Reduction of the short-term availability of copper, lead and zinc in a contaminated soil amended with municipal solid waste compost

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ABSTRACT

The effect of two municipal solid waste composts on the availability of Cu, Pb and Zn in a soil contaminated in the laboratory was evaluated. An agricultural acid soil developed on granite was amended with the composts at two rates (3% and 6% dry weight), contaminated with $1000\,mg\,kg^{-1}$ of Cu, Pb and Zn, and incubated in the laboratory for three months. Determinations of soil pH, $CaCl_2$-extractable and EDTA-extractable Cu, Pb, and Zn were run monthly during the incubation. At the end, a leaching test (TCLP) and selective extractions were performed for these elements. The analysis of the $CaCl_2$-extractable elements demonstrated a strong capacity of both composts to decrease the solubility of the metals added to the soil, specially for Cu and Pb. The percentage of reduction of the soluble forms with respect to the initial addition was higher at the highest rate of compost, and reached 99% for Cu and Pb, and 80% for Zn in the compost-amended soil, whereas the soil without amendment was able to reduce Cu availability by a 94%, but not Zn or Pb availability. The TCLP test showed that compost also reduced the leachability of the three elements. Nevertheless, EDTA extracted a major amount (around 90%) of the elements added in all the treatments. Given that EDTA has a strong ability to extract elements bound to organic matter, it can be hypothesized that the main mechanism of the observed insolubilization was the formation of low-solubility organo-metallic complexes with both soil and compost organic matter. The selective extractions confirmed that compost reduced the exchangeable fraction of the elements, and that the organically bound fraction (pyrophosphate-extractable) was the main one for the three elements.

1. Introduction

The recycling of the organic matter contained in municipal solid waste (MSW) as an amendment for agricultural soils after composting is a feasible option for conserving the organic matter levels in soil and also for improving soil quality and productivity [1–6]. However, MSW composts can in some cases introduce contaminants in the soil, because they may present high concentrations of toxic trace elements, especially when mechanically sorted organic fraction is used for their production, instead of the separately collected waste [7,8]. Yet, it can be hypothesized that the high organic content of MSW compost and the affinity of some toxic elements for organic matter could in some cases make compost act as a sink for contaminants. This fact could be of beneficial application both in the remediation of contaminated soils and in the treatment of industrial wastewaters. Several authors have suggested the use of residual materials such as compost for in situ remediation of

heavy metal contaminated soils, as the least ecologically damaging and least expensive remediation technique [9,10]. Compost has been reported as having a great potential for retaining trace elements in non-available forms [8], potentially reducing their overall bioavailability and toxicity due to several processes, including raising soil pH, complexation, sorption, precipitation, or a combination of them, thus providing an effective soil remediation technique [11,12]. However, some drawbacks may happen with this technique, namely the potential mobilization of some elements (in particular Cu) associated to dissolved organic matter [13,14], and the re-release of the immobilized elements after compost organic matter mineralization in the long term. These drawbacks can in fact be avoided, first, because high loads of dissolved organic matter are expected only when low-stabilized organic materials are employed, as their concentrations decrease with compost maturity. Besides, the mineralization of mature compost proceeds in general at a low rate [15–18], and there is no evidence that trace element availability increases with time in compost-amended soil as a result of organic matter mineralization [8]. Therefore, employing non-stabilized organic materials for this purpose should be avoided in order to keep the potential drawbacks at a minimum.

In this work, samples from the Ap horizon of an agricultural acid soil developed on granite were amended with two MSW com-

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posts at two rates (3% and 6% dry weight), contaminated with 1000 mg kg^{-1} of Cu, Pb and Zn, and incubated at 23 °C in the laboratory for three months, in order to assess the reduction in the availability of these elements, the role played by the compost addition, and the major mechanisms involved in the reduction, as well as to test the hypothesis that compost organic matter plays a key role in the reduction of their availability.

2. Materials and methods

2.1. Soil

The soil used in the experiments was a cropped soil developed over granite, located in the Pedroso hill (Santiago de Compostela, NW Spain, 43° N and 8° W), 180 m above the sea level, under an oceanic climate (mean annual temperature 12.3 °C; mean annual rainfall 1900 mm). Similar soils in the area are classified as Haplic Umbrisols [19] or Humic Dystrudepts [20]. A composite sample from the top 10 cm of the Ap horizon of the soil was taken in February 2008. For the analysis of the general properties of the air-dried soil, the methods described by Guitián and Carballas [21] were followed. The particle size distribution was determined by wet sieving and the pipette method. Soil pH was determined in a water suspension 1:2.5 sample:solution ratio and in KCl 0.1 N. Total organic carbon was determined on ground sample by wet dichromate oxidation and titration with ferrous ammonium sulphate. Total N was determined on ground sample on an elemental analyzer LECO (CHN-1000). For total Cu, Zn and Pb analysis, 0.2 g of the ground sample were digested with 1 mL HF, 5 mL HNO$_3$, and 4 mL HCl in pressure digesters at 120 °C in a microwave oven CEM MDS2000, and the extracts analyzed by flame atomic absorption spectrometry (Varian SpectraAA 220FS).

2.2. Composts

Two composts were employed: MSWC is an aerobic compost obtained from the source-separated organic fraction of MSW, provided by an industrial composting facility in Galicia (Spain). MSGW is a commercial compost obtained from source separated MSW mixed with green waste, supplied by an industrial composting facility in Catalunya (Spain). For the analysis of the general properties of the composts the Spanish version of the European methods for the characterization of soil amendments and substrates [22–25] was followed. Briefly, pH was determined in aqueous extracts (substrate/extractant ratio: 1/5, v/v) of fresh samples. Total organic matter (OM) was determined by weight loss on ignition of dried ground samples at 450 °C, and total organic C (TOC) calculated multiplying OM by a factor 0.58. Total N was measured by Kjeldahl digestion of dried ground samples and steam distillation [26]. Total Cu, Pb and Zn were determined after digestion of dried ground sample with HCl and HNO$_3$ (3:1 ratio), and the extracts were analyzed for Cu, Zn, and Pb using flame atomic absorption spectrometry (Varian SpectraAA 220FS). Dissolved organic carbon (DOC) was determined by the wet dichromate oxidation method after 1 h extraction with distilled water with a solid:liquid ratio of 1:10 [27].

2.3. Incubation experiment

The soil was mixed by hand with each compost at two rates: 3% and 6% (dry weight), roughly equivalent to 60 and 120 t ha^{-1}. The soil alone and the mixtures with compost were contaminated with a solution containing Cu(NO$_3$)$_2$·3H$_2$O, Pb(NO$_3$)$_2$ and Zn(NO$_3$)$_2$·6H$_2$O (Panreac S.A., Barcelona, Spain), in order to obtain a final concentration of 1000 mg kg^{-1} (dry weight) for each element in all samples (treatments are listed in Table 1). Three replicates

Table 1
Treatments assayed in the incubation experiment.

Key	Treatment
S	Soil
CS	Contaminated soil
CS L3	Contaminated soil with 3%MSWC
CS L6	Contaminated soil with 6% MSWC
CS M3	Contaminated soil with 3% MSGW
CS M6	Contaminated soil with 6% MSGW

of each treatment were placed on 0.5-L plastic pots and incubated at 23 °C in the laboratory during 90 days. Their moisture was maintained throughout the experiment around 80% of their field capacity, replacing weight losses with distilled water.

Composite samples were taken monthly at random from each pot, and air-dried for analysis. Soil pH (in water and KCl) was determined as explained above, and Cu, Pb and Zn forms and availability were determined as follows.

2.3.1. Availability analysis

For the determination of immediately available Cu, Zn and Pb, 2 g of air-dry soil were extracted with 20 mL of 0.01 N CaCl$_2$, shaken for 3 h, and filtered [28]. The potentially available elements were extracted with EDTA (ethylene diamine tetraacetic acid), following the method by Lakanen and Erviö [29]. 5 g of air-dry soil were shaken for 1 h in 50 mL of a solution of 0.5 M ammonium acetate and 0.02 M EDTA at pH 4.65, centrifuged at 700 × g for 15 min, and filtered. The extracts from both methods were analyzed for Cu, Zn, and Pb using flame atomic absorption spectrometry (Varian SpectraAA 220FS).

2.3.2. Leaching test

At the end of the incubation, a leaching test was performed following the toxicity characteristic leaching procedure (TCLP) according to the EPA Method 1311 [30]. The extraction was performed using a 1:10 solid:water ratio with aqueous acetic acid adjusted to pH 4.93. Samples were shaken in a rotary shaker at 30 rpm during 18 h at 23 °C. After the extraction step, samples were centrifuged at 2000 rpm during 15 min and filtered by 0.45 μm, and Cu, Zn and Pb were determined in the extracts using flame atomic absorption spectrometry (Varian SpectraAA 220FS).

2.3.3. Selective extractions

At the end of the incubation, the following selective extractions for Cu, Pb and Zn were performed:

- Exchangeable elements (Cu$_A$, Pb$_A$, Zn$_A$). 10 g of soil were shaken for 1 h in 50 mL of 1 M ammonium acetate at pH 7 [31]. The elements displaced by this reagent are assumed to provide an estimate of the exchangeable elements.
- Pyrophosphate-extracted elements (Cu$_P$, Zn$_P$, Pb$_P$). One hundred millilitres of 0.1 M Na-pyrophosphate were added to 1 g of soil and the resulting suspension was shaken for 16 h [32]. Five drops of 0.04% Superfloc were added to the extract before centrifugation in order to produce the flocculation of clay. Sodium pyrophosphate is known to be a highly effective extractant for metal–humus complexes and is assumed to recover organically bound elements.
- Oxalic–oxalate-extracted elements (Cu$_o$, Pb$_o$, Zn$_o$). 1 g of soil was shaken for 4 h in 50 mL of 0.2 M oxalic acid–ammonium oxalate at pH 3 [33]. This reagent extracts those elements associated with organic and inorganic non-crystalline soil components.
- Ascorbic–oxalic–oxalate-extracted elements (Cu$_{AO}$, Pb$_{AO}$, Zn$_{AO}$). Fifty millilitres of a solution of 0.2 M oxalic acid–ammonium oxalate plus 0.1 M ascorbic acid (pH 3.25) were added to 1 g of soil and shaken for 30 min in a water bath at 96 °C [34]. In addition to the elements bound to both organic and inorganic non-crystalline

Table 2
Soil and composts main properties. OM: total organic matter.

	Soil	MSWC	MSGW
pH_w	5.0	8.2	9.2
pH_{KCl}	4.1	–	–
OM (g kg^{-1})	50	397	429
Total C (g kg^{-1})	29	230	248
Total N (g kg^{-1})	3	15	17
C/N	10	15	14
DOC (g kg^{-1})	–	5.7	5.1
Total Cu (mg kg^{-1})	7	829	52
Total Pb (mg kg^{-1})	62	223	62
Total Zn (mg kg^{-1})	22	1149	200

soil components, this reagent extracts those associated with crystalline Al and Fe hydrous oxides.

After the period of shaking, the different extracts obtained were centrifuged at $700 \times g$ for 15 min, and filtered through acid washed filter paper.

- Total elements (Cu_T, Pb_T, Zn_T) were determined as explained above for the soil.

3. Results

3.1. Properties of soil and composts

Table 2 shows the main properties of the soil and composts employed in this work. The soil had a sandy-loam texture (75% sand, 15% silt, 10% clay) and acidic pH (Table 2), as usual in the granitic soils in the area. The composts employed had alkaline pH and similar concentrations of total organic matter (397 and 429 g kg^{-1} for MSWC and MSGW, respectively). The concentrations of DOC (5.7 and 5.1 g kg^{-1} for MSWC and MSGW, respectively), pointed to a higher degree of stability of MSGW, and they both were near to the value of 5 mg g^{-1} considered by many authors as indicative of stable composts [35–37]. The composts differed mainly on their Cu, Pb and Zn concentrations which were much higher in the compost MSWC (52 and 829 mg kg^{-1} for Cu, 62 and 223 mg kg^{-1} for Pb, 200 and 1149 mg kg^{-1} for Zn, for MSGW and MSWC, respectively).

3.2. Incubation experiment

The amendment with both composts alleviated the acidification of soil pH provoked by the addition of the contaminant solution (Table 3). This effect was more pronounced at the highest rates of compost. At the 3% rate, the composts slightly increased the original pH of the soil, while at the rate of 6%, the soil pH was increased in more than one unit, reaching final pH values around 5.5.

Fig. 1 shows the results of the extraction of Cu, Zn and Pb with CaCl$_2$, which is supposed to estimate the short-term available pool of the elements to plants [38]. The unamended soil was able to reduce the solubility of half the Cu added already after the first month of incubation, and reaching at the end of the experiment

Table 3
Evolution of pH in water and KCl throughout the incubation (mean ± standard deviation).

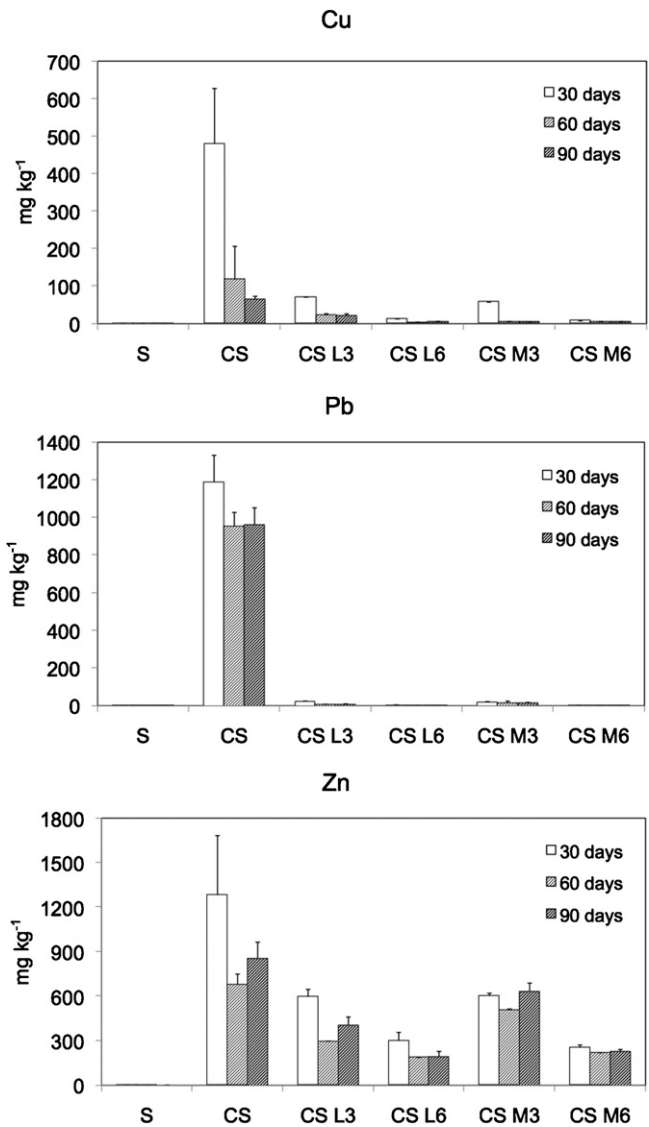| Treatment	Day					
	30		60		90	
	pH_w	pH_{KCl}	pH_w	pH_{KCl}	pH_w	pH_{KCl}
S	4.4 ± 0.0	4.1 ± 0.0	4.2 ± 0.0	4.0 ± 0.0	4.1 ± 0.0	3.9 ± 0.0
CS	3.6 ± 0.1	3.6 ± 0.1	3.7 ± 0.0	3.9 ± 0.0	3.6 ± 0.0	3.8 ± 0.0
CS L3	4.6 ± 0.1	4.4 ± 0.1	4.7 ± 0.1	4.7 ± 0.1	4.7 ± 0.0	4.7 ± 0.1
CS L6	5.5 ± 0.1	5.3 ± 0.1	5.6 ± 0.1	5.5 ± 0.1	5.4 ± 0.1	5.5 ± 0.1
CS M3	4.8 ± 0.1	4.7 ± 0.2	4.7 ± 0.1	4.8 ± 0.2	4.7 ± 0.1	4.7 ± 0.2
CS M6	5.5 ± 0.0	5.6 ± 0.1	5.6 ± 0.0	5.6 ± 0.0	5.5 ± 0.0	5.5 ± 0.0

Fig. 1. Evolution of CaCl$_2$-extractable elements (mg kg^{-1}) throughout the incubation (bars represent standard deviation of the mean).

a 94% reduction of the spiked concentration. In turn, the concentrations of Pb and Zn remained in values close to the initial ones during the whole incubation, with only a slight reduction with time, showing that the soil had lower capacity to reduce their solubility as compared to Cu.

Despite their different total Cu, Pb and Zn contents, the addition of both composts reduced the immediate availability of Cu, Zn and Pb in a similar manner, and their effect took place mainly during the first two months of incubation. The reduction observed in availability was proportional to the rate of compost, and the increment of the compost rate from 60 to 120 t ha^{-1} produced in most cases reductions in the extractable concentrations of the elements higher than 50%. Lead was the element for which the composts showed the highest remediation potential, as the reduction of availability reached almost 100% at the end of the incubation. Copper fixation was also very high, reaching almost a 100% reduction of the initial concentrations, although in this case, the whole effect cannot solely be attributed to the addition of compost, as the unamended soil was able to reduce Cu availability by almost a 94%. The lowest effect was that observed for Zn, although the reduction of availability for this element reached near 80% at the highest rates of both composts.
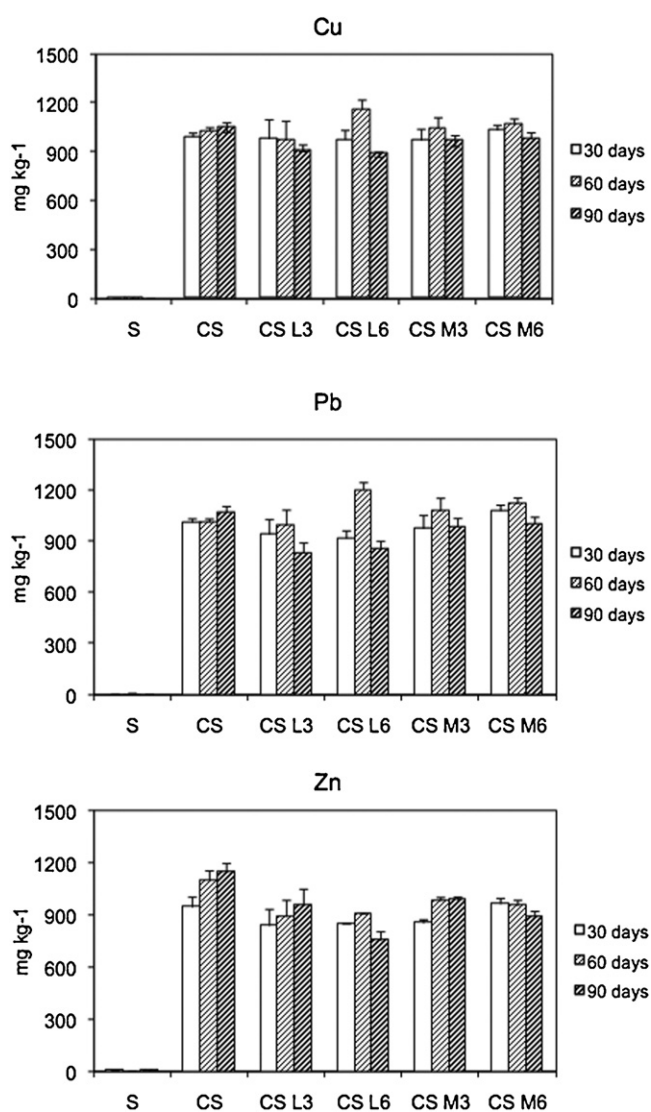
Fig. 2. Evolution of EDTA-extractable elements (mg kg^{-1}) throughout the incubation (bars represent standard deviation of the mean).

Table 5
Selective extractions of Cu, Pb and Zn (mg kg^{-1}) after the third month of incubation (mean ± standard deviation).

	Cu_A	Cu_P	Cu_O	Cu_{OA}	Cu_T
S	nd	3 ± 0.9	6 ± 0.4	5 ± 0.1	16 ± 2
CS	171 ± 12	902 ± 40	1024 ± 52	1002 ± 79	1198 ± 48
CS L3	87 ± 4	833 ± 226	999 ± 55	854 ± 50	1200 ± 26
CS L6	60 ± 4	866 ± 20	916 ± 81	829 ± 76	1303 ± 30
CS M3	91 ± 3	955 ± 56	1017 ± 75	917 ± 49	1230 ± 34
CS M6	56 ± 5	829 ± 95	932 ± 121	902 ± 78	1407 ± 69

	Pb_A	Pb_P	Pb_O	Pb_{OA}	Pb_T
S	nd	nd	nd	8 ± 1	25 ± 3
CS	365 ± 19	881 ± 16	589 ± 19	608 ± 13	1342 ± 25
CS L3	209 ± 18	795 ± 155	198 ± 9	305 ± 7	1324 ± 35
CS L6	140 ± 5	789 ± 160	155 ± 12	285 ± 7	1391 ± 55
CS M3	224 ± 59	908 ± 47	252 ± 15	282 ± 7	1342 ± 70
CS M6	195 ± 35	848 ± 50	159 ± 12	294 ± 2	1521 ± 22

	Zn_A	Zn_P	Zn_O	Zn_{OA}	Zn_T
S	3 ± 0.2	11 ± 1	8 ± 0.2	16 ± 0.3	73 ± 11
CS	514 ± 32	980 ± 43	903 ± 59	970 ± 88	1117 ± 41
CS L3	297 ± 13	820 ± 75	790 ± 62	774 ± 78	1196 ± 23
CS L6	177 ± 10	896 ± 97	622 ± 53	710 ± 62	1360 ± 142
CS M3	314 ± 10	901 ± 41	890 ± 59	822 ± 27	1239 ± 108
CS M6	187 ± 18	772 ± 60	775 ± 129	767 ± 88	1371 ± 72

Cu_A, Pb_A, Zn_A: ammonium acetate extractable Cu, Pb, Zn; Cu_P, Pb_P, Zn_P: pyrophosphate-extractable Cu, Pb, Zn; Cu_O, Pb_O, Zn_O: oxalic/oxalate-extractable Cu, Pb, Zn; Cu_{OA}, Pb_{OA}, Zn_{OA}: ascorbic/oxalic/oxalate-extractable Cu; Cu_T: total Cu, Pb, Zn; nd: not detected.

In contrast, the amounts of Cu, Pb and Zn extractable in EDTA (Fig. 2) kept in values around 1000 mg kg^{-1}, which roughly corresponded to the amounts of the initial spike, for all samples and at all times during the incubation. Thus, and despite the reduction of immediate solubility observed in the CaCl$_2$ extraction, an effect due to the addition of compost was not observed for this pool of extractable elements.

The results of the TCLP test (Table 4) showed that the soil itself had an important capacity for decreasing Cu and Pb mobility, but much lower for Zn. After three months of incubation only a minor part of the Cu and Pb initially added remained in immediately

Table 4
TCLP leaching test for Cu, Pb and Zn (mg kg^{-1}) after the third month of incubation (mean ± standard deviation).

	Cu	Pb	Zn
S	nd	nd	nd
CS	323 ± 27	150 ± 13	959 ± 56
CS L3	37 ± 6	5 ± 1	541 ± 5
CS L6	11 ± 3	nd	219 ± 28
CS M3	34 ± 7	7 ± 2	464 ± 16
CS M6	25 ± 2	6 ± 1	351 ± 21

nd: not detected.

mobile forms in the unamended soil, whereas for Zn the leachable fraction was almost equal to the initial spike. The addition of compost strongly reduced the mobile forms of the three elements with respect to the unamended soil, with the more marked effect for Cu and Pb. In all cases, the effect was higher the higher the rate of compost employed. These results are in agreement with those observed for the CaCl$_2$ extractable elements, confirming the reduction of the immediate availability due to compost addition.

Table 5 shows the results of the selective extractions performed. Problems were found with the oxalic–oxalate extractions, for it is usual that the concentrations in these extracts are higher than in the pyrophosphate extract. However, in this case, this occurred only for Cu, whereas the concentrations for Zn were very similar, and far lower for Pb. This points to a problem of precipitation of Pb and Zn oxalates, given the low degree of solubility of these compounds [39,40], so the use of extractants based on oxalate must be considered carefully when studying contaminated soils.

In theory, the following operationally defined fractions could be determined for each element (M): M_E = exchangeable elements (M_A); M_{OM} = elements associated with organic matter ($M_P - M_A$); M_{IA} = elements associated with amorphous inorganic components ($M_O - M_P$); M_C = elements associated with crystalline oxides ($M_{OA} - M_O$); and M_R = residual elements incorporated in the crystalline structure of minerals ($M_T - M_{OA}$). In this case, and given the operational problems found for Pb and Zn, for which the fractions linked to inorganic components could not be calculated accurately, we calculated the exchangeable and organically bound fractions of these elements as explained, but the residual fraction was not calculated, as it can be seen that these calculations would lead to the overestimation of the residual fraction. For Cu, the calculations were made as usual.

As seen in Table 6, the presence of compost decreased the exchangeable fraction of the three elements, and higher reductions were observed at the highest rate of compost. Here, Cu was the element with the lowest exchangeable pool, which represented a low percentage of the total (near 6% in the soils with the highest rate of compost), while the concentrations for Pb and Zn were higher in

Table 6
Cu, Pb and Zn fractions (mg kg^{-1}) after the third month of incubation (mean ± standard deviation).

	Cu_E	Cu_{OM}	Cu_{IA}	Cu_C	Cu_R
S	nd	3 ± 1	4 ± 0.4	nc	10 ± 2
CS	171 ± 12	731 ± 52	122 ± 38	nc	173 ± 118
CS L3	87 ± 4	746 ± 227	166 ± 70	nc	202 ± 34
CS L6	60 ± 4	805 ± 25	51 ± 35	nc	386 ± 50
CS M3	91 ± 3	864 ± 53	62 ± 32	nc	214 ± 76
CS M6	56 ± 5	773 ± 96	103 ± 42	nc	475 ± 90
	Pb_E	Pb_{OM}	Pb_{IA}	Pb_C	Pb_R
S	nd	nd	nd	8 ± 1	17 ± 4
CS	365 ± 19	516 ± 30	nc	nc	nc
CS L3	209 ± 18	586 ± 146	nc	nc	nc
CS L6	140 ± 5	649 ± 159	nc	nc	nc
CS M3	224 ± 59	683 ± 94	nc	nc	nc
CS M6	195 ± 35	653 ± 15	nc	nc	nc
	Zn_E	Zn_{OM}	Zn_{IA}	Zn_C	Zn_R
S	3 ± 0.2	9 ± 11	nd	5 ± 0.4	58 ± 11
CS	514 ± 32	467 ± 70	nc	nc	nc
CS L3	297 ± 13	523 ± 93	nc	nc	nc
CS L6	177 ± 10	719 ± 110	nc	nc	nc
CS M3	314 ± 10	587 ± 33	nc	nc	nc
CS M6	187 ± 18	585 ± 73	nc	nc	nc

Cu_E, Pb_E, Zn_E: exchangeable Cu, Pb, Zn; Cu_{OM}, Pb_{OM}, Zn_{OM}: Cu, Pb, Zn bound to organic matter; Cu_{IA}, Pb_{IA}, Zn_{IA}: Cu, Pb, Zn bound to amorphous inorganic materials; Cu_C, Pb_C, Pb_C: Cu, Pb, Zn bound to crystalline Fe and Al hydrous oxides; Cu_R, Pb_R, Zn_R: residual Cu, Pb, Zn; nd: not detected; nc: not calculated.

Fig. 3. Comparison of EDTA-extractable and pyrophosphate-extractable elements after the third month of incubation.

all cases. Again, these results confirm the reduction of short-term availability observed in the TCLP test and the CaCl$_2$ extraction. The organically bound fraction was higher than the exchangeable fraction, representing in most cases over 50% of the total, and it was not affected by the addition of compost at any rate. This shows again that an important fraction of the elements was linked to organic matter, in good agreement with the results of the EDTA extraction. As for the fraction linked to inorganic components, for Cu it was smaller in size to the organic pool, and totally associated to the amorphous components. A consistent effect of the composts on this pool was not observed. Finally, part of the added Cu went into non-extractable (residual) forms, and it was observed that both composts increased the size of this fraction proportionally to the rate added.

4. Discussion

The addition of a highly concentrated solution containing Cu, Pb and Zn to an acid cropped soil rich in organic matter had as main effects a strong decrease of soil pH, and increments in both the total concentrations and availability of the three elements. It has to be noted that the conditions in the contaminated soil, this is, strongly acidic pH (under 4) and high concentrations of potentially toxic metals, are similar to those existing in contaminated soils affected for example by mine waste disposal or acid mine drainage [41,42]. After a three-month incubation the availability of the three elements, determined after extraction with CaCl$_2$, decreased progressively, with the highest reduction for Cu. These changes took place without modifications in the soil pH, thus demonstrating the existence of inherent mechanisms in the soil for decreasing the availability of these elements.

The addition of compost to the contaminated soil produced changes in the extractability and leachability of the three elements with respect to the contaminated unamended soil. The immediate availability, assessed by means of a extraction with CaCl$_2$, was strongly reduced for the three elements, but specially for Cu and Pb, which achieved reductions leading to final concentrations com-
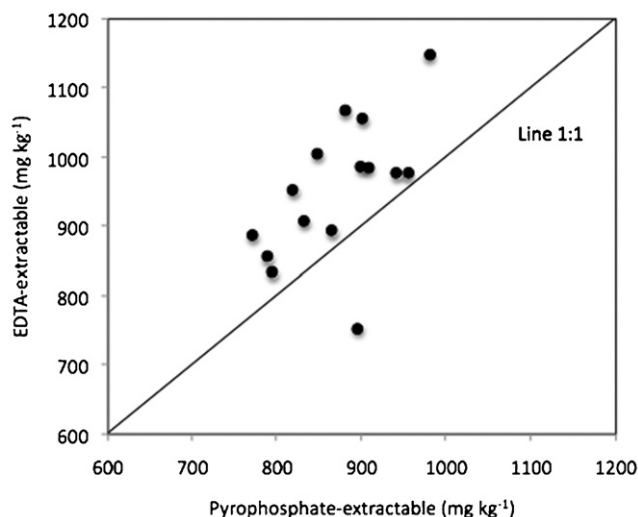
parable to those in the non contaminated soil. The leachability, assessed by the TCLP test, was also reduced in the compost-amended soils for the three elements, and especially for Cu and Pb. These two extractions assess the immediate environmental risk, and their results were highly coincident, so it is unarguable the role of compost addition on the reduction of the immediate availability of Cu, Pb and Zn. This is in line with the findings of other researchers in the direction that compost inputs to contaminated soils containing large fractions of labile elements reduce their overall bioavailability [8,11,12]. It is also remarkable that despite the large differences existing in the metal contents between the two composts, which were much higher for MSWC, they reduced the availability of Cu, Pb and Zn in a similar manner. This is suggesting that, at least at the rates employed here, the composts will not act as sources of contaminants.

The exchangeable fraction of Cu, Pb and Zn was also reduced in the compost-amended soils with respect to the unamended soil, but the size of this pool was in all cases higher than in the non-contaminated soil. An important amount of the spiked Cu, Pb and Zn went to this fraction, but it decreased with the addition of compost, while at the same time, the organically bound (pyrophosphate-extractable) fraction increased. This suggests that compost decreases the mobility/availability of these elements by displacing them from exchange sites to less labile forms, such as metal–MO complexes, this is, increasing the strength of union to the soil matrix.

The extractions with EDTA, a strong complexant used to estimate potential availability, and pyrophosphate, used to estimate the pool of elements associated to organic matter, showed that most of the spiked elements remained in these pools, with a much lower effect of compost than seen for the other procedures employed for the determination of availability. In comparison to CaCl$_2$ for example, ammonium acetate-EDTA is a relatively harsh extractant which removes most of the major element pools, including soluble, exchangeable, sorbed and organically bound, and some bound in oxide form and to clay minerals [43]. In comparison, sodium pyrophosphate extracts the exchangeable plus the organic-associated elements. The results of the pyrophosphate and the EDTA extractions were very similar, but EDTA extracted amounts of the three elements which were in general slightly higher than those extracted by pyrophosphate (Fig. 3). Although EDTA is commonly employed to estimate the potentially plant-available pools of elements, it has been recently pointed out that it extracts higher

quantities than plants are able to take up, therefore overestimating immediate phytoavailability [38,44,45], and our results seem to confirm this point.

Problems with the selective extraction methods avoided to determine accurately the fraction of Pb and Zn which are associated to inorganic Fe, Mn or Al components. Although this fraction was not very important for Cu, there are funded reasons to believe that there may be an important fraction of Pb and Zn in this pool, as fractionation studies of composts and contaminated soils have demonstrated [46–50]. For that reason, searching for selective extraction methods which can be applicable also to highly polluted soils seems very important, specially if some methods might give a wrong idea about the potential mobility of pollutants as a result of an incorrect fractionation.

The comparison of the results of the different extraction procedures suggests indeed a key role of organic matter in the reduction of the availability of Cu, Pb and Zn. As commented above, complexing agents such as EDTA mainly solubilize elements held as sorbed and organically bound phases [43], whereas neutral salts such as $CaCl_2$ displace elements weakly bound to soil components or in soil solution [45]. In consequence, the differences found between the amounts of Cu, Pb and Zn extracted by both methods can be explained assuming that the elements are mainly bound to compost and soil organic matter. Although it is true that the increments in soil pH induced by the composts had surely an important role in reducing availability, Cu and Pb were virtually rendered unavailable in the soil amended with compost, even though the pH increment induced by the compost was not drastic, and pH values were in all cases in a range (near 5.5 or less) where the availability of most metals is high [51]. Therefore, an additional role of mechanisms other from precipitation due to increased pH must be considered for the observed availability reduction.

Sorption is the mechanism more likely to produce the observed reductions in the availability of the three elements. Sorption on SOM by means of complexation, especially with humic and fulvic acids, represents possibly the most important retention mechanism for Cu in soils [52,53]. In a recent work, Pérez-Novo et al. [54] demonstrated that organic matter has a stronger effect on Cu sorption that on Zn sorption, by studying acid soils in which organic matter had been removed by treatment with H_2O_2. The fact that in our work the effect of compost was less marked for Zn than for Cu is indeed confirming the role of sorption on organic matter and not only pH, in the reduction of availability.

Several researchers have shown the potential of compost as a sorbent for Cu, Pb or Zn. Grimes et al. [55] assessed the binding potential of Cd, Cu, Pb and Zn salts by compost in batch sorption studies, finding that the relative binding of the added metals was in the following order: Pb > Cd = Cu > Zn. In a similar study of heavy metal leachability and retention by compost produced from wood, straw and vegetable wastes, Song and Greenway [56] also reported the high sorption affinity of compost for heavy metals, which followed this sequence of affinity: Pb > Cr > Cu > Ni ≥ Cd ≥ Zn, and suggested that humic substances were likely to be the main sites of metal sorption. Kocasoy and Güvener [57] also observed the high retention capacity of compost for Cu and Zn, obtaining percentages of removal of 92% for Cu and 67% for Zn in batch experiments with metal solutions. Similarly, O'Dell et al. [58] found a high binding capacity of yard waste compost for Cu and Zn, while Nwachukwu and Pulford [10] found that the affinity of Cu, Zn and Pb for different soil amendments, including compost and green waste compost, was in the order Pb > Cu ≫ Zn, with the highest effectiveness for the green waste compost.

As seen, the strong sorption of Cu and Pb to compost emerges as a consistent characteristic from the scientific literature, and most researchers agree that Zn is less strongly sorbed to organic matter than Cu; this is due to the stronger binding sites for Cu by virtue of its lower electronegativity and higher charge-to-radius ratio [59,60], and also to the higher affinity of Zn for iron oxides. However, most works studying compost sorption have been performed in laboratory tests with aqueous solutions, so the effect of compost when added to soil cannot be accurately estimated. What is new here is to determine that incorporating 3% or 6% compost to a soil can have such drastic effects on the short-term metal mobility. Thus, our results point out the potential of composts as low-cost sorbents for the remediation of contaminated soils. Even in the case of an eventual release of contaminants in available forms once organic matter mineralization advances, the demonstrated initial reduction of availability due to compost addition poses the greatest interest for the restoration of contaminated soil, because of the potential alleviation of metals toxicity and availability during the first moments of restoration, when plant establishment must be achieved.

5. Conclusions

The addition of municipal solid waste compost at rates of 3% or 6% to a soil artificially contaminated with Cu, Pb and Zn allowed to drastically reduce the availability of these elements, as shown by their extractability in $CaCl_2$ 0.01 N. The solubility of Cu and Pb was reduced by almost 100%, whereas the reduction for Zn reached 80%. The leachability of the three elements, assessed by the TCLP method, also decreased as an effect of compost addition. In contrast, the extractability of the elements in EDTA was not affected by the addition of compost.

In what concerns the metal distribution in chemical phases the exchangeable forms of the three elements, as the most mobile ($CaCl_2$, TCLP), decreased as a consequence of the incorporation of compost. The fraction associated with organic matter (pyrophosphate-extractable) was always the most important, representing over half of the total, and together with the results of the EDTA extraction, confirms that the mechanism of availability reduction was probably the association of Cu, Pb and Zn with organic matter.

These results show that – at least in the short term – the amendment of metal-contaminated sites with compost could be an effective methodology for soil remediation due to the reduction of the mobility and availability of potentially toxic elements.

Acknowledgements

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