

# Chemical Fractionation of Trace Elements in a Metal-Rich Amphibolite Soil Amended with Municipal Solid Waste Composts

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## Abstract

**Purpose** The high concentrations of metals naturally present in soils developed on mafic and ultramafic rocks such as amphibolite could be mobilized in response to modification of soil physicochemical properties after compost amendment. However, so far, research with this type of soils is insufficient. With the objective of understanding the potential risk associated to trace elements in this case, we have studied the chemical distribution of trace metals in an amphibolite agricultural soil amended with several composts and incubated during 3 months in the laboratory.

**Materials and Methods** An agricultural acid soil developed on amphibolites was amended with 5% (dry weight) of five commercial composts (produced mainly from municipal solid wastes) and incubated in the laboratory during 90 days. Trace element potential mobility and bio-availability in the soils were studied by means of chemical analyses: extraction of immediately available trace elements with 0.01 N CaCl<sub>2</sub> and the normalized BCR sequential extraction procedure.

**Results and Discussion** High concentrations of 0.01 N CaCl<sub>2</sub> soluble metals occurred in the non-amended soil (especially Zn and Ni), that decreased after compost addition for Pb, Zn, Ni and Cd, with no effect on Cu and Cr. In general, composts had little effect on the BCR fractionation of the trace elements, because of their high native

concentrations in the studied soil. Even so, the addition of the composts with the highest metal contents increased the oxidizable (organic matter-bound) and reducible (iron oxides-bound) fractions of soil Cu and the soluble and reducible fractions of soil Zn and Ni. None of the composts modified Pb fractionation, which was mostly found in the reducible fraction, nor that of Cr, present in more than 80% in the residual non-extractable fraction.

**Conclusion** This study showed that, in soils developed over metal-rich parent materials such as amphibolites, chemical fractionation of metals after compost amendment is more influenced by the nature of the metals previously present in soil than by the composition of the composts.

**Keywords** Compost · Soil pollution · Mafic rocks · Heavy metals

## Introduction

The use of organic amendments for maintaining soil fertility is as old as agriculture. Nowadays, the evolution of society towards a more urban-based way of life has modified the cycles of organic matter, from short and closed ones (when food production and consumption are close), to longer, more complex ones. Sources of organic matter that were produced in the past close to the agricultural fields where they were needed, are now far from them, associated to urban centres where they pose an environmental problem, in many cases. Although the modern use of chemical fertilizers, pesticides, selected seeds and other advances has made organic amendments no longer essential for the productivity of agricultural systems, organic matter plays a key role in soil functions other than short-term crop production. Thus, it is essential for proper operation and maintenance

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of soil quality to recover and recycle the organic matter present in wastes. As a consequence, composting of organic wastes and recycling of compost in agricultural fields has spread worldwide and is regarded as a necessary technology. Composts from a variety of origins are nowadays being produced and used as amendments in agriculture [1, 2]. However, the relative novelty of the use of these products, in addition to the diversity in their composition and properties makes it necessary a careful examination of their effects on the soil-plant system.

Compost use has many advantages, most of them related to the increment of soil organic matter contents after its application as organic amendment. This leads to changes in physical, chemical and biological properties of soils, often with positive effects such as improved conditions for plant growth, increase of nutrient availability, or reduction of the mobility of inorganic pollutants [1, 3–6]. However, the use of certain composts, such as those produced from urban wastes, can raise serious concerns about the environmental impact of this practice [7]. Although many studies point out the positive effects of amendments issued from urban wastes [1], these composts may present high concentrations of potentially toxic trace elements, such as Cu, Zn or Cr, especially when mechanically-sorted organic fraction is used for their production, instead of the separately collected waste [8].

The environmental risk derived from the agricultural use of compost relies to a great extent on the behaviour of trace elements once they reach the soil, which is a function of (i) their concentrations and chemical forms in compost, and (ii) their interactions with soil components. In addition, compost often modifies the physicochemical conditions of soil, in particular its pH and organic matter content, two properties with a strong influence on the fate of trace elements in soil by affecting their solubility. Besides the possible contribution of metals to soil by adding compost, the mobility and bioavailability of trace elements previously present in the soil can be modified by the changes of soil physicochemical properties induced by compost. Under these circumstances, studies in compost-amended soils are necessary in order to accurately estimate the potential risks of this agricultural practice. In this sense, the particular properties of each soil are decisive. Evaluation of trace elements dynamics in compost-amended soil needs previous knowledge on soil natural trace element contents, which is intimately related to lithology. An example of the importance of lithology are soils developed on mafic and ultramafic rocks such as amphibolites or serpentinites, naturally enriched in trace elements, in particular Ni and Cr [9]. The origin of metals in soils derived from these parent materials is lithogenic, so they cannot be considered as polluted, although they may surpass the threshold levels allowed for addition of organic amendments to agricultural soils

[10]. Therefore, careful and thorough evaluation of metal mobility and bioavailability in these soils is particularly necessary.

This is the case for the soils developed on the amphibolites in the area of Santiago de Compostela (NW Spain). These amphibolites are a part of the massif of mafic and ultramafic rocks known as the Ordes Complex, that also includes biotite schists, serpentinites and gabbros [11]. The soils developed on this material present a residual enrichment in Fe and Al, an almost complete removal of alkaline cations [12] and significant amounts of highly reactive components, such as poorly crystalline mineral constituents and organo-metal complexes [13, 14]. Despite their high metal contents [15], these soils have been widely employed for agricultural production for centuries, due to great soil depth and the smooth relief of the landscape over these materials [16, 17].

The modification of soil physicochemical properties that are a common consequence of compost amendment, mentioned above, can become extremely important in the case of amphibolite soils: the high amount of metals naturally present in the soils could be mobilized at any moment in response to those changes. However, to the best of our knowledge no studies have dealt with the behaviour of metals in these kind of soils after compost amendment. With the objective of understanding the potential risk of trace elements in this case, we have studied the chemical distribution of trace metals in an agricultural amphibolite soil amended with several composts and incubated during 3 months in the laboratory.

## Materials and Methods

### Soil

The soil used in the experiment was a cropped soil developed on amphibolitic colluvial material, located in Santiago de Compostela (NW Spain, 43°N and 8°W), 180 m above 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 Ferrali-Humic Umbrisols or Oxyc Dystrudepts [14]. For the experiment, a composite sample was taken from the top 10 cm of the Ap horizon of the soil. For the analysis of soil pH, texture and total organic carbon (TOC), the methods described by Guitián and Carballas [18] were followed. The particle size distribution was determined by wet sieving and the pipette method, after organic matter and iron oxides destruction. Soil pH was determined in a water suspension (1:2.5 sample:solution ratio). Total organic carbon was determined by wet dichromate oxidation and titration with ferrous ammonium sulphate, and total nitrogen by

the Kjeldahl method. Total Fe, Cu, Pb, Zn, Cr, Ni and Cd were determined after microwave digestion with HF, HNO<sub>3</sub> and HCl at 120 °C and the extracts were analysed using flame atomic absorption spectrometry (Varian SpectraAA 220FS).

## Composts

Four municipal solid waste composts and a manure vermicompost were used: MSWC1 was obtained by anaerobic fermentation of the biodegradable fraction of municipal solid waste (MSW), separated before collection, followed by an aerobic composting step, to stabilize the incompletely digested residue. MSWC2 was obtained by composting the source separated organic fraction of MSW. Both MSWC1 and MSWC2 were provided by industrial composting facilities located in Galicia (Spain). MSGW is a commercial compost obtained from source separated biodegradable MSW mixed with green waste, and MGSS is compost obtained from municipal garden trimmings mixed with sewage sludge; they both were supplied by an industrial composting facility located in Catalunya (Spain). Finally, MV is a mixed manure vermicompost supplied by a local producer in Galicia (Spain). For their analysis, the Spanish version of the European methods for the characterization of soil amendments and substrates [19–21] 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. Total elements were extracted after digestion of dried ground sample with HCl and HNO<sub>3</sub> (3:1 ratio), and the extracts were analysed using flame atomic absorption spectrometry (Varian SpectraAA 220FS). More details about compost characterization can be found in Paradelo et al. [22, 23].

## Incubation Experiment

The soil was amended with a 5% (dry weight) of each one of five composts, roughly equivalent to 100 Mg compost ha<sup>-1</sup> and a N input between 0.5 g kg<sup>-1</sup> (compost MV) and 0.9 g kg<sup>-1</sup> (compost MGSS). Three replicates of each treatment plus a control consisting of non-amended soil were placed on 0.5-L plastic pots and incubated at 23 °C in the laboratory during 90 days. Moisture was maintained throughout the experiment around 70% of field capacity, replacing weight losses with distilled water. Composite samples were taken monthly at random from each pot, and air-dried for analysis. For the determination of immediately available trace elements (Cu, Pb, Zn, Cr, Ni, Cd), 2 g of

air-dry soil were extracted with 20 mL of 0.01 N CaCl<sub>2</sub>, shaken for 3 h, and filtered [24].

Cu, Pb, Zn, Ni and Cr distribution in chemical fractions was assessed monthly, following the BCR sequential extraction procedure as described by Rauret et al. [25]. This method consists of three steps and a residual extraction, and defines four fractions: an acid-soluble fraction, a reducible fraction that is mainly associated to iron and manganese oxides, an oxidizable fraction associated to organic matter, and a non-extractable fraction which is associated to silicates and other mineral material. The extraction procedure is as follows:

### Step 1 (Extraction A, Acid Soluble Fraction)

a 1 g sample was shaken for 16 h in 40 mL of 0.11 M acetic acid solution. The extract was separated from the solid residue by centrifugation at 3000 g for 30 min. The extracted solution was stored in a refrigerator at 4 °C until analysis. The residue was washed by adding 20 mL of deionised water, shaking for 20 min and centrifuged as before.

### Step 2 (Extraction B, Reducible Fraction)

The washed residue from the first step was shaken for 16 h in 40 mL of 0.5 M hydroxylammonium chloride solution adjusted to pH 1.5 by the addition of 2 M nitric acid. The extract was separated and stored as in the first step. The residue was washed as in the first step.

### Step 3 (Extraction C, Oxidizable Fraction)

10 mL of 8.8 M hydrogen peroxide solution were slowly added to the residue from the second step. The mixture was digested for 1 h at 22 °C and then for 1 h at 85 ± 2 °C and the volume of the liquid was reduced to less than 3 mL. A second aliquot of 10 mL of hydrogen peroxide was added, the mixture was digested for 1 h at 85 ± 2 °C, and the volume was reduced to about 1 mL. After cooling, the moist residue was shaken for 16 h in 50 mL of 1 M ammonium acetate solution adjusted to pH 2 with concentrated nitric acid. The extract was separated from the solid residue by centrifugation and decantation as previously, collected in polyethylene bottles and stored at 4 °C until analysis.

### Residual Fraction: (Extraction D, Non-extractable Fraction)

The residue from the third step was digested with *aqua regia* following the recommendations of Pueyo et al. [26]. In this case, the amount of acid used to attack 1 g of sample was reduced to 7.0 mL of HCl (37%) and 2.3 mL of HNO<sub>3</sub> (70%), in order to keep the same volume to mass ratio.

Cu, Pb, Zn, Cr and Ni concentrations in the BCR extracts were determined using an ICP-MS spectrophotometer (VARIAN 820-MS). Blanks were run in parallel to all the determinations. To confirm the accuracy of the extraction procedure and analysis, the certified reference material CRM701 was also analysed in parallel to the soil samples. The recovery of the elements in the different fractions was between 81 and 109% of the certified values.

## Results and Discussion

The amphibolite soil presents a slightly acidic pH and a loamy texture; it is rich in organic matter and iron oxides (Table 1). Edaphic properties are very similar to those reported by Ferro-Vázquez et al. [16] for the surface cycle of a terraced paleosol in the same area. Recent lime additions, that are common in the area, explain the pH value, less acidic than expected. The total concentrations of the six metals analysed (Cu, Zn, Pb, Cr, Ni and Cd) are slightly higher than the mean values for soils developed over similar parent material in the region [15], and surpass the values allowed in the EU Directive for amendment with sludge [10].

The five composts presented pH values that ranged from neutral (MGSS) to alkaline (MSGW), and similar TOC contents, with organic matter accounting for approximately half of the dry compost weight. Regarding total trace element contents, Zn and Cu were the most abundant in all the composts, followed by Pb, Cr and Ni, and last, Cd. It has to be highlighted that Cr and Ni contents are higher in the soil than in the composts, an unusual fact that is related

here to their abundance in the parent material. According to the Spanish regulation for compost use [27], the composts MV and MSGW would be categorized as class C composts, and therefore could not be used in agricultural soils at rates higher than 5 Mg ha<sup>-1</sup>, whereas MSWC1, MSWC2 and MGSS could not be used as organic amendments, since they surpass the allowed levels for several elements. Even so, these metal-rich composts were employed in the study in order to obtain metal loads that are not negligible compared to the high metal contents of the amphibolite soil.

The effect of compost addition on pH and soil organic carbon (SOC) content during the incubation is shown

**Table 2** Soil pH and organic carbon (SOC) at the beginning and at the end of the incubation experiment

	pH <sub>w</sub>		SOC (g kg <sup>-1</sup> )	
	Initial	Final	Initial	Final
Control soil	6.0±0.1	5.1±0.1	39±2	39±3
Amended soil				
MSWC1	6.9±0.2	6.2±0.2	46±0.2	44±2
MSWC2	6.7±0.1	6.4±0.2	47±5	46±4
MSGW	6.7±0.2	6.6±0.2	49±3	43±3
MGSS	6.6±0.2	6.3±0.1	50±2	47±1
MV	6.8±0.2	6.1±0.3	44±0.3	37±0.5

Mean ± standard deviation (n = 3)

MSWC1 and MSWC2 composts obtained from source separated organic fraction of municipal solid waste, MSGW compost obtained from source separated organic fraction of municipal solid waste mixed with green waste, MGSS compost obtained from municipal garden trimmings mixed with sewage sludge, MV manure vermicompost

**Table 1** Properties of soil and composts

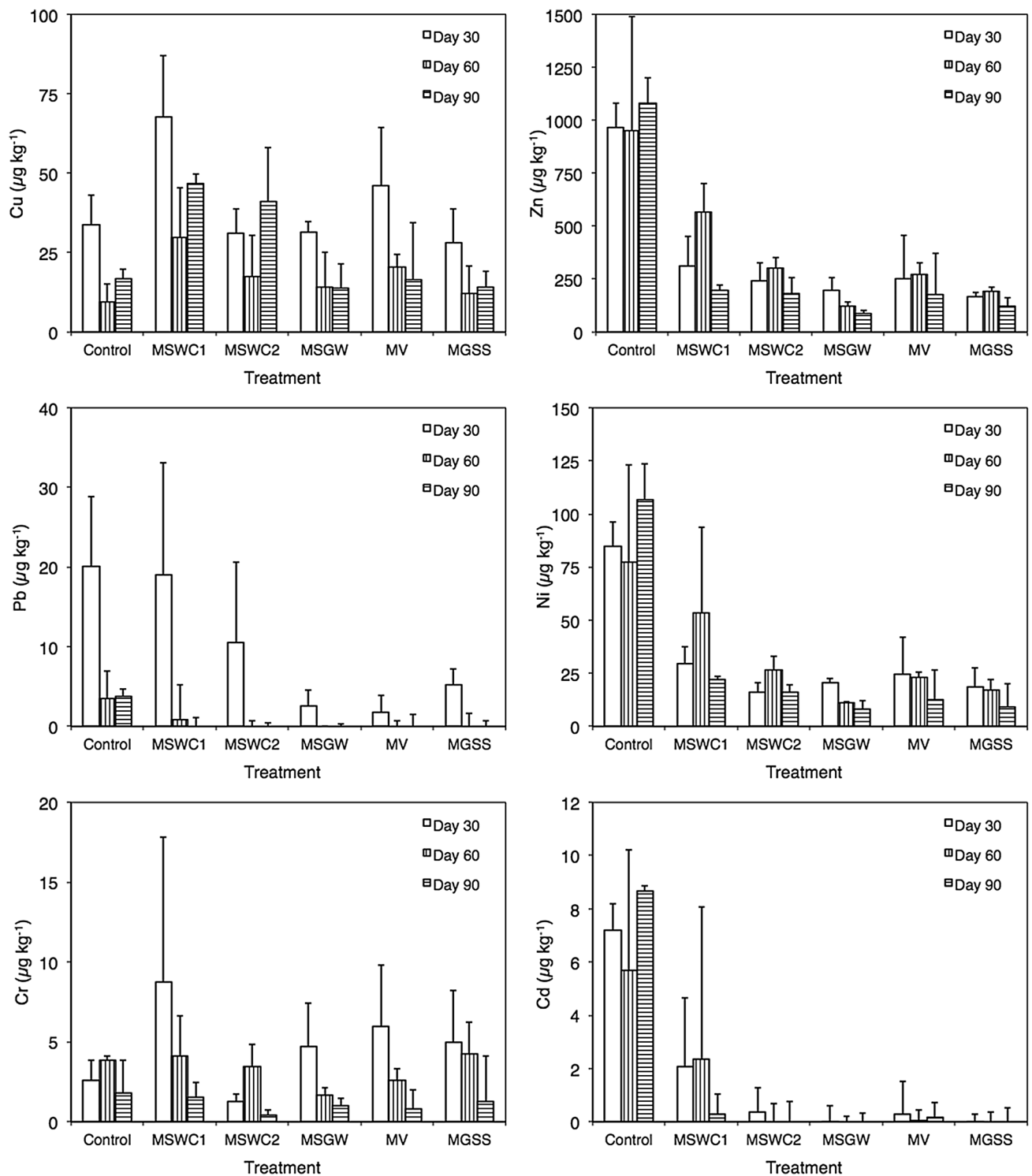
	pH <sub>w</sub>	Sand g kg <sup>-1</sup>	Clay g kg <sup>-1</sup>	Texture	OC g kg <sup>-1</sup>	Fe g kg <sup>-1</sup>	Cu mg kg <sup>-1</sup>	Zn	Pb	Cr	Ni	Cd
Soil	6.0	403	208	Loamy	39	86	97	151	63	190	73	1.7
Reference <sup>a</sup>	–	–	–	–	–	–	50	66	32	129	66	0.16
EU directive <sup>b</sup>	–	–	–	–	–	–	50	150	50	100	30	1.0
Composts												
MSWC1	8.4	–	–	–	280	–	325	608	188	80	57	3.5
MSWC2	8.2	–	–	–	230	–	829	1149	223	77	75	3.1
MSGW	9.2	–	–	–	248	–	52	200	62	17	25	2.1
MGSS	7.3	–	–	–	298	–	688	896	180	68	71	2.7
MV	7.9	–	–	–	217	–	144	689	33	23	27	2.0
Class C compost <sup>c</sup>	–	–	–	–	–	–	400	1000	200	300	100	3

OC total organic carbon, MSWC1 and MSWC2 composts obtained from source separated organic fraction of municipal solid waste, MSGW compost obtained from source separated organic fraction of municipal solid waste mixed with green waste, MGSS compost obtained from municipal garden trimmings mixed with sewage sludge, MV manure vermicompost

<sup>a</sup>Mean metal contents of soils developed over similar geological material in the region [15]

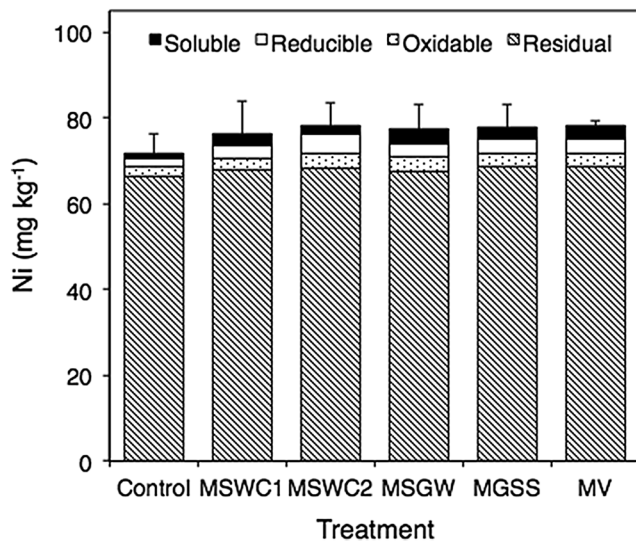
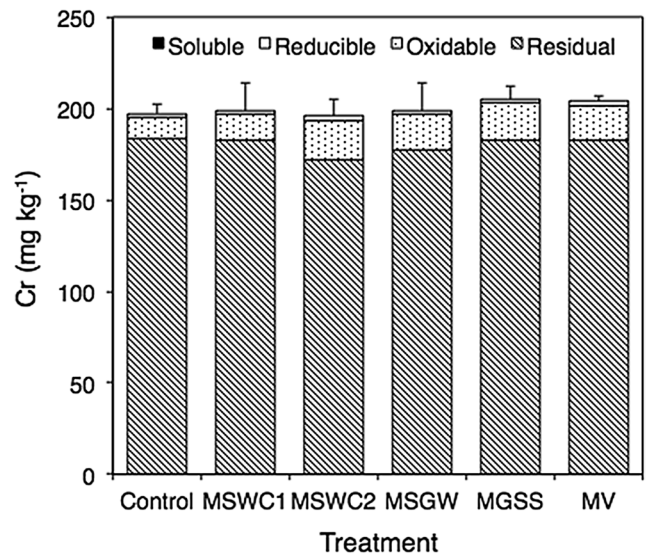
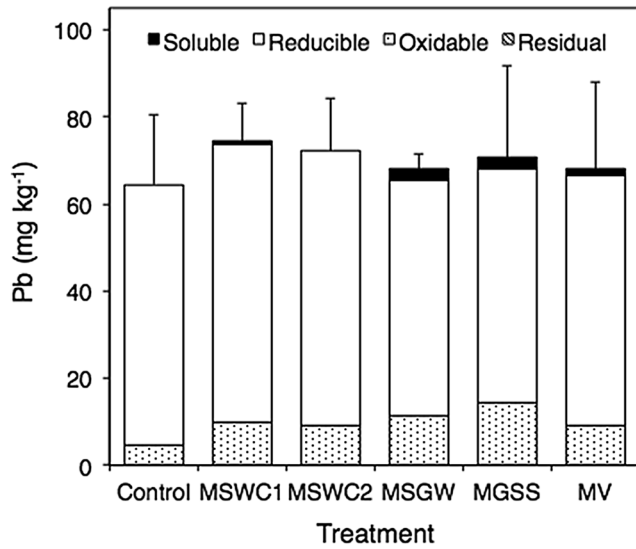
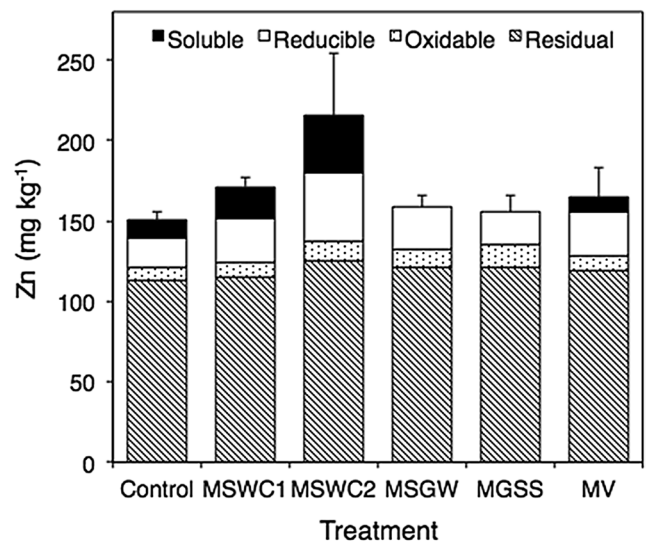
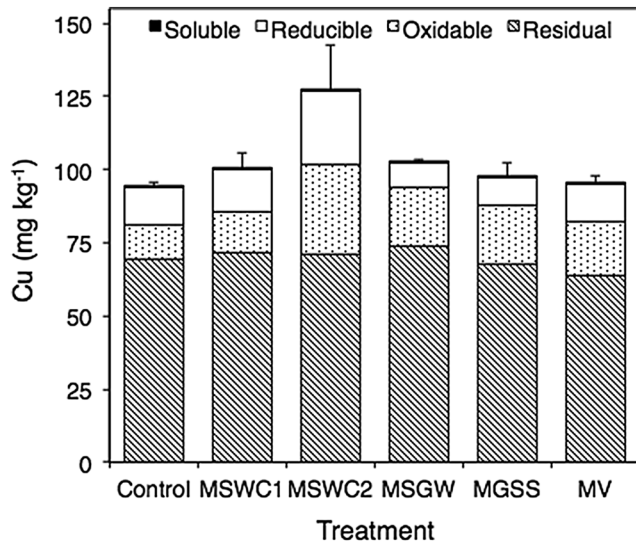
<sup>b</sup>Maximum trace element concentrations in agricultural soils receiving sewage sludge according to the EU Directive 86/278/CEE [10]

<sup>c</sup>Maximum trace element concentrations allowed in the Spanish Fertilizers Law for organic amendments [27]



**Fig. 1** Evolution of 0.01 N CaCl<sub>2</sub>-extractable trace elements during the incubation after 30, 60 and 90 days. Bars represent the confidence intervals in the *t* test at *p* < 0.05 (n=3). MSWC1 and MSWC2 composts obtained from source separated organic fraction of municipal

solid waste, MSGW compost obtained from source separated organic fraction of municipal solid waste mixed with green waste, MGSS compost obtained from municipal garden trimmings mixed with sewage sludge, MV manure vermicompost



**Fig. 2** Concentrations of trace elements in the BCR fractions after 90 days of incubation. Cd is not shown because concentrations in all fractions were under the detection limits. Bars represent the confidence interval for the total metal contents in the *t* test at  $p < 0.05$  ( $n = 3$ ). *MSWC1* and *MSWC2* composts obtained from source separated organic fraction of municipal solid waste, *MSGW* compost obtained from source separated organic fraction of municipal solid waste mixed with green waste, *MGSS* compost obtained from municipal garden trimmings mixed with sewage sludge, *MV* manure vermicompost

in Table 2. All the composts increased SOC, as well as soil pH in about one unit with respect to the control soil. This liming effect of compost in acid soils is commonly observed [28] and it is due to the buffering capacity of organic matter, as well as to the presence of significant amounts of carbonates in urban wastes [23, 29]. Also, a progressive reduction of soil pH happened throughout the incubation in all the treatments, that is likely an effect of acidification due to  $\text{CO}_2$  release during OM mineralization.

Regarding the immediate environmental risk posed by metals, assessed by the concentrations of immediately available trace elements solubilised in the  $\text{CaCl}_2$  extraction (Fig. 1), different trends were observed for each element considered. First, the non-amended soil presented high concentrations of soluble metals, in particular Zn and Ni. Compost addition did not modify soluble Cu and Cr with respect to the control soil, but a decrease of soluble Pb, Zn, Ni and Cd concentrations was observed. A reduction of solubility of Pb, Zn, Cd, Ni in compost-amended soils has often been found in this kind of studies, due to the combined action of metal complexation with OM and increasing pH [6, 8]. This reduction of metal solubility after compost addition is a fact of use for the treatment of contaminated soils [6, 30–33]. In turn, the lack of reduction on Cu mobility (even an increase was observed in the case of *MSWC1*) despite the high affinity of Cu for organic matter, is likely a consequence of the formation of soluble complexes of Cu with dissolved organic carbon [34], that has also been observed in compost-amended soils [35, 36].

Regarding the distribution of the metals in the fractions of the BCR procedure, there were no changes in the compost-amended soils throughout the incubation period, and therefore only the results after the third month of incubation are shown (Fig. 2). Compost addition did not increase total trace element contents of the soil in most cases (Fig. 2): due to the high previous contents in the amphibolite soil, only the composts *MSWC1* and *MSWC2* (those with the highest metal contents) increased total Cu and Zn concentrations in the soil, by about 10% for Cu and 30% for Zn. This is a very unusual fact, in contrast with what is typically observed in compost-amended soils [1, 8].

Copper was found mainly in the residual fraction (>50% of the total) in non-amended soil and in all the treatments. The second fraction in importance was the oxidizable (bound to organic matter), a result of the great affinity of this element for organic matter [37]. Zinc was also mostly found in the residual fraction in all soils. The second fraction in importance was either the reducible (iron oxide-bound), in the control soil and in the treatments with *MGSS*, *MSGW* and *MV* composts, or the soluble fraction in the soil amended with *MSW* composts (*MSWC1* and *MSWC2*). Zinc is frequently the element where the largest increase in labile forms is reported when composted urban wastes are applied to soil, particularly under acidic soil conditions [38]. Therefore, any increase of pH after compost addition can be extremely relevant, as zinc affinity for the surfaces of Fe and Mn oxides increases when soil pH raises [8, 39].

Regarding Pb, it showed a very different behaviour compared to the other elements studied. In this case, the reducible fraction was the most important in all treatments, with almost no contribution from the residual fraction. This is an evidence of a non-lithological origin of Pb in these soils, which may be attributed to contamination in the past due to the combustion of leaded gasoline. Besides, the preferential association of Pb with the reducible fraction show the high capacity of the Fe oxides to fix Pb in amphibolite soils. In contrast with Pb, but similarly to Cu and Zn, the residual fraction was largely the most important one for Cr and Ni (>80% total), showing a predominantly and almost exclusive lithological origin in this soil. Still, it is interesting to highlight that all treatments with compost presented important amounts of Ni in the soluble fraction, what shows that this element is of concern from an environmental point of view.

An interesting point regarding trace element availability in the compost-amended soils is that the first step of the BCR scheme (the acid-soluble fraction) and the  $\text{CaCl}_2$  extraction produced some results that might seem contradictory, although both methods are thought to estimate immediately available elements. In particular, from the BCR extraction it seems that composts increase Zn and Ni immediate availability with respect to the non-amended soil, whereas the  $\text{CaCl}_2$  extraction shows a clear reduction of the solubility of these two elements. This apparent contradiction is due to the ambiguous significance, in terms of availability, of the acid-soluble fraction of the BCR scheme. Being a stronger extraction (acetic acid) than the  $\text{CaCl}_2$  extraction, it is expected to mobilise not only water-soluble and exchangeable elements, but also elements immobilized in carbonates, and thus it can overestimate availability. Indeed, the analysis of the composts used here following the BCR scheme has shown that the elements extracted in this fraction are higher than those extracted in

water or other mild extractions, especially for Zn, Pb, and Ni [23].

Overall, differences in metal fractionation and availability were larger among elements than among treatments. Chemical fractionation of trace elements in compost-amended soil was in this case clearly inherited from the fractionation in the soil, with only a small influence from the compost added. This is in contrast with what happens in most types of agricultural soils, where composts increase metal concentrations and mobility due to larger metal contents with respect to the soil [8]. Even so, two of the composts had a larger effect than the others with respect to the non-amended soil. The composts MSWC1 and MSWC2 modified substantially Cu and Zn chemical fractionation, especially in the case of MSWC2, that presented the highest Cu and Zn contents among all composts (Table 1).

Despite these relatively minor differences attributable to compost properties, our results illustrate the importance of parent material in the behaviour of potentially toxic elements in some compost-amended soils. In a previous work [40] we have already discussed how national regulations for agricultural use of organic amendments should take into account soil properties, and specifically the geochemical backgrounds, when establishing maximum metal concentrations allowed in compost or the maximum admissible load for each element. The wide differences in metal contents among soils developed over different parent materials [15], as well as the fact that compost properties have only a limited effect on trace elements mobility in these naturally metal-rich soils, justify the need for including edaphic properties in these regulations, following the direction initiated by the EU Directive about sewage sludge application [10].

## Conclusions

The addition of several composts to an acid, metal-rich soil developed on amphibolite, increased soil pH and organic carbon during a 3 month laboratory incubation, and reduced immediate availability of Pb, Zn, Ni and Cd, with no effect on Cu and Cr. The composts had little effect on the chemical fractionation of these trace elements, which is in part due to their previous high concentrations in the amphibolite soil. After 90 days of incubation, two of the composts increased slightly the oxidizable (organic matter) and reducible (iron oxides) fractions of soil Cu, and the soluble and reducible fractions of soil Zn, at the expense of the residual fraction. None of the composts modified the distribution of Pb, which was mostly found in the reducible fraction, nor that of Cr or Ni, present in more than 80% in the residual non-extractable fraction. MSW composts clearly were the ones increasing most the

environmental risk, as they increased the soluble fractions of most elements more than the rest of composts. Among the elements studied, the highest environmental risk is related to Zn, given that it is the element with the highest concentrations in readily available soluble forms. The study shows that, in soils developed over metal-rich parent materials such as amphibolites, chemical fractionation of metals after compost amendment is more influenced by the nature of the metals already present in soil than by the composition of the composts employed.

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