaches a linear model and  $K_f$  becomes equal to the  $K_d$  value, which remains constant across the range of concentrations. If  $N>1$ , sorption at low metal concentrations may be inhibited by a competing reaction within ligands in the solution, such as soluble organic compounds.  $N<1$  indicates the presence of high affinity sites that govern metal sorption at low metal concentrations in the sample.

The metal sorption isotherm was fitted to a linear equation for the concentration range in which a constant slope of  $C_{sorb}$  vs.  $C_{eq}$  could be considered. This was the case for the overall concentration range for the amendments investigated here. Therefore, a  $K_{d,linear}$  value was derived for all amendments and metal combinations, and for all times examined.

## 3. Results and discussion

### 3.1. Changes in soil properties during the ageing process

#### 3.1.1. Initial conditions

Table 1 summarises the relevant physicochemical parameters of contaminated soils, as well as total and water-soluble metal concentrations. Soils had very low loss on ignition (LOI) values associated with low organic matter content, low DOC and low CEC values. The S15 soil exhibited a mildly acidic pH, but it also contained significant carbonate content, which

guaranteed a significant buffering capacity and resulted in the highest ANC value of all of the examined soils. The RIB soil also had a mildly acidic pH but exhibited negligible carbonate content and low ANC values. The ALJ soil had an acidic pH (lower than 4), which accounted for the negative ANC values.

Regarding total metal content, S15 contained the highest metal concentrations for all metals, followed by ALJ. To evaluate the degree of contamination within the three soils, total metal concentrations were compared with reference levels (maximum allowable concentrations for non-polluted soils) established by the Junta de Andalucía. These values are relevant because the target contaminated soils originated from this region and are subject to its regulation (see Table S1 in the Supplementary Material). Based on this criteria total metal concentrations in the three soils (except for Ni in RIB) exceeded the reference levels. However, total metal concentrations in the RIB soil all fell below the intervention limits for agricultural soils. For this reason, while metal concentrations in the RIB sample exceeded reference levels, they did not require remediation. In contrast, the S15 and ALJ soils required remediation because their total metal concentrations exceeded the intervention limits, and in certain cases were so bad they exceeded the limits for industrial use (Cu, Pb and Zn for both soils and Cd for S15 soil). Of the water-soluble metal concentrations, S15 exhibited the highest Cd concentrations, which represented the highest Cd extraction yield of the soils examined (greater than 50% of the total Cd content). The ALJ and RIB soils contained much lower Cd concentrations, which led to lower extraction yields (5% and 8%, respectively). Extractable Pb concentrations in all soils were high for the ALJ and S15 soils, although the related extraction yields were lower than 1%. This low extractability was also observed for Cu in the S15 and RIB soils, while the Cu extraction yield was significantly higher in the ALJ soil (20%). Water extraction yields for Zn were relatively low in S15 and RIB (2% and 3%, respectively), while they were approximately 11% for ALJ. However, despite its low extraction yield, the extractable Zn concentration in the S15 soil was extremely high (6000 meq kg<sup>-1</sup>). The extractable yield for

Ni was low in the RIB and S15 soils, and it was approximately 17% in the ALJ soil. Water-soluble metal concentrations for the soils were compared with the European Council limits for the management of wastes (see Table S1 in the Supplementary Material) (European Council 2003). Under these regulations, the RIB soil is classified as a non-hazardous waste, while the high water-soluble concentrations of all metals in the ALJ soil and of Cd and Zn in the S15 soil resulted in these soils being classified as hazardous wastes. Thus, decreasing water-soluble metal concentrations would be an excellent management practice for these soils.

### *3.1.2. The effect of ageing on selected soil properties*

Selected soil parameters (pH, ANC and DOC) were monitored during the ageing period and are summarised in Table 1 through a comparison of the T0 and T2 samples. Soil pH remained constant during the ageing experiments for the ALJ and S15 soils. In contrast, the RIB soil acidified significantly (1.3 pH units) by the end of the ageing period studied. This behaviour may relate to a partial oxidation of the pyrite present in the RIB soil, which can result in soil acidification (Lacal 2003). This process was not observed in the ALJ soil, which also contained considerable pyrite content, because it had a much lower initial pH (2.2).

The ANC values of all soils remained roughly constant throughout the ageing period. The significant relative decrease in ANC noticed in the RIB soil was likely due to the acidification of the sample. The DOC content in all soils remained low throughout the ageing process and even decreased slightly at the end of the study period.

## **3.2. Changes in amendment properties during the ageing process**

### *3.2.1. Initial conditions*

Table 2 summarises some physicochemical parameters of the amendments. All amendments exhibited an alkaline pH, and had higher FC (all over 100%) and CEC values than the soils. MOW2 had a high ANC value, much higher than that found in the soils and nearly one order



of magnitude higher than that of the biochars. LOI content ranged from 60% in MOW2 to approximately 95% in the two biochars. Conversely, MOW2 had the highest DOC content, followed by BS and BF. The latter had a much lower DOC content, which was of the same order of magnitude as the soil samples. The LOI and DOC content in the amendment samples did not correlate, indicating that the ratio between solid and soluble organic matter strongly varied depending on the amendment.

The total metal content in the three amendments was low, much lower than the maximum concentration established for the addition of organic amendments to agricultural soils in Spain (BOE 2005). MOW2 consistently exhibited the highest total metal concentrations, whereas BS had the lowest. In most cases, the low metal concentrations in the amendments resulted in the dilution of total metal concentrations in the soil+amendment mixtures, with the exception of MOW2 added to RIB, where both samples had similar total metal concentrations for certain metals.

Although extraction yields of water-soluble metal concentrations for the amendments could occasionally be greater than those for the soils, the resulting concentrations were systematically lower than those obtained from the soil samples. Given the dose of amendments applied to soils and the low soluble metal content in these amendments, the contribution of the amendments to the pool of water-soluble metals in the soil+amendment mixtures was considered negligible. Comparing the metal soluble concentrations of the amendments with the European Council's limits for the management of wastes (European Council 2003) indicated that the three amendments would be classified as non-hazardous waste.

### *3.2.2. The effect of ageing on selected amendment properties*

Certain parameters (pH, ANC, CEC and DOC) were monitored during the ageing period and are summarised in Table 2 by comparing the T0 and T2 samples. The pH of the amendments

remained reasonably constant within the alkaline range, although a moderate decrease of 0.7 pH units was recorded for the BS biochar. The slight decrease in this pH may be related to the formation of acid organic functional groups associated with the natural oxidation of organic matter, which has a lower impact on samples with an already low pH (Hale et al. 2011).

The slight increase in the CEC and ANC values for the T2 samples, suggested the oxidation of functional groups on the surface of the organic amendments, which was consistent with reported data (Mukherjee et al. 2014). These two latter parameters were correlated ( $R=0.82$ ), thus confirming that the functional groups responsible for the CEC were also responsible for the buffering capacity of the amendments. Finally, slight increases or decreases in DOC content were observed depending on the examined amendment, indicating that DOC was not strongly affected by the ageing process.

### *3.2.3. Changes in the sorption capacity of amendments due to the ageing process*

Changes in the sorption capacity of the amendments during the ageing experiments were also tested for Cd and Cu, because sorption patterns may provide significant information that partially justifies changes in the metal leaching patterns of the soil+amendment mixtures. The isotherms obtained at T0, T1 and T2 are presented in Figure S1 in the Supplementary Material. Table 3 summarises the main sorption parameters of Cd and Cu derived from the data and fitting of the respective sorption isotherms.

Sorption data for the T0 samples indicated that the  $K_d$  parameter varied within a short range according to changes in the initial metal concentrations for all of the amendments. Differences between  $K_{d,min}$  and  $K_{d,max}$  values were generally lower than 2-fold. For Cd, amendment sorption capacity decreased in the following order: MOW2 > BS > BF. This was similar to the sequence of CEC and ANC values in the amendments, suggesting that exchange sites played a key role in Cd sorption. In the case of Cu, the  $K_d$  values were inverse to the DOC content of the amendments and followed the sequence BF > BS > MOW2. This behaviour

was consistent with the high affinity of Cu to form stable complexes with organic ligands in solution.

The obtained isotherms were satisfactorily fitted with the Freundlich equation with  $R^2 > 0.99$ . In the case of Cd,  $N$  values were always lower than 1, indicating sorption of Cd at high affinity sites in low concentrations, but at lower affinity sites in higher concentrations. This suggests that ionic exchange mechanisms may govern sorption. That is,  $K_d$  was predicted to continuously decrease with increasing initial Cd concentrations. Moreover, the  $K_f$  values were lower than  $K_{d,min}$ , since they were derived from an extrapolated scenario in which  $C_{eq}$  is 1 meq L<sup>-1</sup>, in this case for  $N < 1$ . For Cu, BF exhibited  $N < 1$ , indicating sites of decreasing affinity as Cu concentrations increased, as was observed for Cd. The amendments with higher DOC contents (MOW2 and BS) exhibited  $N > 1$ , suggesting that, at low concentrations, Cu was mostly associated with organic matter in solution, whereas when initial Cu concentrations increased, the competitive role of dissolved organic matter decreased and the sorption of Cu increased. As a result,  $K_f$  values for these cases were generally higher than  $K_{d,max}$ , because this value was also derived by extrapolating the  $C_{sorb}$  vs.  $C_{eq}$  isotherm to a  $C_{eq}$  value of 1 meq L<sup>-1</sup>, but for  $N > 1$ .

As the  $K_f$  estimation was strongly dependent on the  $N$  value, and a direct comparison of the metal+amendment scenarios would be compromised, comparisons were better made by fitting sorption data to a linear model. Thus,  $K_{d,linear}$  could be calculated for all cases at the lowest metal concentration values, resulting in a satisfactory fit, where  $R^2 > 0.9$ . The fitted  $K_{d,linear}$  parameters resulted in the same relative sequence of sorption among amendments as  $K_{d,min}$  and  $K_{d,max}$  for both Cd and Cu. Therefore,  $K_{d,linear}$  was considered a robust parameter in the evaluation of the effect of ageing on an amendment's sorption capacity. In general, minor variations were observed in the  $K_{d,min}$  and  $K_{d,max}$ , and consistent variations were observed for  $K_{d,linear}$  as a result of ageing, which were consistent with the minor changes in the physicochemical parameters of the amendments, including pH, DOC, ANC and CEC. The

consistent increase in  $K_{d,linear}$  for Cd in the BS biochar was an exception. This suggests that the sorption capacity of the amendments may be reasonably stable (or even increasing) over the ageing period. The relatively high  $K_d$  values observed in a few cases (e.g., Cd-MOW2, or Cu in biochars) should be considered an additional factor affecting metal availability in soil+amendment mixtures.

### **3.3. Changes in soil+amendment mixture properties during the ageing process**

#### *3.3.1. Initial conditions*

The effect of soil amendments on selected soil properties (pH, ANC and DOC) is summarised in Table S2 (T0 samples) (see the Supplementary Material). Every mixture had either a similar or higher pH than the untreated soils. The amendments with the greatest effect on pH were not those with the highest pH, but those with the highest ANC, that is, those with the highest buffering capacity. Accordingly, changes in pH and ANC were more relevant in soils with lower ANC values. The addition of amendments led to a minor increase in the pH of the S15 soil mixtures because this soil already had a high ANC. In the case of the RIB soil, which had a lower ANC, the amendments led to a slight increase in the pH of the resulting mixtures (1.1 for MOW2, 0.7 for BF and 1.6 for BS). Changes in the pH of the ALJ soil were strongly dependent of the amendment used. The addition of MOW2 resulted in a strong increase in soil pH (2.5 units of pH), whereas biochars had no effect on the mixture's pH because the buffering capacity of these two amendments was insufficient to have an effect on such an acidic soil. The same reasoning can be used to explain changes in ANC after amendments were added. Soil mixtures with MOW2 resulted in increased ANC values. The largest impact was seen in the ALJ soil, which had the lowest ANC, and the smallest effect occurred in the S15 soil, which already possessed high ANC levels. The RIB-BS mixture exhibited a minor decrease in pH after the ageing period (T2 samples), which was consistent with the pH decrease observed for the RIB soil and the BS amendment. The rest of the cases exhibited

non-significant changes in pH and ANC as a result of the ageing experiment, which was consistent with the absence of significant variations in the pH and ANC values observed in the relevant amendments and soils.

With respect to DOC, the addition of MOW2 and BS amendments led to a slight increase in the DOC concentrations in the mixtures at T0 for untreated soils, as was expected based on the higher DOC levels in those amendments; in contrast, this parameter was not significantly modified by the addition of BF. Based on our observations, the ageing process did not lead to a significant or consistent modification of DOC in the soil+amendment mixtures.

### *3.3.2. Changes in water extractable metal concentrations due to the addition of amendments and ageing*

Figure 1 summarises the leaching of target metals in the soil+amendment mixtures (T0 samples), with untreated soil taken as a control, as well as the effect of ageing on metal leaching in soils and soil+amendment mixtures (T1 and T2 samples).

#### *The case of the S15 soil*

At the initial time (T0), leaching of all metals in the S15 soil was very low (within the 0.05-3% range), with the exception of Cd (50%). The high total metal concentration suggested that metal concentrations in the extracts were likely very high, despite the low extraction yields, as was the case for Zn (approximately 6000 mg kg<sup>-1</sup>) and for Cd (approximately 500 mg kg<sup>-1</sup>). As expected by the already low extraction yields and high buffer capacity of this soil, a slight decrease in metal extractability was only observed for Cd and Zn when MOW2 and BS amendments were added to the soil; the effect was less pronounced for BF. These changes could be partially explained by the fact that BS and MOW2 had high  $K_d$  (Cd) values, even greater than those expected in soils (Sauvé et al. 2000), and a similar sorption pattern in the amendments could be anticipated for Zn based on the similarity of their sorption behaviour

with that of Cd. For Cu and Pb, non-significant changes occurred after the application of the amendments; thus, no additional role on decreasing metal extractability could be attributed to sorption mechanisms.

Ageing of the S15 samples did not change the amendments' effect pattern, which was consistent with the lack of changes in the amendment properties due to the ageing process. Major changes observed between the T0 and T2 samples in the extractability of specific metals were attributed to changes in the metal-soil interactions caused by the drying-wetting cycles. The drying process accelerated the process of natural attenuation, during which the metals are able to be sorbed by inner sphere mechanisms instead of outer sphere mechanisms because of the loss of water molecules, causing them to become less reversibly sorbed (Gerson et al. 2008).

#### *The case of the RIB soil*

At the initial time (T0 samples), metal extraction yields for the RIB soil followed the same trend as observed for the S15 soil. The relatively low metal concentrations in the extracts were related to both low total metal concentration and low extraction yields. Pb and Cu exhibited the lowest extraction yields (<0.5%), while Ni and Zn were also in the low value range (2% and 3%, respectively). On the other hand, Cd had the highest, but still moderated extraction yield (8%). As anticipated, the significant changes in the pH and ANC values in the RIB mixtures caused by the addition of the amendments resulted in a significant decrease in leachable concentrations of Zn, Cd and Ni in the mixtures when compared with the untreated soil. However, the minor role of the specific sorption increase should not be disregarded, especially for Ni and Cd. In this case, MOW2 and BS provoked larger reductions in the extraction yield than BF, which was consistent with their greater  $K_d$  related to Cd. The amendments had a minor effect on the extractable concentrations of Cu and Pb, despite the

changes in pH and ANC, because of the extremely low extraction yields for these metals in the RIB soil.

With respect to the effect of the ageing on metal extractability, the decrease in the leachable concentrations of metals persisted over time in the soil+amendment mixtures, even when slight increases in the extractable concentrations were observed in the soil without amendments (as was the case of Zn). Further decreases over time were observed for Ni and Cd. As already observed for the S15 soils, this confirmed the stability of the amendments added to contaminated soils over time.

#### *The case of the ALJ soil*

At the initial stage (T0 samples), high concentrations of Cu, Pb and Zn were observed in the extracts due to the low pH value of this soil. Given the total metal concentration, this led to metal extraction yields in the untreated ALJ soil that were generally higher than those for the other two soils: 5%, 20%, 17% and 11% for Cd, Cu, Ni and Zn, respectively. The exception was Pb, which also had an extremely low extraction yield (lower than 0.5%). The addition of the MOW2 amendment led to a significant decrease in leachable concentrations of all metals, as this material increased the pH of the soil by more than two units. Conversely, no change was observed after the addition of BS and BF because the ANC of these amendments was insufficient to increase the pH of such an acidic soil.

In general, the changes in metal extractability observed in the soil+amendment mixtures at T0 were maintained throughout the ageing process. Therefore, the positive effect of the MOW2 amendment and the leachability pattern of the other two mixtures were constant even after being subjected to the ageing process.

#### **4. Conclusions**

In the present study minor changes in the physicochemical properties of organic amendments occurred during the ageing process. In general, minor increases in CEC and ANC due to the ageing process were observed, whereas pH and DOC content remained almost constant. The sorption capacity of the amendments was generally not affected by ageing either. Once the soils were amended, the addition of the compost and the biochars led to a beneficial effect, decreasing metal extractability in the resulting mixtures, especially in the soils in which pH and ANC increased. Moreover, DOC did not significantly change in the mixtures during the ageing period. Of the amendments, the MOW2 compost seemed to be the most promising material. Decreases in extractable metal concentrations observed at the initial stage were maintained throughout the ageing period tested, revealing that the effect of the amendments would persist over time, as required for a robust soil remediation strategy.

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**Table 1** Main parameters of soils

Parameter	S15	RIB	ALJ
pH	6.3	6.4	2.2
ANC (meq kg <sup>-1</sup> )	1960	60	-440
Moisture (%)	7.9	1.1	1.3
FC (%)	34	29	21
LOI (%)	0.9	1.0	1.0
DOC (mg L <sup>-1</sup> )	12	21	18
CaCO <sub>3</sub> (%)	16	<l.q.	<l.q.
CEC (cmol <sub>c</sub> kg <sup>-1</sup> )	13	6.9	3.0
Sand (% , wrt mineral matter)	63.9	76.5	34.2
Clay (% , wrt mineral matter)	9.5	7.2	18.2
Cd (mg kg <sup>-1</sup> )	TC 10200	4	15
	WS 5140	0.3	0.8
Cu (mg kg <sup>-1</sup> )	TC 16430	120	1610
	WS 8.1	0.6	330
Ni (mg kg <sup>-1</sup> )	TC 150	26	60
	WS 4.9	0.6	9.9
Pb (mg kg <sup>-1</sup> )	TC 91520	260	12370
	WS 43	0.5	60
Zn (mg kg <sup>-1</sup> )	TC 275500	350	3295
	WS 6030	9.8	360
<i>Effect of aging in selected soil properties</i>			
pH	T0 6.3	6.4	2.2
	T2 6.4	5.1	2.2
ANC (meq kg <sup>-1</sup> )	T0 1960	60	-440
	T2 1865	25	-350
DOC (mg C L <sup>-1</sup> )	T0 10	20	20
	T2 5	10	15

ANC: acid neutralization capacity; FC: field capacity; LOI: loss on ignition; DOC: dissolved organic carbon; CEC:cation exchange capacity

TC: total content; WS: water soluble; l.q.: limit of quantification

**Table 2** Main parameters of amendments

Parameter		MOW2	BF	BS
pH		8.1	8.6	9.4
ANC (meq kg <sup>-1</sup> )		4180	420	725
Moisture (%)		6.0	4.5	6.0
FC (%)		175	116	100
LOI (%)		60	95	95
DOC (mg L <sup>-1</sup> )		475	10	220
CEC (cmol <sub>c</sub> kg <sup>-1</sup> )		65	25	55
Cd (mg kg <sup>-1</sup> )	TC	6.4	1.2	0.6
	WS	0.4	0.8	0.1
Cu (mg kg <sup>-1</sup> )	TC	150	33	20
	WS	7.3	0.4	0.2
Ni (mg kg <sup>-1</sup> )	TC	75	15	1.6
	WS	0.9	<1.q.	<1.q.
Pb (mg kg <sup>-1</sup> )	TC	175	4.2	1.7
	WS	1.9	1.6	1.0
Zn (mg kg <sup>-1</sup> )	TC	430	75	105
	WS	2.1	9.2	0.8
<i>Effect of aging in selected amendment properties</i>				
pH	T0	8.1	8.6	9.4
	T2	8.0	8.3	8.7
ANC (meq kg <sup>-1</sup> )	T0	4180	420	725
	T2	4915	515	790
CEC (cmol <sub>c</sub> kg <sup>-1</sup> )	T0	65	25	55
	T2	85	30	60
DOC (mg L <sup>-1</sup> )	T0	475	10	220
	T2	390	6	245

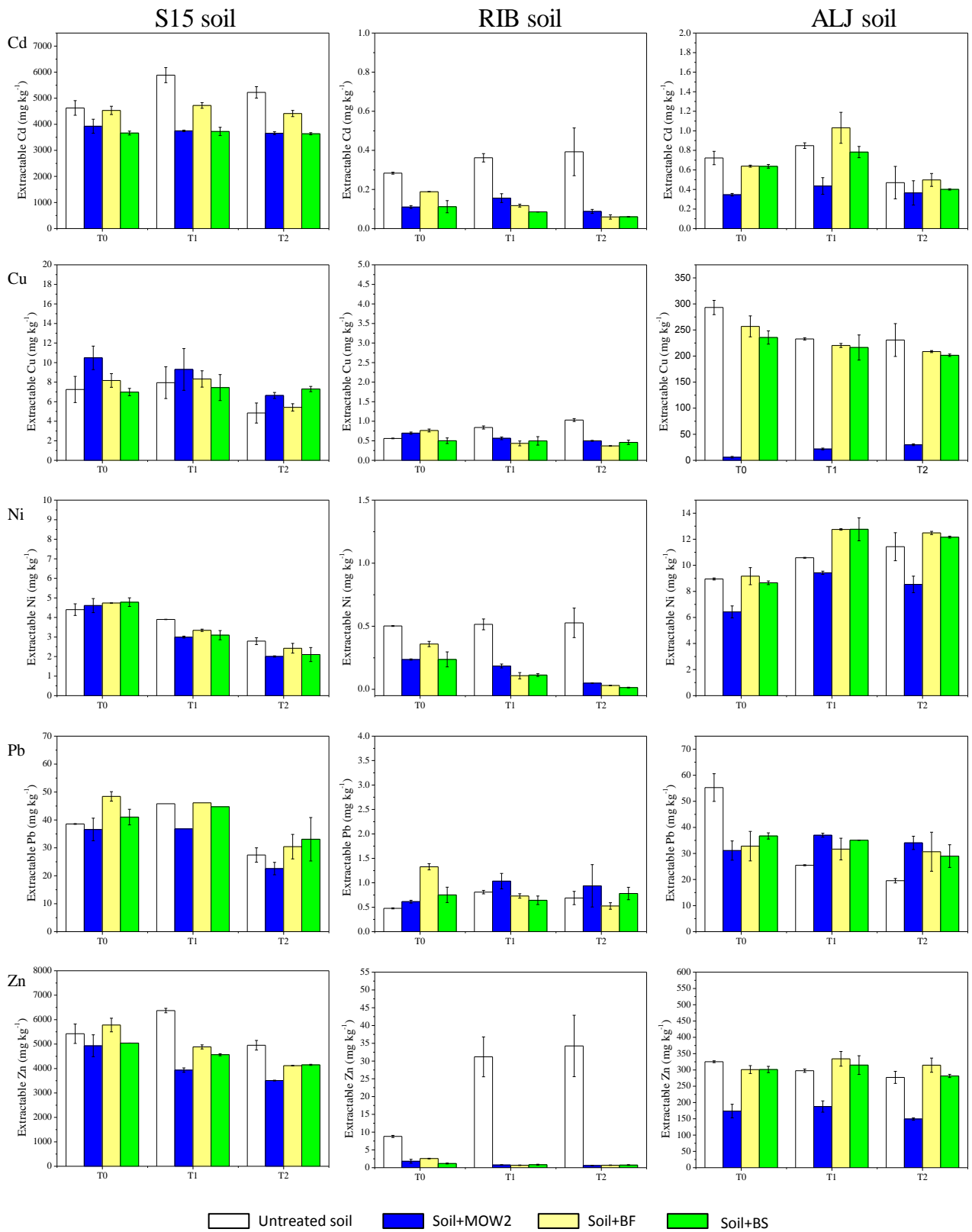
ANC: acid neutralization capacity; FC: field capacity; LOI: loss on ignition; DOC: dissolved organic carbon; CEC: cation exchange capacity

TC: Total content; WS: Water soluble; l.q.: limit of quantification

**Table 3** Sorption parameters of amendments

Metal		$K_{d,min}$ (L kg <sup>-1</sup> )	$K_{d,max}$ (L kg <sup>-1</sup> )	$K_f$	$N$	$K_{d,linear}$ (L kg <sup>-1</sup> )
<b>Cd</b>						
MOW2	T0	2320	3265	1040 (170)	0.81	2640 (90)
	T1	2440	3510	1020 (190)	0.81	2790 (70)
	T2	2190	3525	1010 (110)	0.83	2400 (80)
BF	T0	170	320	80 (20)	0.64	240 (10)
	T1	150	270	80 (10)	0.67	200 (10)
	T2	100	210	60 (5)	0.67	125 (10)
BS	T0	770	1410	325 (10)	0.76	860 (50)
	T1	1725	3205	680 (60)	0.79	1830 (100)
	T2	1640	3320	500 (150)	0.73	1700 (170)
<b>Cu</b>						
MOW2	T0	915	1445	4840 (670)	1.30	1715 (60)
	T1	825	1530	5760 (1440)	1.32	1740 (40)
	T2	620	1585	3250 (1830)	1.27	1365 (110)
BF	T0	2605	4860	610 (70)	0.72	2350 (310)
	T1	3930	8200	900 (100)	0.70	4750 (320)
	T2	2535	7370	540 (40)	0.66	3180 (240)
BS	T0	1770	2255	2590 (1170)	1.04	2140 (50)
	T1	1405	2630	3280 (1560)	1.09	2140 (50)
	T2	1495	2415	3375 (1950)	1.07	2370 (80)

**Fig. 1** Effect of aging on the leaching of heavy metals in soils and soil+amendment mixtures. Error bars indicate one standard deviation.



# Supplementary material

## Effect of ageing on the availability of heavy metals in soils amended with compost and biochar: evaluation of changes in soil and amendment properties

Andrea Venegas, Anna Rigol, Miquel Vidal

### Material and methods

#### Sample characterisation

The pH of each soil and amendment was measured in deionised water using a solution-to-solid ratio of 10 mL g<sup>-1</sup>. Field capacity (FC) was determined by wetting the samples until a saturated paste was obtained, and then the paste was centrifuged at 0.33 bar (75 x g during 30 min). The samples were then dried at 105°C to constant weight. The resulting weight loss was the FC. Particle size distribution was determined using the pipette method and was based on the varying settling velocity in a fluid medium of the different particle sizes (Burt, 2004).

The buffering capacity of the samples was examined using a pH titration test (CEN/TS, 2006). This test also allowed for the determination of the acid neutralisation capacity (ANC) of the samples, which is defined as the quantity of an acid or base (meq kg<sup>-1</sup>) required to shift the initial pH of a sample to a pH of 4. First, the initial pH of each sample (2 g) was measured in a 1:100 sample/deionised water ratio. Then, consecutive additions of 200 µL of 1 mol L<sup>-1</sup> HNO<sub>3</sub> or 1 mol L<sup>-1</sup> NaOH were made, and the pH of the suspension was measured after the sample was stirred for 40 min following each addition. The acid and base additions were repeated until the pH range of 2–12 had been covered.



The cationic exchange capacity (CEC) of the amendments and soils was determined by extraction using ammonium acetate (Bower et al., 1952). 5 g of the sample was put in contact with 30 mL of 95% ethanol, and the resulting suspension was shaken end over end for 5 min and then centrifuged. This procedure was repeated three times to remove the soluble salts, and the supernatants were discarded. 30 mL of 1 mol L<sup>-1</sup> ammonium acetate were added to the remaining solid, and the suspension was again shaken end over end for 5 min and centrifuged. This step was repeated three times, and the supernatants were collected in the same flask. The exchangeable cations (Ca, Mg, K, Na) in the supernatant were determined using ICP-OES, and the CEC was calculated as the sum of the exchangeable cations.

The loss-on-ignition (LOI) of the samples was determined as the loss of weight of 3 g of soil (or 10 g of amendment) at 450°C for 16 h. The soil (or amendment) had been previously oven-dried overnight at 110°C. The dissolved organic carbon (DOC) content was quantified in the water extracts obtained by equilibrating 6 g of the sample with 60 mL of deionised water for 48 h. Then, the samples were centrifuged and filtered through a 0.45-µm filter, and the DOC content was determined from a water extract that had been previously acidified to pH 2 with HCl. A total organic carbon analyser (Shimadzu TOC-50000) was used to determine DOC.

The total content of trace elements in the soil samples was determined through soil digestion in a closed microwave digestion system (Milestone Ethos Touch Control) following a procedure adapted from EPA 3052 (USEPA, 2008). Briefly, 0.3 g of the sample were weighed in a PTFE vessel, and 6 mL of 69% HNO<sub>3</sub>, 3 mL of 40% HF and 2 mL of 30% H<sub>2</sub>O<sub>2</sub> were added in the first stage. The temperature was gradually increased from 25°C to 190°C over 15 min, and then the sample was held at a constant temperature for 30 min. After a cooling time of 10 min, 16 mL of 5% H<sub>3</sub>BO<sub>3</sub> were

added to mask the free fluoride ions present in the solution and re-dissolve the fluoride precipitates; and the resulting suspension was subjected to the same digestion procedure as in the first stage. After cooling the extracts to room temperature, they were diluted with deionised water to a final volume of 50 mL and stored at 4°C until analysis.

The water-soluble metal content was quantified from the water extracts obtained after equilibrating a known amount of sample with deionised water in a 1:10 solid:liquid ratio (DIN, 1984) for 48 h at room temperature. Then, the samples were centrifuged, and the water extract was decanted, filtered and stored at 4°C until analysis. Metals were determined in the solutions by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Perkin–Elmer Model OPTIMA 3200RL. The following emission lines were used for each element determined (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 mg L<sup>-1</sup> Cd; 0.01 mg L<sup>-1</sup> for Cu; 0.1 mg L<sup>-1</sup> for Ni; 0.2 mg L<sup>-1</sup> for Pb and 0.025 mg L<sup>-1</sup> 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 µg L<sup>-1</sup> for Cd; 0.1 µg L<sup>-1</sup> for Cu; 0.2 µg L<sup>-1</sup> for Ni; 0.05 µg L<sup>-1</sup> for Pb and 0.2 µg L<sup>-1</sup> for Zn.

**Table S1** Reference levels and intervention limits ( $\text{mg kg}^{-1}$ ) for agricultural and industrial soils regulated by the Junta de Andalucía (1999) and water soluble contents ( $\text{mg kg}^{-1}$ ) regulated by Decision 2003/33/CE of the European Council (2003) for the acceptance of waste at landfills

Junta de Andalucía				EC Decision 2003/33/CE		
Reference level <sup>a</sup>		Intervention limit <sup>b</sup>		Inert waste	Non-hazardous waste	Hazardous waste
		Agricultural soils (pH < 7)	Industrial soils			
Cd	2	7	30	0.04	1	5
Cu	50	300	1000	2	50	100
Ni	40	200	750	0.4	10	40
Pb	100	350	2000	0.5	10	50
Zn	200	600	3000	4	50	200

<sup>a</sup>Maximum allowable concentration for non-polluted soils, which indicates that 90% of soils from the region present lower contents.

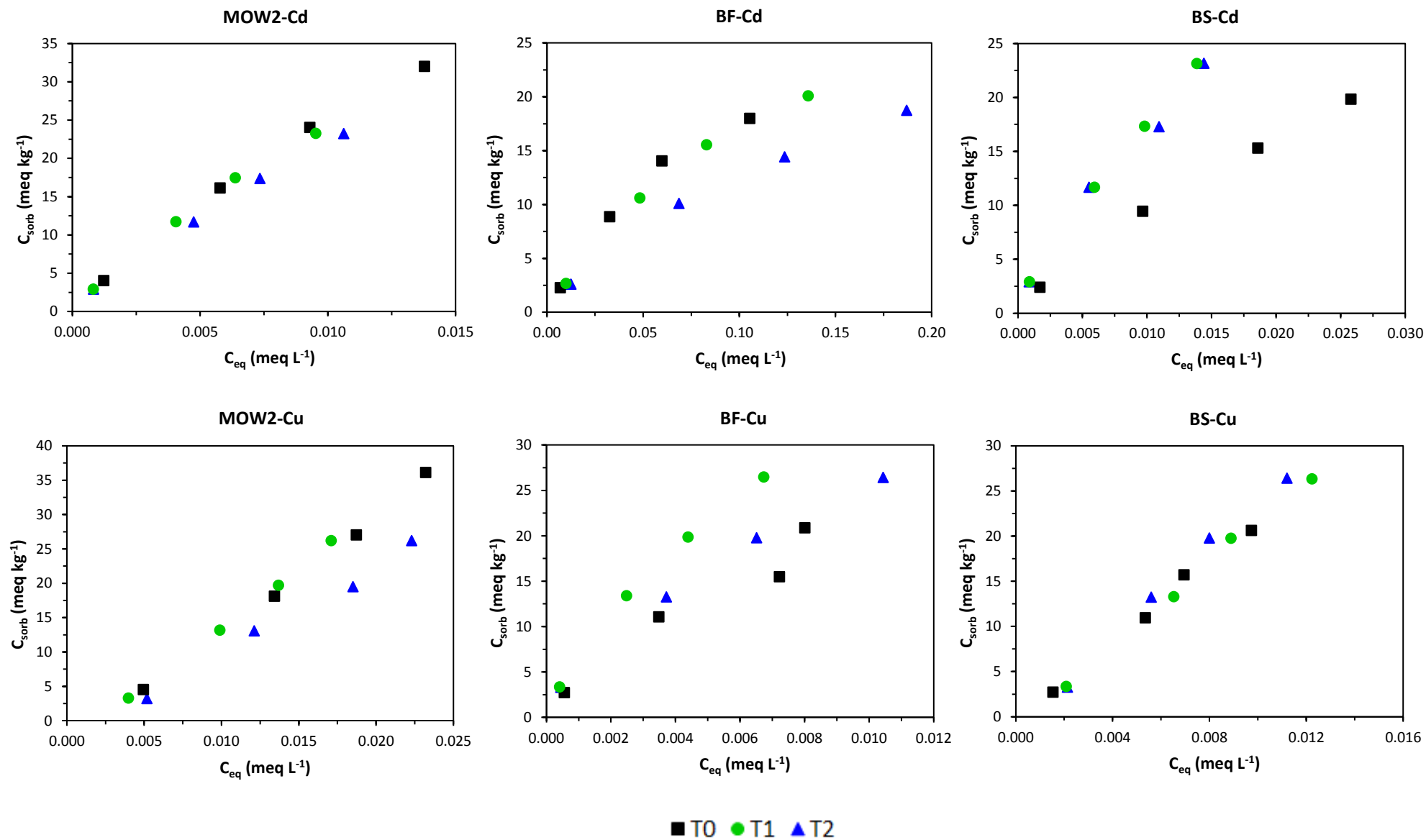
<sup>b</sup>Threshold concentration above which the soil is considered contaminated with dangerous levels and urgent remediation process is required.

**Table S2** Effect of aging in selected properties of the soil+amendment mixtures

		S15-MOW2	S15-BF	S15-BS	ALJ-MOW2	ALJ-BF	ALJ-BS	RIB-MOW2	RIB-BF	RIB-BS
pH	T0	6.6	6.3	6.4	4.7	2.1	2.0	7.5	7.1	7.6
	T2	6.6	6.4	6.4	4.3	2.0	2.0	7.7	6.9	7.3
ANC (meq kg <sup>-1</sup> )	T0	2260	2070	1740	35	-245	-260	305	90	95
	T2	2370	1855	1790	15	-310	-220	360	60	95
DOC (mg C L <sup>-1</sup> )	T0	30	10	25	25	15	35	40	15	45
	T2	30	8	12	20	13	20	30	10	20

ANC: acid neutralization capacity; DOC: dissolved organic carbon

**Fig. S1** Sorption isotherms of Cd and Cu in the amendments at increasing aging time



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