

Valorization of a treated soil via amendments: fractionation and oral bioaccessibility of Cu, Ni, Pb, and Zn

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Abstract The present study aims to transform a treated soil (TS) into a more desirable resource by modifying physico-chemical properties via amendments while reducing toxic metals' mobility and oral bioaccessibility. A hydrocarbon-contaminated soil submitted to treatment (TS) but still containing elevated concentrations of Cu, Ni, Pb, and Zn has been amended with compost, sand, and $Al_2(SO_4)_3$ to render it usable for horticulture. Characterization and sequential extraction were performed for TS and four amended mixtures (AM1-4). P and K availability and metal bioaccessibility were investigated in TS and AM2. Amendment improved soil properties for all mixtures and yielded a usable product (AM2 20 % TS, 49 % compost, 30 % sand, 1 % $Al_2(SO_4)_3$) satisfying regulatory requirements except for Pb content. In particular, AM2 had improved organic matter (OM) and cation exchange capacity (CEC), highly increased P and K availability, and reduced total metal concentrations. Furthermore, amendment decreased metal mobile fraction likely to be plant-available (in $mg\ kg^{-1}$, assumed as soluble/exchangeable + carbonates fractions). For AM2, estimated Pb bioavailability decreased from $1.50 \times 10^3\ mg\ kg^{-1}$ (TS) to $238\ mg\ kg^{-1}$ (52.4 % (TS) to 34.2 %). Bioaccessible concentrations

of Cu, Ni, and Zn ($mg\ kg^{-1}$) were lower in AM2 than in TS, but there was no significant decrease for Pb. The results suggest that amendment improved soil by modifying its chemistry, resulting in lower metal mobile fraction (in %, for Cu and Zn) and bioaccessibility (in %, for Cu only). Amending soils having residual metal contamination can be an efficient valorization method, indicating potential for reducing treatment cost and environmental burden by rendering disposal/additional treatment unnecessary. Further studies including plant bioavailability are recommended to confirm results.

Keywords Metals · Oral bioaccessibility · Metal mobility · Sequential extractions · Soil contamination · Soil valorization

Introduction

Metals, unlike hazardous organic compounds, cannot be degraded (McLean and Bledsoe 1992). Once present in soil, they can be adsorbed onto the soil constituents, transported via runoff into rivers or lakes, or leach into the groundwater; subsequent exposure to these substances can lead to accumulation and/or toxicity in plants, animals, and humans (Mulligan et al. 2001). The toxicity of certain metals and metalloids (such as lead (Pb), cadmium (Cd), and arsenic (As)) to plants, animals, and humans even in low levels of exposure has been previously demonstrated (ATSDR 2007). Other elements including copper (Cu), nickel (Ni), and zinc (Zn) are essential soil micronutrients that can become

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toxic if their uptake exceeds threshold doses (ATSDR Agency for Toxic Substances and Disease Registry 2004; ATSDR 2005a; ATSDR 2005b).

Metals immobilization is generally promoted by mechanisms of adsorption and precipitation (Evans 1989; McLean and Bledsoe 1992). pH affects several mechanisms of metal retention and mobilization in soils. Particularly for Pb, Ni, Zn, and Cu, their adsorption in soils tends to increase with pH (McLean and Bledsoe 1992). The presence of organic matter (OM) also affects metal mobilization and plant bioavailability via the formation of metal-OM complexes (van Herwijnen et al. 2007). In particular, Pb is adsorbed to various soil constituents to a greater extent than the other metals especially when pH is greater than 6; and it reacts with clays, phosphates, sulfates, carbonates, hydroxides, and OM which results in a reduction of its solubility (McLean and Bledsoe 1992). Similarly, but to a lesser extent than Pb, Cu is also highly retained in soils but complexation with soluble organic ligands may increase its solubility. Ni and Zn are mainly retained via adsorption mechanisms and both metals can potentially form complexes with inorganic and organic ligands.

Soil pollution is an extensive problem. In some cases, the quantity of contaminated soil to deal with can be very high, which may result in enormous treatment and/or disposal costs. In the province of Quebec (Canada), treatment of hydrocarbon (HC)-contaminated soils in treatment centers via *ex situ* technologies such as bioventilation can cost between 40 and 250 CAN \$ per ton depending on HC and other contaminants concentrations, with *in situ* treatment being generally costlier. More than one million tons of HC-contaminated soils are treated every year in treatment centers in Quebec, and regulations and management practices do not allow returning the excavated and treated soil to the original site. Since there are few possibilities to reuse or valorize the treated soils, a common method to deal with relatively low levels of HCs and metals is to use them as landfill cover material, where more than five million tons of soil have been utilized as such between 2006 and 2011 (Recyc-Quebec 2013). Because of limited landfill space, it currently costs an additional 20 CAN \$ per ton on top of initial treatment costs to dispose of treated soils in a landfill. This practice is not only a waste of a potential valuable resource that could be suitable for reuse following valorization but also a burden on scarce landfill space (almost 25 % of total material buried in landfills according to Recyc-Quebec).

Mixing contaminated material with amendments can be promising in its conversion from expensive-to-manage waste material to a resource (Pollmann et al. 2010), and valorization of soils via amendments is supported in provincial regulations if specific conditions are satisfied (MDDEP 2012). Compost amendment to treated soils can reduce soil solution concentrations of potentially toxic elements and raise soil pH and nutrient levels (Madejón et al. 2006; Farrell et al. 2010; Farrell and Jones 2010). It can also minimize future heavy metal contamination through runoff and erosion, following establishment of vegetation (Pérez-de-Mora et al. 2007; Schwab et al. 2007), and reduce contaminant bioavailability for plants (Castaldi et al. 2005) and animals (Brown et al. 2004). However, following compost amendment, rapid leaching of metals could also be induced (Farrell et al. 2010). Therefore, increased risk due to heavy metal leaching in the presence of organic amendments should be carefully considered (Schwab et al. 2007).

When children play outdoors, they may unintentionally ingest soil by putting dirty hands and objects in their mouths or may deliberately eat soil (Ljung et al. 2007). Oral bioavailability is the fraction of a contaminant that reaches the systemic circulation from the gastrointestinal tract after ingestion, and oral bioaccessibility is the fraction of the substance solubilized in the gastrointestinal tract and is thus available for absorption (Ruby et al. 1996). For compost-amended soils intended to be used for horticultural purposes, an assessment of oral bioavailability via bioaccessibility testing (considering human exposure following incidental ingestion of soils) should be performed.

Amended soils with adequate pH and OM content can optimize nutrient availability and plant growth while minimizing toxic element plant bioavailability and human oral bioaccessibility, and therefore can be efficiently used as top cover in horticulture. Regrettably, valorization of soils with relatively low levels of metal contamination via soil amendments has not been studied in detail. Successful valorization may render high quantities of treated soil usable in horticulture as enrichment. The objective of this study is to assess the effect of amendment on (1) soil characteristics (physico-chemical properties, metal concentrations, and fractionation) and on (2) oral metal bioavailability using an *in vitro* gastrointestinal method for a treated soil (TS)

coming from a soil treatment facility (in order to determine if a usable final product for horticulture can be obtained). TS has been subjected to ex situ chemical oxidation and successfully cleaned-up for hydrocarbons but still contains some Cu, Ni, Pb, and Zn. TS and four different amended mixtures (AMs) have been characterized for soil properties and metal content, and metal fractionation has been determined via sequential extraction. Furthermore, TS and one selected AM (AM2) were tested for nutrient availability and gastrointestinal bioaccessibility.

Experimental

Sample handling and preparation

The experimental work was performed using TS (fraction $<250\ \mu\text{m}$ as received) obtained from Northex Environnement Inc. located in Contrecoeur (Quebec, Canada). The components of AMs were chosen based on availability, particle size distribution, OM content, and the provincial norms regarding chemical properties for mineral amended soils (requiring $10\% < \text{OM} < 30\%$, $6 < \text{pH} < 7$, cation exchange capacity (CEC) $\geq 10\ \text{meq}\ 100\ \text{g}^{-1}$, electrical conductivity (EC) $< 3.5\ \text{dS}\ \text{m}^{-1}$, phosphorus (P) $> 41\ \text{mg}\ \text{kg}^{-1}$, potassium (K) $> 108\ \text{mg}\ \text{kg}^{-1}$ (BNQ Bureau de Normalisation du Québec 2001)) and environmental criteria for amended soils for horticultural use (requiring Cu $< 100\ \text{mg}\ \text{kg}^{-1}$, Ni $< 52\ \text{mg}\ \text{kg}^{-1}$, Pb $< 70\ \text{mg}\ \text{kg}^{-1}$, Zn $< 200\ \text{mg}\ \text{kg}^{-1}$, Salmonella: absent (MDDEP 2012)). AMs were prepared in 500 mL polypropylene copolymer (PPCO) tubes. Approximately 100 g of each AM was prepared in duplicates in separate tubes.

Four components were selected to constitute AMs: TS, compost, sand, and $\text{Al}_2(\text{SO}_4)_3$. The compost was mainly used to increase the OM content and was provided by Northex Environnement (OM content of the compost 31.1 % (w/w); moisture content 50 %). The compost was sieved to obtain $< 2\ \text{mm}$ fraction. Sand (Ottawa Sand by Unimin Corporation, quartz) was used to increase porosity, and $\text{Al}_2(\text{SO}_4)_3$ (certified ACS) was used to adjust the pH of AMs. In total, four AMs were prepared (% by weight): AM1 (69 % compost, 20 % TS, 10 % sand, 1 % $\text{Al}_2(\text{SO}_4)_3$), AM2 (49 % compost, 20 % TS, 30 % sand, 1 % $\text{Al}_2(\text{SO}_4)_3$), AM3 (69 % compost, 30 % TS, 1 % $\text{Al}_2(\text{SO}_4)_3$), and AM4 (49 %

compost, 30 % TS, 20 % sand, 1 % $\text{Al}_2(\text{SO}_4)_3$). Following preparation, AMs were dried at $45\ ^\circ\text{C}$ overnight and were then gently crushed in an agate mortar with a pestle for homogenization. They were finally sieved to obtain $\leq 2\ \text{mm}$ fraction and stored at $4\ ^\circ\text{C}$ for a few weeks prior to analysis.

Sample physicochemical properties

TS and AMs were characterized for their pH, EC, moisture content, CEC, total carbon (TC), and total organic C (TOC). pH was determined according to method D4972-13 (ASTM International 2013) in deionized water using a solid-to-liquid ratio of 1:4. Measurements (Accumet AR-25 pH meter with an Accumet 13-620-285 combination Ag/AgCl electrode) were performed at 24 and 48 h following sample agitation for 30 min. EC was determined in deionized water using a solid-to-liquid ratio of 1:10 (conductivity meter model Professional Plus, YSI). Moisture content was measured for all samples following evaporation at $105\ ^\circ\text{C}$ in an oven (Isotemp Model 175, Fisher). CEC was measured using the sodium acetate method (pH 8.2) (Chapman 1965). TC and inorganic C were measured by combustion with an induction furnace (LECO). TOC was calculated as the difference between TC and inorganic C. OM content was calculated multiplying TOC by 1.724 (MDDEP 2012). TS and AM2 were also tested for their available P and K content via the Mehlich-III extraction method (CPVQ 1997). Salmonella count was performed on AM2 according to the method required by the Centre d'Expertise en Analyse Environnementale du Québec (method MA.700-Sal-PA1.0) (CEAEQ 2013). Total P, total K, Al, Fe, Mg, and Ca were determined according to method MA.200-Mét.1.2 (CEAEQ 2014). Kjeldahl N was determined according to the standard method 4500- N_{org} (Clesceri et al. 1999).

Metals characterization, fractionation, and gastrointestinal bioaccessibility

Total concentrations of Pb, Cu, Ni, and Zn in AMs were determined following the acid digestion protocol described by Balasoiu et al. (2001) with minor modifications. Amount of 1.4 g of AM was placed in a Teflon beaker. A 1 h acid digestion was performed on a hot plate at $350\ ^\circ\text{C}$ with 40 mL of HNO_3 . The sample was allowed to cool at room temperature for 30 min, then 20 mL HClO_4 and 1 mL HF were added. The digestion

continued at 350 °C on the hot plate until approximately 5 mL of digestate remained in each beaker. At the end, the digestate was left to cool, diluted to 100 mL in a volumetric flask, and then filtered (0.45 µm PVDF filter). The total metal concentrations were measured using atomic absorption spectroscopy (AAS) (Perkin Elmer, AAnalyst 200; measured detection limits (DLs) in mg L⁻¹ were 0.003 for Cu, 0.002 for Ni, 0.01 for Pb, and 0.001 for Zn).

The sequential extraction procedure of Tessier et al. (1979) described and used by Zagury et al. (1999) with minor modifications was performed on TS ($n=2$) and AMs ($n=3$). The following fractions of metals were determined: soluble and exchangeable (F1, extracted with 1 mol L⁻¹ MgCl₂), bound to carbonates or specifically adsorbed (F2, extracted with 1 mol L⁻¹ NaOAc, pH=5), bound to iron (Fe) and manganese (Mn) oxides (F3, extracted with 0.04 mol L⁻¹ hydroxylamine hydrochloride in 25 % (v/v) with HOAc), bound to OM (F4, released by HNO₃ 0.02 mol L⁻¹ and H₂O₂ 30 % (w/v)), and residual (F5, acid digestion with HF 48 % (w/v), HNO₃ 70 % (w/v) and HClO₄ 70 % (w/v)). The sequential extractions were performed on 1.4 g of sample in 50 mL PPCO tubes. After adding extracting solution, the tubes were shaken using a mechanical wrist-action shaker (Burrell Scientific Model 75). Liquid-solid separations were performed by centrifuging (Beckman Model J2-21) at 5000 × g for 30 min. Metal concentrations in supernatant were analyzed via AAS following filtration (0.45 µm PVDF filter). The residue was rinsed with 8 mL of deionized water, shaken, and centrifuged for 30 min. The second supernatant was removed, filtered, and analyzed. The solid residue was then used in the subsequent extraction step.

Gastrointestinal bioaccessibility of metals was determined in AM2 (in <250 µm and <2 mm fractions) and in TS (<250 µm, as received) via the IVG method (Rodriguez et al. 1999) with small modifications (Pouschat and Zagury 2006; Girouard and Zagury 2009). For AM2, in addition to <2 mm fraction, <250 µm size fraction was also tested as it is representative of the fraction which adheres to children's hands (USEPA 2012). Amount of 150 mL of gastric solution was transferred to 250 mL beakers (0.15 mol L⁻¹ NaCl by Anachemia and 1 % w/v pepsin by Sigma-Aldrich in deionized water). The pH was adjusted to 1.80 ± 0.05 with 2 mol L⁻¹ HCl and was maintained during the gastric phase. One gramme of soil was added to the beaker with gastric solution agitated by padded stirrers

at 100 rpm and placed in a water bath at 37 °C. After 1 h, 10 mL of gastric solution was collected. Then, pH was adjusted to 5.5 ± 0.05 using saturated NaHCO₃ solution, and the intestinal phase was conducted for 1 h following addition of 10 mL of deionized water, porcine bile extract (0.525 g; Sigma-Aldrich, no. B-8631), and porcine pancreatin (0.053 g; Sigma-Aldrich, no. P-1750) to each beaker. After 1 h, 10 mL of intestinal solution was collected. Aliquots were centrifuged at 5000 × g, filtered (0.45 µm PVDF filter), and analyzed for metals via AAS.

Quality assurance/quality control

All glassware was soaked in 10 % (v/v) HNO₃ bath for at least 8 h before the analyses and then was rinsed three times with distilled water followed by three times with deionized water. All reagents were of analytical grade or better. All experiments were conducted in duplicates or triplicates. Cu, Ni, Pb, and Zn concentrations in procedure blanks for total metals, fractionation, and bioaccessibility tests were either below or very close to method DLs. When found necessary, corrections were made by subtracting metal concentrations measured in procedure blanks from the results for first and second steps in sequential extraction. In order to evaluate analysis variability, the standard deviations (SD) of replicates for each analyzed sample were calculated. Overall, SD values were satisfactory (mostly within ±20 % range of analyzed values).

Accuracy and precision of the acid digestion procedure were assessed by analyzing soil reference material SRM 2710 (US National Institute of Standards and Technology) in triplicate. For total metal content, measured values (in mg kg⁻¹, Cu 2.85 × 10³ ± 215, Zn 6.33 × 10³ ± 487, Pb 5.99 × 10³ ± 557, Ni 21.6 ± 0.2) were consistent with certified values (Cu 2950 ± 130, Zn 6952 ± 91, Pb 5532 ± 80, Ni 14.3 ± 7), and the recovery percentages were acceptable compared to certified values (97, 91, 108, and 151 % for Cu, Zn, Pb, and Ni, respectively). SRM 2710 was also submitted to the sequential extraction (Cu (F1 to F5, in mg kg⁻¹) 104, 912, 469, 925, 395; Ni 3.6, 2.3, 3.5, 0.6, 20.9; Pb 1.34 × 10³, 1.06 × 10³, 1.30 × 10³, 1.03 × 10³, 1.12 × 10³; Zn 888, 471, 2.50 × 10³, 379, 2.40 × 10³). Results were comparable to previous findings for Cu, Pb, and Zn (Ho and Evans 1997), and recovery percentages ((sum of all fractions ÷ total concentration) × 100) were satisfactory (Cu 98.4 %, Ni 117 %, Pb 97.7 %, Zn 105 %). SRM 2710 was also tested for bioaccessibility

of metals via the IVG protocol. Gastrointestinal bioaccessibility values were 43.6 % for Cu (similar to the value 46.5 %±2.8 reported by Pouschat and Zagury (2008)), below DL for Ni (<2.1 %), 1.6 % for Pb, and 5.4 % for Zn.

Results and discussion

Sample physicochemical properties and contaminant characterization

Physico-chemical characteristics of TS, compost, and AMs are given in Table 1. TS is a neutral soil (pH=6.45) with moderate values for TOC (1.69 %), OM content (2.91 %), CEC (18.5 meq 100 g⁻¹), and conductivity (1.52 dS m⁻¹). Following amendment with compost, Al₂(SO₄)₃, and sand, changes in some physico-chemical characteristics have been observed. While pH values of AMs stayed in neutral range (6.26–7.11), electrical conductivity increased (2.84–3.52 dS m⁻¹). Furthermore, OM greatly increased in AMs (range 11.0–18.5 %) in comparison to TS, which may better support plant growth as well as improve soil structure. Compost is an effective way to build soil OM via amendment (Cooperband 2002), and the compost used for amendment had very high OM (31.1 %), resulting in elevated OM in AMs. Finally, following amendment with compost, CEC largely increased in all AMs (range 48.0–78.6 meq 100 g⁻¹), which is favorable for plant nutrient uptake as exchangeable cations may become available to plants. Generally, the CEC of any soil is considered to come principally from the OM and clay fraction (Balasoïu et al. 2001).

Concentrations of certain soil macro- and micronutrients were also determined in TS and AMs,

and results showed an improvement in available nutrients following amendment. TS was rich in various soil nutrients (Ca=67,900 mg kg⁻¹, total P=995 mg kg⁻¹, total K=1400 mg kg⁻¹, Kjeldahl N=732 mg kg⁻¹, Al=9480 mg kg⁻¹, Fe=20,300 mg kg⁻¹, Mg=7530 mg kg⁻¹). The compost was also nutrient-rich, where concentrations for P and N were particularly high (Ca=43,800 mg kg⁻¹, total P=3800 mg kg⁻¹, total K=9700 mg kg⁻¹, Kjeldahl N=14,800 mg kg⁻¹, Al=7610 mg kg⁻¹, Fe=3120 mg kg⁻¹, Mg=4300 mg kg⁻¹). Although total concentrations of P and K were high in TS, laboratory tests showed that these nutrients may not be available to plants. In fact, in TS, Mehlich-III-extractable P was <1 mg kg⁻¹ and Mehlich-III-extractable K was only 124 mg kg⁻¹. Mehlich-III extraction was also performed on one selected AM (AM2). Following amendment, available P increased to 178 mg kg⁻¹ (from below DL in TS), and available K increased to 1472 mg kg⁻¹ (from 124 mg kg⁻¹ in TS).

Soil metal characterization shows that TS was mainly contaminated with Pb (2.37×10³ mg kg⁻¹) and, to a lesser extent, with Cu, Ni, and Zn (Table 2). The total Cu, Ni, Pb, and Zn concentrations in compost were low: 34, 13, 24, and 133 mg kg⁻¹, respectively. The other two amendments, Ottawa Sand and Al₂(SO₄)₃ (ACS grade), contained negligible amounts of metals. Therefore, metal concentrations were lower in AMs than in TS as expected, due to dilution effect from adding material to TS with low metal concentrations. Particularly, Cu, Ni, and Zn concentrations were comparable to their typical background concentrations in soils of Quebec (40, 50, and 110 mg kg⁻¹, respectively (Ministère du Développement Durable de l'Environnement et des Parcs 1998)), being around or slightly above those values. On the contrary, albeit being lower than in TS, all AMs still had high Pb

Table 1 Physico-chemical characteristics of treated soil (TS), compost, and four amended mixtures (AM1–4) (mean±standard deviation (SD), n=2)

| Sample | pH (–) | Total organic C (%) | Organic matter (%) | CEC (meq 100 g ⁻¹) | EC (dS cm ⁻¹) |
|---------|----------|---------------------|--------------------|--------------------------------|---------------------------|
| TS | 6.45±0.3 | 1.69±0.0 | 2.91±0.0 | 18.5±0.0 | 1.52±0.4 |
| Compost | 7.42±0.1 | 18.0±3.4 | 31.1±10 | 125 ^a | 1.67±0.3 |
| AM1 | 6.26±0.4 | 10.1±1.8 | 17.5±5.4 | 78.0±6.2 | 3.52±0.2 |
| AM2 | 6.96±0.1 | 6.35±2.8 | 11.0±8.4 | 48.0±0.5 | 3.24±0.4 |
| AM3 | 7.10±0.1 | 10.7±0.5 | 18.5±1.5 | 78.6±7.1 | 2.84±0.5 |
| AM4 | 7.11±0.1 | 6.55±0.6 | 11.3±1.7 | 54.5±0.5 | 3.39±0.1 |

^a n=1

content ($714\text{--}1.19 \times 10^3 \text{ mg kg}^{-1}$). It should be noted that the actual (measured) concentrations of Cu, Ni, Pb, and Zn in AMs were generally higher than the theoretical concentrations (calculated from metal concentrations in TS and compost from composition data). This could be due to a less complete acid digestion of the compost when digested separately as a result of its very high OM content.

Overall, the laboratory analyses have shown that among the four AMs, the mixture AM2 (49 % compost, 20 % TS, 30 % sand, 1 % $\text{Al}_2(\text{SO}_4)_3$) satisfied the provincial norms regarding chemical properties for mineral-amended soils (BNQ Bureau de Normalisation du Québec 2001) and environmental criteria for amended soils for horticultural use (MDDEP 2012) for its OM, pH, CEC, and EC; P and K availability; metal content (except for total Pb); and *Salmonella* count (none detected).

Fractionation of metals

Generally speaking, the sequential extractions (Table 2) carried out for AMs yielded good recovery percentages (range for Cu 90–146 %, Ni 94–152 %, Pb 94–137 %, Zn 85–151 %) and precision (see SD values). However, the recovery values of metals for AM3 were consistently higher (between 129 and 151 %). It is possible that the acid digestion was incomplete for this particular sample.

Overall, metal concentrations in various fractions were lower in AMs than in TS, which could be attributed to amending TS with material having lower metal concentrations. It is necessary to compare percentage distributions of fractions in order to conclude whether lower concentrations are simply due to dilution effect (indicated by no significant changes in percentages) or due to more significant changes in soil chemistry following amendment (causing shifts between different fractions for a metal). This comparison showed that there were differences in terms of percentage distributions for various fractions (Fig. 1) between TS and AMs particularly for Pb and, to a lesser extent, for Cu and Ni. These differences are discussed in detail for each metal in the following paragraphs. In terms of metal mobility, the sum of F1 and F2 fractions (representing potentially mobile fraction and therefore likely to be available to plants) was generally lower (in mg kg^{-1}) for all metals in AMs than in TS and particularly for Pb ($1.50 \times 10^3 \text{ mg kg}^{-1}$ for TS vs. $175\text{--}382 \text{ mg kg}^{-1}$ for AMs). Considering percentage distribution of F1 + F2

fractions, the results for TS and AMs varied especially for Cu (7.3 % for TS vs. 1.6–3.0 % for AMs) and Pb (52.4 % for TS vs. 22.1–34.3 % for AMs), suggesting that amendment has led to improvement in soil chemistry beyond dilution, lowering the mobility of these metals. Consequently, the higher percentages of these metals were associated, in general, to less mobile fractions (F4 and F5) in AMs compared to TS.

In general, there were important shifts between certain fractions for Cu, Ni, and Pb, indicating changes in soil physico-chemical properties beyond dilution effect. To start, Cu was associated to less mobile fractions in all samples. A large percentage of Cu (83.9 %) was bound to organic matter (F4) and residual (F5) fractions in TS. The combined percentage bound to these fractions (F4 + F5) was significantly higher in AMs (93.9–95.1 %). Potentially mobile fraction (F1 + F2, 7.3 % in TS) as well as F3 (8.9 % in TS) were consequently lower in AMs (F1 + F2, 1.6–3.0 %; F3, 3.0–3.2 %). The results indicated that following amendment, there was a shift for Cu fractionation from F2 and F3 to mainly F4 fraction which already binds the majority of Cu. The affinity of Cu to OM (Balasoiu et al. 2001) in artificially contaminated soils containing peat moss and the low proportion of Cu in soluble and exchangeable fractions in organic soils (Pouschat and Zagury 2008) have been previously reported. The increase in Cu percentage found in F4 in the present study can be explained by the higher OM content in AMs resulting from amendment with compost. This is further supported by the higher levels of Cu in F4 for AM1 and AM3 containing 69 % compost (Cu in F4, 51.9 and 66.0 mg kg^{-1} , respectively) than for AM2 and AM4 containing 49 % compost (Cu in F4, 40.2 and 49.6 mg kg^{-1} , respectively).

The potentially mobile fraction for Ni (F1 + F2) was very low both in TS and AMs (around 3 %). The main difference between the results for TS and AMs was in fraction F4 (18.7 vs. 39.8–53.4 %). Ni fractionation changed following amendment (a shift from F3 and F5 fractions towards F4 fraction), which may indicate an affinity of Ni to OM for these amended soils due to higher OM content.

Although Pb is highly problematic due to its high toxicity as well as elevated total concentrations in many contaminated sites, the bioavailable Pb fraction is usually very low due to the strong association with OM, Fe-Mn oxides, clays, and precipitation (as carbonates, hydroxides, phosphates) (Miller et al. 2008). It is also

Table 2 Total concentrations and fractionation of Cu, Ni, Pb, and Zn in treated soil (TS (<250 μm fraction as received), n = 2) and four amended mixtures (AM1–4 (<2 mm fraction), n = 3) (mean ± SD)

| Metal | Sample | Fraction 1 | | Fraction 2 | | Fraction 3 | | Fraction 4 | | Fraction 5 | | Sum of fractions | Recovery ^a (%) | |
|-------|--------|------------------------|--------|------------------------|--------|------------------------|--------|------------------------|--------|------------------------|--------|------------------|---------------------------|------------------------|
| | | (mg kg ⁻¹) | (%) | (mg kg ⁻¹) | (%) | (mg kg ⁻¹) | (%) | (mg kg ⁻¹) | (%) | (mg kg ⁻¹) | (%) | | | (mg kg ⁻¹) |
| Cu | TS | ± 2.30 | ± 0.01 | 11.6 | ± 0.45 | 15.0 | ± 1.70 | 8.9 | ± 0.39 | 64.2 | ± 33.3 | ± 0.72 | 19.7 | 113 |
| | AM1 | ± 14.0 | 0.74 | ± 0.02 | 1.0 | 0.44 | ± 0.08 | 3.2 | ± 6.90 | 72.5 | ± 16.2 | ± 3.50 | 22.6 | 90 |
| | AM2 | ± 12.0 | 0.84 | ± 0.09 | 1.6 | 0.71 | ± 0.09 | 3.1 | ± 1.60 | 77.8 | ± 8.31 | ± 4.50 | 16.1 | 97 |
| | AM3 | ± 4.80 | 0.85 | ± 0.05 | 1.0 | 0.79 | ± 0.05 | 3.0 | ± 7.10 | 74.2 | ± 18.7 | ± 8.60 | 21.0 | 146 |
| Ni | AM4 | ± 17.0 | 0.82 | ± 0.08 | 1.1 | 0.80 | ± 0.09 | 3.1 | ± 0.26 | 67.5 | ± 19.9 | ± 5.10 | 27.1 | 90 |
| | TS | ± 19.0 | <0.02 | 7.00 | ± 0.25 | 3.6 | ± 2.20 | 35.0 | ± 0.50 | 18.7 | ± 84.2 | ± 26.0 | 42.7 | 152 |
| | AM1 | ± 3.20 | <0.02 | 1.77 | ± 0.20 | 2.9 | ± 0.30 | 17.7 | ± 3.10 | 50.8 | ± 17.6 | ± 6.60 | 28.6 | 97 |
| | AM2 | ± 10.0 | <0.02 | 1.90 | ± 0.20 | 3.9 | ± 1.00 | 25.5 | ± 1.00 | 53.4 | ± 8.30 | ± 6.30 | 17.2 | 100 |
| Pb | AM3 | ± 5.30 | <0.02 | 2.29 | ± 0.16 | 2.9 | ± 0.73 | 19.2 | ± 4.80 | 50.3 | ± 22.0 | ± 9.40 | 27.6 | 129 |
| | AM4 | ± 14.0 | <0.02 | 2.22 | ± 0.32 | 2.9 | ± 0.91 | 24.2 | ± 1.10 | 39.8 | ± 25.1 | ± 4.10 | 33.1 | 94 |
| | TS | ± 24.0 | 16.4 | ± 0.30 | 0.6 | 1.48 × 10 ³ | ± 12.0 | 40.5 | ± 1.90 | 5.0 | ± 57.9 | ± 0.43 | 2.0 | 2.86 × 10 ³ |
| | AM1 | ± 37.0 | 5.56 | ± 0.26 | 0.7 | 169 | ± 9.30 | 31.5 | ± 95.0 | 15.0 | ± 249 | ± 38.0 | 31.5 | 791 |
| Zn | AM2 | ± 125 | 35.0 | ± 4.50 | 5.0 | 203 | ± 20.0 | 34.1 | ± 4.00 | 21.5 | ± 70.5 | ± 5.70 | 10.2 | 693 |
| | AM3 | ± 105 | 9.80 | ± 4.80 | 0.8 | 306 | ± 22.0 | 34.0 | ± 15.0 | 24.2 | ± 228 | ± 48.0 | 17.5 | 1.30 × 10 ³ |
| | AM4 | ± 301 | 43.3 | ± 5.30 | 3.8 | 338 | ± 16.0 | 30.8 | ± 4.00 | 19.2 | ± 185 | ± 10.0 | 16.3 | 1.13 × 10 ³ |
| | TS | ± 23.0 | 0.19 | ± 0.00 | 0.1 | 33.3 | ± 5.00 | 58.1 | ± 0.11 | 11.5 | ± 71.3 | ± 1.20 | 20.7 | 344 |
| Zn | AM1 | ± 22.0 | 3.34 | ± 5.20 | 1.8 | 15.5 | ± 2.70 | 55.8 | ± 7.50 | 15.7 | ± 32.9 | ± 6.20 | 18.1 | 182 |
| | AM2 | ± 27.0 | 1.42 | ± 0.14 | 1.1 | 13.7 | ± 7.60 | 60.4 | ± 0.32 | 14.2 | ± 16.7 | ± 9.60 | 13.4 | 125 |
| | AM3 | ± 16.0 | 0.90 | ± 0.06 | 0.4 | 15.4 | ± 5.00 | 56.8 | ± 14.0 | 19.6 | ± 38.1 | ± 16.0 | 16.5 | 230 |
| | AM4 | ± 50.0 | 1.51 | ± 0.18 | 0.9 | 16.3 | ± 26.0 | 53.1 | ± 1.30 | 11.6 | ± 40.3 | ± 9.80 | 24.5 | 165 |

^aSum of all fractions ÷ total concentration) × 100

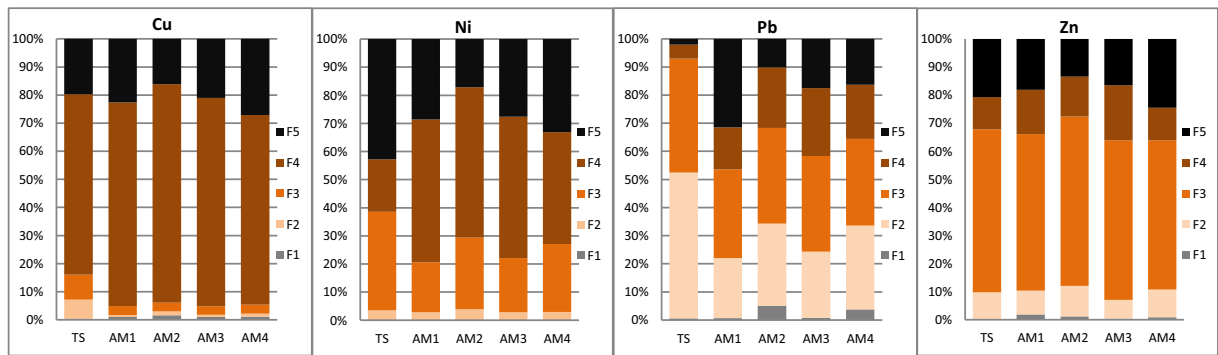


Fig. 1 Distributions of fractions of Cu, Ni, Pb, and Zn in treated soil (TS, $n=2$) and four amended mixtures (AM1–4, $n=3$) (fractions in %; soluble and exchangeable (F1), bound to carbonates or

specifically adsorbed (F2), bound to Fe and Mn oxides (F3), bound to organic matter (F4), residual (F5))

known that only a small amount of the total Pb in soils may be taken up by plants, and the translocation of Pb from roots to tops is greatly limited unlike some other metals like Cu and Zn (Angelova et al. 2010). In the present study, Pb in TS and AMs was associated more with potentially mobile fraction (F1+F2) than Cu and Ni. In TS, Pb was mainly present in the F2 fraction (bound to carbonates or specifically adsorbed, 51.8 %), followed by F3 (associated with Fe and Mn oxides, 40.5 %). In AMs, the fractionation for Pb largely changed, with shift from F2 (decreased to 21.4–29.8 %) and F3 (decreased to 30.8–34.1 %) to F4 and F5 (F4+F5 increased from 7.1 % for TS to 31.6–46.4 % for AMs). Potential mobile fraction has largely decreased following amendment (from 52.4 % in TS to 22.1–34.3 % in AMs).

Finally, Zn was found mainly associated to F3 and had a low percentage of potentially mobile fraction (F1+F2; 9.7 % for TS, 7.1–12.1 % for AMs). In contrast to Cu, Ni, and Pb, the sequential extraction results were similar for TS and AMs.

In summary, important differences were observed between TS and AMs in terms of Cu, Ni, and Pb fractionation. Particularly for Pb and for Cu, the potentially mobile fraction (F1+F2) was lower in AMs in comparison to TS. This indicates a potentially lower mobility of these toxic elements from soil to plants, which is favorable for reuse. This being said, plant studies are recommended to confirm this interpretation.

Metals bioaccessibility

Metal gastrointestinal bioaccessibilities for TS, AM2, and AM2 sieved to $<250 \mu\text{m}$ (to obtain the fraction

likely to adhere to children's hands) are presented in Table 3. Overall, bioaccessible concentrations (in mg kg^{-1}) and per cent bioaccessibilities (calculated by dividing bioaccessible concentration by total concentration, expressed as %) of Cu, Ni, Pb, and Zn were low, predicting limited bioavailability in a case of potential human exposure. In $<250 \mu\text{m}$ fraction for AM2, the total concentrations of metals were higher (in $\text{mg kg}^{-1} \pm \text{SD}$; Cu 63.0 ± 24 , Ni 61.0 ± 23.0 , Pb 982 ± 374 , Zn 133 ± 50.0) than in $<2 \text{ mm}$ fraction (Table 2). The bioaccessible concentrations and percentages of all metals in $<250 \mu\text{m}$ fraction were also higher than in the $<2 \text{ mm}$ fraction.

The key finding from the bioaccessibility determination was that bioaccessible concentrations (in mg kg^{-1}) were lower in AM2 than TS for Cu, Ni, and Zn, which will lead to lower risk for AM2 when exposure to these soils is considered. The difference in concentrations was particularly large for Cu (11.9 mg kg^{-1} in AM2 vs. 51.2 mg kg^{-1} in TS), followed by Zn and Ni. The levels of Pb were not significantly different when comparing TS ($<250 \mu\text{m}$) and AM2 ($<250 \mu\text{m}$) (81.9 ± 2.7 and 71.3 ± 27.2 , respectively). Per cent bioaccessibility values for TS and AM2 were also different, and the nature of this difference was metal-specific. For Cu, per cent gastrointestinal oral bioaccessibility decreased following amendment (33.8 % for TS vs. 18.9 % for $<250 \mu\text{m}$ and 13.1 % AM2 for $<2 \text{ mm}$ fraction). Percentages for Cu fractionation in relatively more mobile F2 and F3 were lower, and less mobile F4 was higher in AM2 in comparison to TS; therefore, a lower Cu bioaccessibility could be expected. On the contrary, for Ni and Pb, it was observed that per cent bioaccessibility was higher for AM2 than for TS (Table 3). For Ni,

Table 3 Gastrointestinal bioaccessibility of Cu, Pb, Ni, and Zn in treated soil (TS) and amended mixture 2 (AM2) (in mg kg⁻¹ as mean \pm SD, and in %; $n=3$)

| Soil | Cu | | Ni | | Pb | | Zn | |
|-------------------------------|---------------------|------|---------------------|------|---------------------|-----|---------------------|------|
| | mg kg ⁻¹ | % | mg kg ⁻¹ | % | mg kg ⁻¹ | % | mg kg ⁻¹ | % |
| TS (<250 μ m as received) | 51.2 \pm 2.20 | 33.8 | 18.6 \pm 0.80 | 8.9 | 81.9 \pm 2.70 | 3.4 | 33.0 \pm 5.80 | 10.5 |
| AM2 (<2 mm) | 8.30 \pm 1.30 | 13.1 | 7.30 \pm 0.30 | 11.9 | 56.5 \pm 1.60 | 5.8 | 11.3 \pm 3.30 | 8.5 |
| AM2 (<250 μ m) | 11.9 \pm 0.60 | 18.9 | 13.0 \pm 1.40 | 21.2 | 71.3 \pm 27.2 | 7.3 | 12.0 \pm 7.70 | 9.0 |

residual fractions for TS and AM2 were very different (F5 42.7 vs. 17.2 %), and this difference may partially explain higher bioaccessibility in AM2. For Pb, although a higher percentage was associated to potentially less mobile F4 and F5 fractions in AM2 (21.5 and 10.2 %, respectively) than TS (5.0 and 2.0 %, respectively), the bioaccessibility (%) was slightly higher. This might be due to the possibility that Pb bioaccessibility is being controlled mainly by the F1 fraction (5.0 % for AM2 and 0.6 % for TS). Finally, for Zn, the per cent bioaccessibility values for samples TS and AM2 were similar in agreement with the comparable sequential extraction results. In summary, although the bioaccessible concentrations of Cu, Ni, and Zn in AM2 were lower than in TS, only Cu per cent bioaccessibility significantly decreased in AM2.

In terms of human exposure to contaminated soil, a child is the critical receptor. The <250 μ m soil fraction is the representative fraction which adheres to children's hands (USEPA United States Environmental Protection Agency 2000) and is also commonly used to determine bioaccessibility when dealing with metal-contaminated soils (Ruby et al. 1996; Rodriguez et al. 1999; Girouard and Zagury 2009). Soil ingestion rate value recommended by the USEPA (2011) is 100 mg day⁻¹ as general population central tendency value for soil and dust. By using this value and considering a normal daily soil ingestion scenario (unintentional ingestion of soil) assuming outdoor play, chemical daily intake (CDI) was calculated by taking mean body weight of a child between 1- and 2-year-old as 11.4 kg (USEPA 2008) and considering daily exposure (365 days year⁻¹). This CDI has been compared to a reference value, above which toxic effects are assumed to occur.

For the scenario of children's soil ingestion, the bioaccessible concentration of Pb (71.3 mg kg⁻¹ for AM2 (<250 μ m fraction)) multiplied by ingestion rate (100 mg day⁻¹) and divided by body weight

(11.4 kg) yields a CDI of 0.63 μ g kg⁻¹ of bw day⁻¹. According to van Engelen et al. (2006), tolerable daily intake of Pb is 3.6 μ g kg⁻¹ of bw day⁻¹. The calculated CDI, falling below this value, indicates acceptable exposure. Thus, it can be said that oral daily exposure to AM2 for children would not cause a significant risk for the scenario of normal soil ingestion. However, due to the unique toxicological profile of Pb indicating a potential of causing adverse effects in even very low blood concentrations (i.e. below 5 μ g dL⁻¹, Lanphear et al. 2000), some health agencies choose not to state limit values for Pb exposure (i.e. the USEPA does not specify a reference dose for Pb (USEPA 2004)). Therefore, the results presented here should be taken as an initial human health screening assessment and thus be considered with caution to be supported by a more detailed risk characterization study if AM is to be used for horticultural purposes.

Conclusions

The present study showed that a soil previously treated for hydrocarbon removal but still containing metals can be successfully amended with compost, sand, and Al₂(SO₄)₃ to yield a usable amended mixture (in this study, the sample AM2) for horticultural purposes where a primary exposure pathway for humans is the ingestion of soils following contact. More specifically, following amendment, P and K availability increased, cation exchange capacity and organic matter content were improved; and guidelines for pH, conductivity, salmonella count, and metal content (with the exception of total Pb content) were satisfied. Although total Pb was high, potentially mobile Pb which is likely to be plant-bioavailable was much lower in AM2 than in treated soil (238 mg kg⁻¹ vs. 1.50 \times 10³ mg kg⁻¹). Finally, oral

bioaccessibility of Cu, Ni, and Zn (expressed in mg kg⁻¹) was lower. Overall, the findings suggest that the amendment caused changes in soil chemistry, improving the soil by lowering the sum of mobile fractions (F1 + F2 in %, for Cu and Zn) and bioaccessibility (in %, for Cu only). Associated calculated risk for oral exposure to Pb for children was found acceptable despite the fact that amendment did not significantly decrease Pb oral bioaccessibility. That being said, plant bioavailability studies and additional oral bioaccessibility tests using amended mixtures to support more detailed risk characterization studies are suggested as the next step. Additional research on amending moderately metal-contaminated treated soils (long-term fate of metals in amended soils, weathering of organic matter on bioavailability and bioaccessibility, ecological risk assessment) should help enable their valorization, while significantly cutting further treatment and disposal costs.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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