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Effects of compost application on soil vulnerability to heavy metal pollution

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Abstract

Soil vulnerability to heavy metal pollution is low in soils exhibiting an ability to strongly adsorb heavy metals on their geochemical fractions. Organic matter (OM) is among other components of soils, one of the most effective sorbing fractions. Compost addition is often used for soil remediation thereby enriching the soil with OM. However, compost is often enriched with heavy metals and thereby may induce adverse effects on the soil and plants growing in them. Compost-derived dissolved organic matter (DOM) can mobilize heavy metals. The balance between two contrasting effects of compost—mobilization and immobilization of heavy metals—was studied under the conditions of adsorption–desorption batch experiment. Metal adsorption to different geochemical fractions of soil treated with compost was examined by a combined batch-adsorption experiment and a sequential extraction procedure. Compost-derived DOM mobilized Cu at low loading levels, whereas adsorption of Cd and Pb was not decreased by DOM application. Compost was found to be a source of an important reducible oxides fraction (RO—sorbing and fixation fraction) and also of the OM geochemical fractions that most commonly immobilizes heavy metals. The Langmuir and Freundlich models employed in our study exhibited a good fit for most of data the experimental data obtained on bulk samples. Adsorption of the metals on operationally defined geochemical fractions was described by a linear function in several experimental instances.

Keywords Adsorption isotherm · Adsorption model · Compost · Heavy metal · Sequential extraction protocol · Operationally defined metal fraction

Introduction

The vulnerability of soils to heavy metal pollution is based on their ability to adsorb and/or fix them from any pollution source to their solid phase and desorbing them into the soil solution phase under changing ecological conditions. Lower adsorption capacity and larger likelihood of metal desorption will enhance the soil's vulnerability to pollution. Adsorption is one of the main processes regulating heavy metal availability to plants. It is defined as the accumulation of ions at the interface between a solid phase and the aqueous one (McLean and Bledsoe 1992).

Compost is the product of composting, a partially controlled bio-oxidative process through which highly heterogeneous organic matter (OM) in its solid state is being transformed into humified material (Zmora-Nahum et al. 2007). Compost is often used for soil remediation at sites that are contaminated with heavy metals. Since the contaminant's solubility is related to its mobility and therefore also to its bioavailability, chemical immobilization may reduce environmental risk (Basta et al. 2001). In a study carried out by Basta et al. (2001), the largest reductions in metal extractability and phytoavailability took place when alkaline organic stabilization treatment has been employed (lime-stabilized biosolid and N-Viro Soil). Application of large amounts of these amendments was necessary to prevent development of acidic soil conditions (pH < 6) and to maintain reductions in metal extractability and phytoavailability. Tandy et al. (2009) used compost for soil remediation and found that its addition greatly reduces Pb content in plant shoots due to complexation

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with OM, precipitation with P in the compost equilibration solution and reduced solubility at high pH. Minkina et al. (2011) studied the influence of different amendments (chalk, glauconite, semi-decomposed cattle manure, and their combinations) on the heavy metal pool in polluted soils. They found that metal compound transformation occurs in the contaminated soils for 3 years after the application of the amendments. Processes occurring after application resulted in a decrease in proportion of the most mobile and exchangeable forms and a corresponding increase in the content of firmly bound forms (metals strongly fixed in slightly soluble compounds: hydroxides, carbonates, stable organic and organo-mineral compounds).

The influence of compost on the chemistry of heavy metals in soils is first and foremost connected to its OM properties. Composted OM may be divided into two major components: (i) dissolved organic matter (DOM) and (ii) solid organic matter (SOM), namely that fraction which is insoluble in water, consisting of partially decomposed and non-decomposed plant debris and humic substances (HS).

DOM is usually defined as a mixture of organic molecules that are present in water which has been filtered through a 0.45-μm filter. DOM consists of hydrophilic and slightly more hydrophobic substances that play important roles in different chemical processes in soil. Humic and fulvic acids (HA and FA) are the major components, representing up to 70% of DOM (Weng et al. 2002). DOM is commonly divided into several fractions, according to its solubility, hydrophobicity, and hydrophilicity (Chefetz et al. 1988; Gat 2006). The concentration of DOM in compost is usually ≤ 1000 mg dissolved organic carbon (DOC) per 1 L compost water extract (1:10 solid:liquid ratio) and its level depends on compost maturity (Zmora-Nahum et al. 2007).

Addition of organic amendments (OA) (compost, manure, sewage sludge, etc.) increases DOM concentration in either by acting as a direct source of DOM especially upon their decomposition or by enhancing the solubilization of the soil organic matter (so called priming effect, the increase in soil organic matter microbial decomposition rate after fresh organic matter input to soil) (Fontaine et al. 2003; Bolan et al. 2004).

Irrigation with treated wastewater (TWW) may result in an increase in soil DOM concentration (Fine et al. 2002). However, reduction of DOC due to the priming effect has also been reported (Jueschke et al. 2008). DOM is applied to soils with any OA application and plays an important and unique role in the chemistry of heavy metals in soils. It can reduce the adsorption of the metals to soil surfaces by either competing more effectively for the free metal ion and forming soluble organometallic complexes, or being preferentially adsorbed onto the surfaces instead of the metals with which it is competing. Increased plant uptake of heavy metals has been observed with increasing DOM concentration (Antoniadis and Alloway 2002). Metals have been found bound to the DOM, mainly the high-molecular-weight hydrophobic fractions

(Vaca-Paulin et al. 2006). Metal adsorption to DOM usually fits the Langmuir model (Dudal et al. 2005 and see further on).

Compost OM content may vary from 18 to 86% (Zmora-Nahum et al. 2007) and it is comprised mostly of SOM. Compost SOM is similar to soil HS (Chen et al. 1991). Compost SOM is an important adsorbing agent for heavy metals. OA can contribute to metal immobilization through the formation of stable complexes with OH or COOH groups on the solid surfaces of the organic polymers (Madrid et al. 2007).

The strong metal sorption properties of compost produced from municipal solid waste (MSW) or sewage sludge provide important potential benefits for the remediation of metal-contaminated industrial and urban soils. Compost inputs to contaminated soils containing large fractions of labile elements reduce the overall bioavailability of metals due to sorption processes and thus provide an effective soil-remediation technique (He et al. 1995; Zheng et al. 2004; Smith 2009).

OA application to soil may have two contrasting effects with respect to the fate of the heavy metals: on the one hand, metals may be immobilized by the SOM (and, of course also by the mineral part of the OA); on the other hand, metal mobilization may be facilitated by the DOM released from the OA. The final net mobilization or immobilization depends on the balance of these two contrasting effects (Wong and Zhou 2003).

Sorption of metals by soil is usually described by the Langmuir and/or Freundlich models (Langmuir 1918; Echeverria et al. 1998; Martinez-Villegas et al. 2004; Chaturvedi et al. 2006; Vaca-Paulin et al. 2006). The assumptions for the Langmuir model are the following: (i) all sorption sites in the sorbent particle bind a single molecule of sorbate, (2) all sites are identical (particularly with respect to binding energy), and (III) all are mutually independent (so that the affinity of any site for the sorbate is independent of the amount of sorbate already adsorbed) (Vega et al. 2011). The Freundlich model is based on an empirical law that may be used to describe heterogeneous systems, where the binding energy and affinity change along the sorption process. Use of these models enables evaluating the sorption capacity of the substrate and the sorption intensity by comparing the model parameters obtained for different objects and conditions. According to Appel and Ma (2002), Pb has a greater affinity for soil sorption than Cd. The sorption maxima estimated from the Langmuir equation were greater for Pb than for Cd for most of the soils studied. It was also shown that soil mineralogy is more important for Cd and Pb sorption than the quantity of soil OM.

The main chemical reactions affecting heavy metals availability in soil and hence, soil vulnerability to metal pollution, are (i) metal reaction with Fe and Mn oxides, (ii) metal reaction with SOM, and (iii) metal precipitation with specific anions (phosphates, sulfides, carbonates, etc.) (Basta et al. 2005).

The goals of the present investigation were to (i) differentiate the effects of the water-soluble components of compost

from those of its non-soluble components, on competitive adsorption of Cd, Cu, and Pb by clayey and sandy soils; (ii) examine the metal adsorption on different operationally defined geochemical fractions by combined batch-adsorption experiment and sequential extraction (SE) procedure (combined SE–sorption isotherm analysis, or CSSA; Salim et al. 1996); and (iii) evaluate the influence of OA application on soil vulnerability to heavy metal pollution.

The reasons for selecting Cd, Cu, and Pb as heavy metals of interest for this study are the following: (i) Cd and Pb are widely known as eco-toxic elements. Cd exhibits highly adverse effects on soil biological activity, plant metabolism, and the health of humans and the animal kingdom. Pb is usually strongly adsorbed by soil, but its accumulation in surface soil is of great ecological importance, because Pb greatly limits soil biological activity and at certain environmental conditions, it penetrates the roots and may be translocated into the plants tops (McLean and Bledsoe 1992; Kabata-Pendias and Pendias 2001) and (ii) concerning the importance of the Cu environmental fate investigations, the following citation is pertinent: "Although copper does not belong to the 'heavy metals,' comprising arsenic, cadmium, lead and mercury, that are generally believed to pose the greatest risk of elements to animal health, it is interesting that in Israel, this mildly toxic metal actually causes more health problems than all the other four elements combined" (Shlosberg 2010).

Materials and methods

The following materials were used for the experiment: sandy soil (sand) from Rehovot, Israel (S); clayey soil (sandy clay) from Beit-Elazari, Israel (C); partly stabilized poultry–cow manure (PCM); soluble salts (chlorides) of 3 heavy metals (Cd, Cu, and Pb). The main characteristics of the soils and compost are presented in Tables 1 and 2, respectively. Routine analyses of soils and compost were conducted according to classical methods (Chen et al. 1991). The soil texture was determined by the hydrometer method; carbonate content was determined using a manual calcimeter; EC_{25} and pH were measured in saturated paste extracts using potentiometric method to measure pH and a conductometer (Metrohm, Switzerland) to measure EC_{25}; water content of the saturated paste was determined by the common gravimetric method (drying at 105 °C); cation exchange capacity (CEC) was determined using 0.1 N NaOAc with 0.4 N NaCl as a saturating solution; exchangeable cations were determined using the ammonium acetate method; total organic carbon content of the compost was calculated using OM concentration, determined by loss-on-ignition method at 500 °C, then multiplying the value obtained by a factor of 1.72 (assuming the 58% C content in the OM).

The content of heavy metals in soils, compost, and mixtures, and the distribution of heavy metals among operationally defined geochemical fractions were determined using the procedures, developed in our laboratory: PTA (pseudo-total metals concentration analysis) protocol and modified BCR (Community Bureau of Reference) SE protocol. The details about method development and validation may be found in the "Experimental design" section below, in Online Resource 1 (the section "Quality Control Procedures") and in our previously published work (Rosen and Chen 2014). This protocol was established to extract the following operationally defined geochemical fractions (from the most to least bioavailable ones): water-extractable (WE), exchangeably adsorbed (EXC), associated with carbonates and acetic acid-soluble forms (CARB), occluded by reducible (hydro)oxides of Fe and Mn (RO), associated with organic matter (OM) and a residual fraction (RES). However, the WE step was skipped, because it was reasonable to assume that water-soluble compounds were dissolved during equilibration with the matrix solution. The clayey and sandy soils without any metal addition were subjected to the same adsorption–desorption procedure and the native (background) contents of metals were subtracted from those in the equilibrated solution. The first fraction extracted from the control treatments (0.01 M $CaCl_2$, 24-h shaking at a constant 27 ± 2 °C) was designated "WE+EXC."

The quality control procedures demonstrated, in short, the following results: the PTA protocol demonstrated recovery of 84.1, 94.3, and 85.7% for Cd, Cu, and Pb, respectively, when the BCR-701 certified reference material (CRM) was used. The same CRM was subjected to non-modified (standardized) BCR SE protocol (according to Pueyo et al. 2001). The sum of all extracted fractions (CARB, RO, OM, and RES) was compared to the certified one and the following recoveries were obtained: 96.9, 106, and 96.5% for Cd, Cu, and Pb, respectively.

Heavy metal concentration was measured in the filtered solutions using an axial ICP-OES "Arcos" from Spectro, Germany. Crossflow or concentric nebulizers were used. Measurements were calibrated with Merck ICP standards. The measurement was conducted according to standard EPA method 6010C (2007). Yttrium was added to the samples as an internal standard for matrix-effect compensation. Matrix-matching method was used for sequentially extracted fractions measurements. Background correction with a second-degree polynomial function was used to correct spectral interferences of Al and Fe in the UV (< 180 nm) region.

Figures were made using Excel 2007. The positive and negative bars on the column and line plots present the standard deviation values. We used JMP 7.01.1 for statistical data analysis. Tukey–Kramer test ($\alpha = 0.05$) was used to reveal significant differences between variables (indicated by lowercase letters between treatments on the figures).

Table 1 Selected properties of soils used in the experiment

Parameters		Units	Soil	
			Clayey	Sandy
Texture	Clay	%	37	8
	Silt		16	3
	Sand		47	89
	CaCO$_3$	%	13.2	0.2
Saturated paste	EC25	dS m^{-1}	0.74	0.66
	pH		7.5	7.4
	Wsat.[a]	%	49.7	24.7
CEC		cmol$_c$ kg^{-1}	26.6	7.6
Exchangeable cations	Na	% of CEC	3.8	5.3
	K		2.4	2.8
	Ca		80.5	83.3
	Mg		13.3	8.7
Pseudo-total content of metals (mg kg^{-1})	Cd		<LOQ[b]	<LOQ
	Cu		14.5 ± 0.88	8.4 ± 0.22
	Pb		1.08 ± 0.18	2.12 ± 0.13

[a] Water content of the saturated paste

[b] Less than method limit of quantitation

Experimental design

The soil–OA mixtures were composed as follows: each soil was mixed with PCM compost (both materials were air-dried) in a rate of 20% (*v/v*) and were used as is for equilibration with the solutions containing dissolved heavy metals. The soils and the soil–OA mixtures were equilibrated for 24 h by shaking in solutions with different concentrations of Cd, Cu, and Pb (1, 10, 50, 100, and 200 mg L^{-1}). To prepare the solutions, chlorides of Cd, Cu, and Pb, purchased from Merck, were dissolved in 0.01 M CaCl$_2$ that was used as a matrix solution to facilitate phase separation and to keep ionic strength similar to the natural soil solution (Alumaa et al. 2001). We studied the sorption of heavy

metals under competitive adsorption conditions because the relevant pollution sources are usually multi-metal (Vidal et al. 2009). The soil contamination level resulting from heavy metals addition from 1 to 10 mg L^{-1} was defined as "low" and from 50 mg L^{-1} and higher was defined as "high." The soils and soil-compost mixtures (referred to as "soil" and "soil+compost" treatments) were equilibrated with the series of CaCl$_2$ (0.01 M) solutions containing heavy metals (concentrations from 1 to 200 mg L^{-1}). The soils without compost addition were equilibrated with the solutions of the same metals concentrations, but containing also DOM, extracted from PCM compost (referred to as "soil+DOM" treatment).

After equilibration at 27 ± 2 °C, suspensions were centrifuged and the absorbance (ABS, cm^{-1}) at 300 nm was determined in the supernatant using a Thermo Evolution 300 UV–VIS spectrophotometer. The quantitative relationship between ABS and DOC concentration in the equilibrated solution (mg L^{-1}) was established by means of ABS measurement at 300 nm and DOC measurement with a TOC analyzer (Shimadzu VCPH). The following equations were obtained for the clayey and sandy soil extracts, respectively:

$$DOC, mg\ L^{-1} = (ABS + 0.0239)/0.0111\ (R^2 = 0.99)$$

and

$$DOC, mg\ L^{-1} = (ABS + 0.0325)/0.0116\ (R^2 = 1.0) \quad (1)$$

All of the extracts obtained during the batch experiment were analyzed for light absorbance using a UV–VIS

Table 2 Selected properties of the compost added to soils

Water extract (1:10)	Cd	mg kg^{-1}	<LOQ[a]
	Cu		23.3 ± 1.67
	Pb		<LOQ
	pH		7.87 ± 0.04
	EC$_{25}$	dS m^{-1}	7.5 ± 0.12
	DOC[b]	mg kg^{-1}	31,832 ± 3734
	TOC[c]		251,548 ± 8690
Pseudo-total content of metals	Cd	mg kg^{-1}	0.58 ± 0.03
	Cu		123 ± 7.17
	Pb		3.01 ± 0.15

[a] Less than method limit of quantitation

[b] Dissolved organic carbon, determined in water extract (1:10) passed through 0.45-μm filter

[c] Total organic carbon

spectrometer, then DOC concentration was calculated using the established relationships.

The equilibrated solutions were also analyzed using ICP–OES for metal concentrations ($C_{sol(e)}$). Adsorbed metal concentrations (C_{ads}) were determined by the difference between the initial solution concentrations ($C_{sol(i)}$) and the equilibrated solution concentrations:

$$C_{ads} = C_{sol(i)} - C_{sol(e)} \qquad (2)$$

The Langmuir model (Langmuir 1918) was applied to the obtained data:

$$q = \frac{K^*C^*b}{(1 + K^*C)} \qquad (3)$$

where q is the adsorbed metal concentration (mg kg^{-1}), C is the equilibrated solution concentration (mg L^{-1}), K is the Langmuir constant (L mg^{-1})—the measure of the affinity between adsorbate and adsorbent, and its reciprocal value (1/K) gives the concentration at which half the maximum adsorption capacity of the adsorbent is reached (Martinez-Villegas et al. 2004), and b is the maximum sorption capacity (mg kg^{-1}).

The Freundlich model has the form:

$$q = K^*C^{\frac{1}{n}} \qquad (4)$$

where K is the Freundlich distribution coefficient, related to the total sorption capacity of the soil (L kg^{-1}) and n is the constant that typically has a value of less than 1 (Echeverria et al. 1998). The value of $1/n$ is the sorption intensity (Vaca-Paulin et al. 2006). To treat the experimental data, linear transformation of both of the models was performed (Chaturvedi et al. 2006; Vaca-Paulin et al. 2006). However, the linearization approach has some limitations and may lead to some errors in the parameter estimates. We compared this procedure with a more recent alternative (Bolster and Hornberger 2007), namely, a nonlinear regression calculation using the Microsoft Excel spreadsheet that these authors developed. The obtained model parameters were practically the same. This spreadsheet is able to calculate Langmuir and Freundlich model parameters using the original data of the adsorption experiment and was successfully tested against SAS software. In addition to model parameters, the following measures were calculated: (i) E—goodness-of-fit measure, the model efficiency, the overall indicator of model fit. An E value of 1 indicates a perfect fit to the data; (ii) St. Error—standard error; (iii) 95% confidence intervals (CI) for the fitted parameters (i.e., parameter uncertainties). Poor model fits tend to produce larger parameter uncertainties; (iv) AIC—Akaike's information criterion. The model with the lowest AIC is considered the most likely to be correct (Bolster and Hornberger 2007).

The soil residues were washed three times with deionized water, and the SE procedure was conducted to determine the distribution patterns of the metals adsorbed under different conditions (untreated soil, soil treated with compost, and soil treated with DOM).

On the basis of the obtained data, the CSSA adsorption isotherms were plotted for each geochemical fraction extracted. This method has been proposed by some researchers and defined as (i) CSSA by Salim et al. (1996), (ii) fractional loading isotherm techniques (Han and Banin 2001), or (iii) combined adsorption sequential extraction analysis (CASA) by Dho and Lee (2003). According to this technique, the concentration of adsorbed metal is determined by the appropriate reagent extraction according to the SE protocol used, and the adsorption isotherm is plotted with adsorbed metal concentration (mg kg^{-1}) on the Y axis and equilibrium solution concentration (obtained from the batch-adsorption experiment, mg L^{-1}) on the X axis. This method has an advantage over the bulk sample adsorption study because it allows sorption capacities to be determined for individual components while together in a natural mixture (Salim et al. 1996).

Results and discussion

pH and DOC

After the 24-h equilibration, the pH of the solutions with added metal decreased significantly with increasing metal concentration (Fig. S1 in Online Resource 1). Mainly, the pH decrease is explained by lower pH of the initial solutions with higher metal concentration (pH of CalCl$_2$ 0.01 M solution was decreased from 5.06 to 4.76 while the added metals concentration increased from 1 to 200 mg L^{-1}, respectively; and with DOM addition the pH decreased from 7.15 to 5.01). Thus, with the addition of solutions of 50, 100, and 200 mg L^{-1} metal concentration to the soil, the metal adsorption may also decrease as a result of the pH-dependent negative charge decrease (Dube et al. 2001). According to Christensen (1983), the sorption capacities of the soils are known to increase approximately three times for each increase in pH, of one unit in the pH interval 4 to 7.

All of the pH changes observed were relatively small. However, in a number of instances, they were statistically significant. At high initial metal concentration in the solutions, the DOC concentration decreased significantly, albeit not in all cases (Fig. S2 in Online Resource 1). The obvious reason for this was DOM flocculation at lower pH values. The DOC was found to be significantly ($p < 0.001$) and positively correlated with pH values: $r = 0.75$ and 0.79 for the clayey and sandy soils, respectively. A similar observation was reported by Gomes et al. (2001), when precipitation occurred in solutions with metal concentrations higher than 50 mg L^{-1} added to the soils. At high solution concentrations, metal cations may give rise to DOM precipitation, decreasing the negative charge of the DOM molecules (Guggenberger and Kaiser

2003). It is reasonable to assume that in the case of high levels of metal contamination, the mobilizing effect of DOM on heavy metals will decrease as a result of DOM flocculation.

Adsorption of Cd, Cu, and Pb to soils

Clayey soil without OA or DOM addition adsorbed much more metals than the sandy one, because of higher percent of clay particles (Figs. 1, 2 and 3 Table 1), that enhanced the metal sorption (Dube et al. 2001; Kabata-Pendias and Pendias 2001).

Cd adsorption was not significantly influenced by the addition of DOM, but the presence of compost increased the metal adsorption in the clayey and sandy soils (Fig. 1). The existence of humic material in soils or composts increases sorption of heavy metals. Carboxylic and phenolic groups of the HA and FA can replace their hydrogen ions by metal ions (Dube et al. 2001; Arias et al. 2002; Stevenson 1994).

According to the parameter E (Table S1 in Online Resource 2) for sandy soil, the Freundlich model showed a better fit to the soil and soil+DOM treatment data, whereas the Langmuir model gave a better fit the soil+compost treatment data. For clayey soil, the Langmuir model fit the experimental data better except for the soil+compost treatment, due to the adsorption decrease at the highest initial solution concentration. This decrease can be explained by low Cd adsorption under the competitive adsorption conditions.

When low initial concentrations of Cd (1–10 mg L^{-1}) were added to the clayey and sandy soils, it was retained mainly by the CARB (more than 50%), RO and EXC fractions (Figs. S3 and S4 in Online Resource 1). Sorption of Cd on the acetic acid-soluble CARB fraction with added compost might explain the similar Cd isotherms of the soil+compost treatment of sandy and clayey soils (Fig. 1). At increasing contamination levels, the Cd was retained by more available fractions. It is known from the literature, that the carbonate concentration in the soil solution leads to total Cd precipitation, and no other soil factors are so active in Cd immobilization. (Kabata-Pendias and Pendias 2001), but, at the same time, the

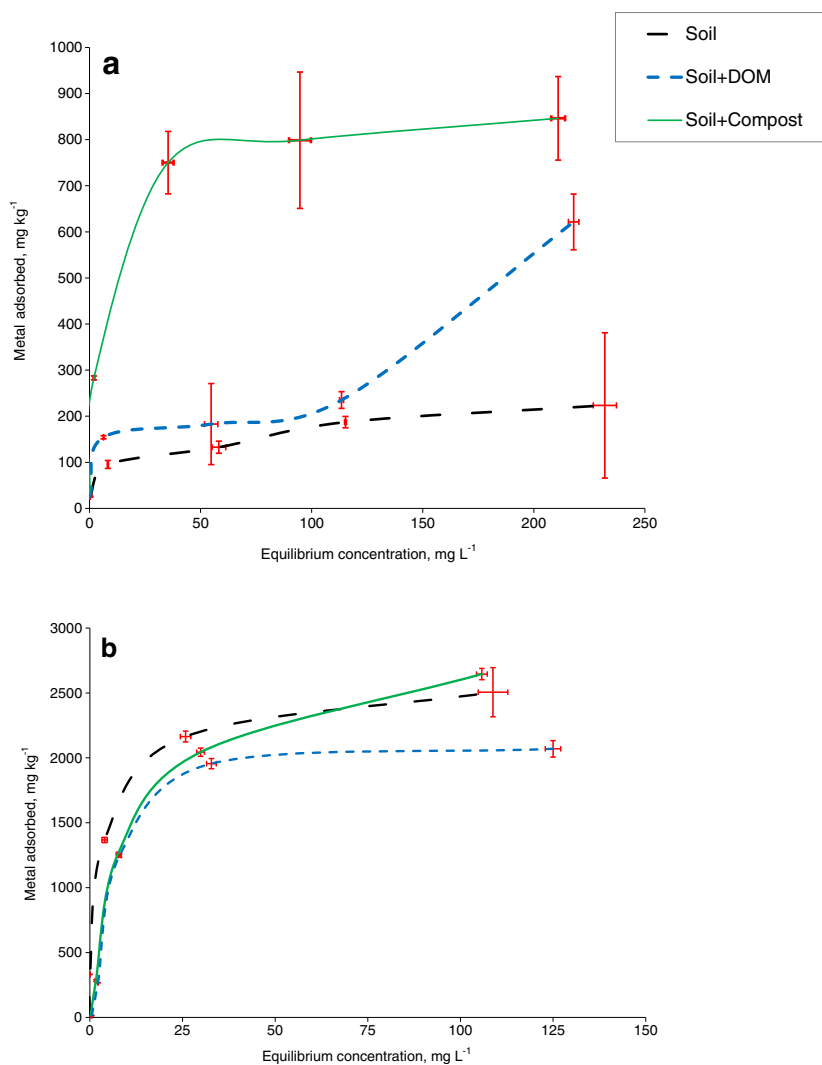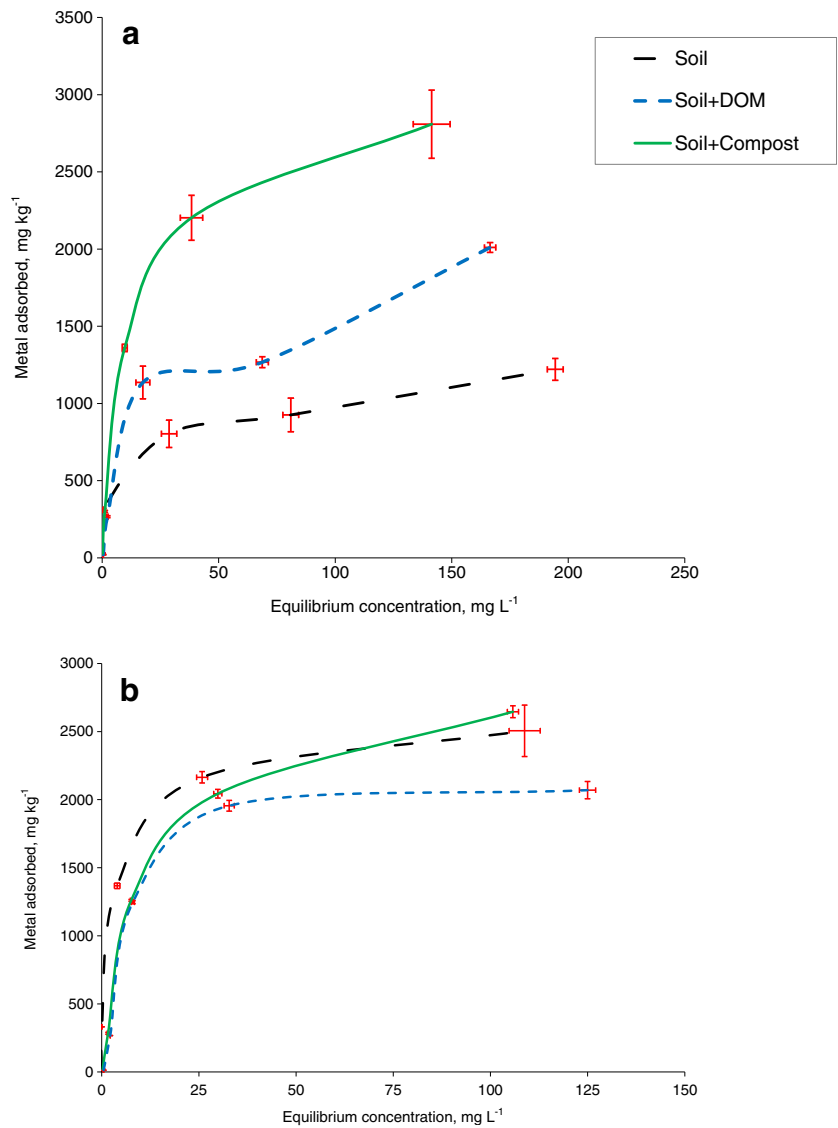**Fig. 1** Isotherms of Cd adsorption on sandy (**a**) and clayey (**b**) soils

Fig. 2 Isotherms of Cu adsorption on sandy (A) and clayey (B) soils

solubility of the metals depends mainly on the metal loading over soil sorbents, pH, and the concentration of inorganic ligands and DOM in the soil solution (Weng et al. 2002).

In all treatments, L-type Cu-adsorption isotherms were observed for sandy soil, whereas they were of the H-type for clayey soil, indicating possible chemical adsorption in both cases (Fig. 2). A DOM mobilization effect was observed on Cu. These data are in agreement with the findings reported by Vaca-Paulin et al. (2006), who found that DOM produced from sewage sludge reduces Cu sorption by the substrate not only because of the higher DOM concentration, but also because of the greater amount of high-molecular-weight hydrophobic fractions, which allow the formation of a soluble Cu–DOM complex. It may be concluded that for clayey soil, compost-derived DOM is less effective at mobilizing Cu at high metal loadings than DOM applied as an extract.

The difference in Cu and Cd adsorption may be explained by different properties of these elements. Cadmium is generally considered as weakly-bonded metal and its major sorption mechanism is cation exchange (Selim 2013). The most important factors which control Cd ion mobility are pH and oxidation potential. Cu, however, is considered as one of the least mobile heavy metals in soil (Kabata-Pendias and Pendias 2001).

Also, electronegativity is an important factor influencing on the metal's adsorption and based on this, the order of bonding preference is the follow: $Cu > Pb > Cd$ (Fontes 2013). Christensen (1983) found that the mixture of Cr, Cu, and Pb effectively reduced the sorption of Cd onto soils and reduced the distribution coefficients for Cd from 2 to 14 times due to competition. Arias et al. (2002) also found a dramatic decrease on the adsorption of Cd^{2+} on kaolin and kaolin-HA complex in the presence of Cu^{2+}. These changes on adsorption can be due to density of charge (the ratio of the ionic charge to the ion's radius). This parameter is bigger for Cu^{2+} than for Cd^{2+}, that is why Cu would be more strongly adsorbed than Cd (Arias et al. 2002).

Fig. 3 Isotherms of Pb adsorption on sandy (**a**) and clayey (**b**) soils
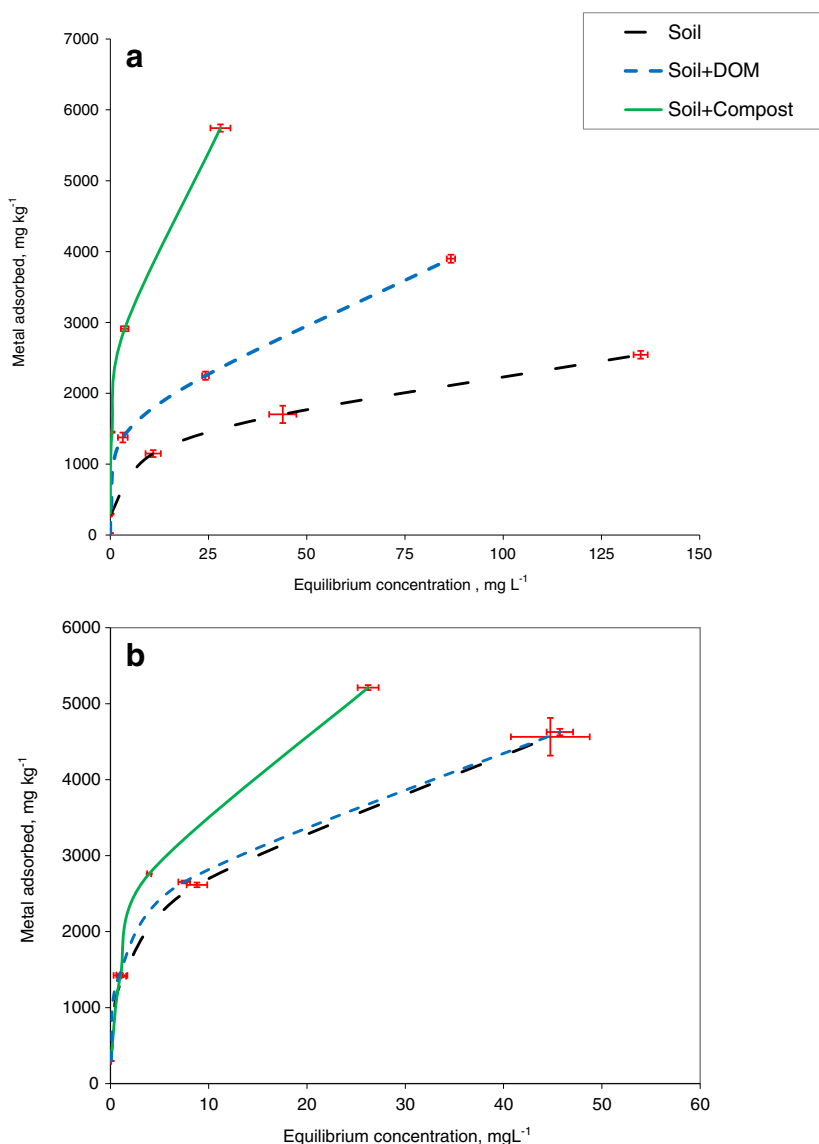
In general, Cu is bound stronger to the mineral and to specific organic constituents of soils compared to Cd. Therefore, the common characteristic of Cu distribution in soil profiles is its accumulation in the top horizon (Kabata-Pendias and Pendias [2001]).

In the sandy soil, application of DOM extract or compost led to an increase in Cu adsorption in comparison to the untreated soil. This increase may have resulted from the improved configuration of the DOM following its interaction with the mineral surface.

In the studied clayey soil, native Cu was distributed among the RES, OM, and RO fractions (Table S2 in Online Resource [2]). In the sandy soil, Cu was distributed among the same fractions, but less metal was found in the RES fraction and more in the OM one. Addition of the DOM extract and compost to soils facilitated Cu transfer to some available metal forms as a WE+EXC

fraction (the concentration of Cu in the DOM extract was subtracted from the results).

The distribution patterns of added Cu are presented in Figs. S3 and S4 in Online Resource [1]. The clayey soil demonstrated more Cu in the EXC fraction than the sandy one, and the sandy soil demonstrated more Cu in the CARB fraction than the clayey one. An increase in initial metal concentration changed the Cu distribution pattern significantly in both soils. The portion in the EXC fraction increased from 14.1 to 53.8% in the clayey soil and from 1.5 to 47.8% in the sandy one (at 1 mg L^{-1} and 200 mg L^{-1} initial metal concentration, respectively). The portion in the CARB fraction also reached a value of more than 30%, while the portions in the other fractions decreased. These two fractions may therefore be defined as the main adsorbents of Cu at higher loading levels, whereas at lower loading levels, the RO fraction was dominant in the studied soils. It may be concluded that under low Cu contamination, the soil is less vulnerable to pollution than

under high contamination, because the RO fraction is known to be less bioavailable than the EXC and CARB fractions (Filgueiras et al. 2002).

DOM addition to the system did not change the Cu distribution pattern significantly. Cu in the OM fraction increased slightly at higher initial metal concentrations, probably indicating Cu adsorption to the flocculated DOM. This process might also explain the higher adsorption of Cu to the sandy soil with DOM addition compared to nontreated soil (Cu adsorption capacity (b) was 2313.9 ± 498.4 and 1224.6 ± 214.8, respectively, Table S1 in Online Resource 2).

The most obvious changes in added Cu distribution patterns were observed in soils treated with PCM compost, where the portion in the OM fraction was significantly higher than that in the nontreated soil OM fraction (Figs. S3 and S4 in Online Resource 1). In the clayey soil under increasing concentrations of metal loading, the portion in the OM fraction was drastically reduced (from 20.7% at 1 mg L^{-1} Cu to 4.8% at 200 mg L^{-1}), but the portions in the RO and RES fractions increased. In the sandy soil, a similar phenomenon was observed: the portion in the OM fraction decreased from 30.8% at 1 mg L^{-1} Cu to 2.9% at 200 mg L^{-1}, and the portions in the RO and CARB fractions increased. The portion in the EXC fraction decreased with compost addition in both soils.

The distribution of native Cu in the studied compost is presented in Table S3 in Online Resource 2. Most of the metal was found in the OM and RES fractions. It can be concluded that a less labile part of the compost provided adsorption sites for the added Cu.

SOM added to the clayey soil with the compost led to a strong decrease in Cu adsorption by the EXC fraction. At the same time, compost addition significantly increased the metal concentration in the CARB, RO, and OM fractions which might be attributed to the compost SOM's influence on Cu adsorption (Fig. S5 in Online Resource 1). The same outcome of compost application was observed in the sandy soil.

The sandy soil retained less Cu than the clayey one, but in contrast to the latter, more metal was adsorbed on the EXC, CARB, and RO fractions during the DOM extract equilibration at initial concentrations higher than 10 mg L^{-1}. At a high Cu contamination level, the DOM's mobilizing influence in the sandy soil was suppressed. This can be explained by DOM flocculation at lower pH (Fig. S2 in Online Resource 1).

At an initial solution concentration of up to 100 mg L^{-1} Pb, the sorption isotherms plotted for the clayey soil treatments could be defined as L-type. This isotherm type indicates a strong interaction between the metal and the soil surface, and probably the inner-sphere complexes forming (Fig. 3). The soil–OA mixture exhibited the highest maximal sorption (b parameter of the Langmuir model), whereas there was no significant difference in b value between the soil+DOM treatment extract and the clayey soil itself (5583 ± 695, 4878 ± 768 and 4824 ± 804, respectively, Table S1 in Online Resource 2). It could be concluded

that DOM does not influence Pb sorption by the studied clayey soil, but the water-insoluble part of the compost (SOM and minerals) increases the metal adsorption. One of the explanations for Pb's affinity to soil with compost is the carboxylic and phenolic groups of the HS (Chaturvedi et al. 2006).

In the case of the sandy soil, the highest maximal sorption (b) of Pb was observed in the soil+compost treatment which was expressed as an L-type isotherm (Table S1 in Online Resource 2). Soil and soil+DOM adsorbed less Pb, but the addition of DOM significantly increased Pb adsorption relative to the nontreated soil. It is likely that Pb had more affinity to the flocculated DOM than to the DOM that remained in solution.

All treatments were described sufficiently well by the Langmuir and Freundlich models (E parameter of 0.8–1, Table S1 in Online Resource 2), except for clayey soil treated with compost, where the Langmuir model fitted the experimental data better than the Freundlich model. It might be concluded that clayey soil, especially that treated with compost, can adsorb more Pb than was used in our experiment.

The distribution patterns of native Pb are presented in Table S2 in Online Resource 2. In the clayey soil, Pb that had been added with the compost was retained by the RO and OM fractions. In the sandy soil, Pb was found in the same fractions. In the studied PCM compost, all of the detected Pb was found in the OM fraction (Table S3 in Online Resource 2). In both soils, the main Pb scavenger was the RO fraction, especially at low initial metal concentrations (1–10 mg L^{-1}). With an increase in the initial metal concentration, there were also increases in the CARB and EXC fractions (Figs. S3 and S4 in Online Resource 1). It could be concluded that Pb added to the studied soils has a higher affinity to more bioavailable soil components. Addition of DOM extract to the clayey soil led to an increase in the EXC fraction at high initial metal concentrations (12.5, 7.5, and 23.1% in the clayey soil, soil+compost, and soil+DOM treatments respectively at 200 mg L^{-1} Pb). In contrast, the addition of compost and DOM extract to the sandy soil decreased the EXC fraction's portion at high initial Pb concentrations.

Clayey soil treated with compost demonstrated a higher portion of Pb in the OM fraction and less EXC- and CARB-retained Pb. The distribution pattern of Pb in the sandy soil treated with compost was similar to that of the clayey one. Addition of DOM slightly increased the Pb adsorption by the more available fraction (EXC), whereas compost addition initiated Pb adsorption by the RO fraction, which was defined as less available. Compost components that are soluble in NH$_2$OH·HCl (RO fraction) are responsible for the high sorption affinity of compost-treated soils for Pb.

CSSA method application

An example of CSSA isotherms plotted for individual operationally defined fractions in comparison to the bulk sample

isotherms is presented in Figs. S5 and S6 in Online Resource 1 (Cu adsorption on clayey and sandy soil, respectively). The parameters of the adsorption models calculated for each operationally defined fraction of the studied soils are presented in Tables S4 and S5 in Online Resource 2. For the concentration range studied, in some cases, the isotherms did not fit the Langmuir model because of a negative slope or intercept value, in contrast to the bulk sample isotherm for those same cases. Some isotherms had a linear shape that allowed calculation of linear model parameters that were not applicable to the bulk sample isotherms (Table S6 in Online Resource 2). Similar observations were reported by Han and Banin (2001), who applied the CSSA method to loessial soil from southern Israel, spiked with soluble forms of heavy metals and incubated for 1 year. The redistribution and transformations of Cu, Cr, Ni, and Zn were demonstrated through the fractional loading isotherms. For all metals studied, the linear model better described metal adsorption in individual solid-phase components than the Freundlich model.

It was difficult to describe the adsorption of Cu on individual fractions of both soils by either the Langmuir or Freundlich model (Figs. S5 and S6 in Online Resource 1). The best fit for the Langmuir model was in the clayey soil for the RO, OM, and RES fractions (E value was 0.64–0.99, Table S5 in Online Resource 2). The maximal sorption in those fractions (parameter b) was observed for the soil–OA mixture. In the sandy soil, the Langmuir model also fitted the experimental data better than the Freundlich model.

The adsorption of Pb on soil fractions was better described by the Langmuir model (E value close to 1, except for the OM and RES fractions in both soils, Table S5 in Online Resource 2). Adsorption on the EXC fraction was sufficiently well described by a simple linear model (Table S6 in Online Resource 2). Maximal sorption in both soils was observed for the soil–OA mixture, except for the CARB and EXC fractions of the clayey soil. It could be concluded that Pb is adsorbed mostly by the soil RO and CARB fractions, whereas compost gives the soil additional OM and RO adsorbing agents.

In the case of Cd, only adsorption on the EXC fraction of clayey soil was well described by both models (E value close to 1, Table S5 in Online Resource 2), whereas DOM and compost addition decreased the Freundlich model's goodness-of-fit (E value was 0.57 and 0.39 respectively, in comparison with 0.89 in untreated soil, Table S5 in Online Resource 2). This indicates high Cd bioavailability at high loading levels.

Conclusions

The adsorption–desorption batch experiment results showed that the influence of DOM on Cu adsorption differs for sandy and clayey soils. High metal affinity to the soil in all

treatments was observed, but at higher metal loading rates, the DOM reduced the adsorption in the clayey soil whereas in the sandy one, at an initial metal concentration higher than 10 mg L^{-1}, the opposite influence was observed. The increased adsorption with the addition of DOM could have resulted from an improved configuration of the DOM following its interaction with the mineral surface.

The adsorption isotherms of Cd did not confirm the DOM mobilizing effect in either soil. In the sandy soil, the DOM significantly increased Cd adsorption. It was also found that in the sandy soil, the DOM significantly increases Pb adsorption at high metal loading rates whereas it did not influence it in the clayey soil. Compost addition significantly increased Pb adsorption relative to the nontreated sandy and clayey soils. This is in accordance with the findings of Weng et al. (2002), who concluded that the DOM-complexed species is generally more significant for Cu and Pb than for Cd.

Under the conditions of the adsorption–desorption experiment, the RO fraction was the main scavenger of Pb in both the soils. At high metal loading rates (> 10 mg L^{-1}), most of the Pb was adsorbed by the CARB and EXC fractions. Compost addition increased the proportion of the RO fraction. The Langmuir and Freundlich models described the Pb adsorption well in both soils except for clayey soil treated with compost, where the Langmuir model showed a better fit to the experimental data. It might be concluded that clayey soil, especially when treated with compost, adsorbs higher concentrations of Pb than were used in our experiment.

Compost addition generally increased the proportion of the RO and OM fractions, reducing metal bioavailability and therefore, soil vulnerability to heavy metals pollution. It can be concluded that the immobilizing effect of compost SOM on heavy metals is usually stronger than the mobilizing effect of DOM that is part of the compost applied to the soil. This is especially important for sandy soils, which have low adsorption ability and higher vulnerability to metal pollution than clayey soils.

References

Alumaa P, Steiness E, Kirso U, Petersell V (2001) Heavy metal sorption by different Estonian soil types at low equilibrium solution concentrations. Proc Est Acad Sci Chem 50(2):104–115

Antoniadis V, Alloway B (2002) The role of dissolved organic carbon in the mobility of Cd, Ni and Zn in sewage sludge-amended soils. Environ Pollut 117:515–521

Appel C, Ma L (2002) Concentration, pH, and surface charge effects on cadmium and lead sorption in three tropical soils. J Environ Qual 31: 581–589

Arias M, Barral M, Mejuto J (2002) Enhancement of copper and cadmium adsorption on kaolin by the presence of humic acids. Chemosphere 48:1081–1088

Basta N, Gradwohlb R, Snethenab K, Schroderab J (2001) Chemical immobilization of lead, zinc, and cadmium in smelter-contaminated soils using biosolids and rock phosphate. J Environ Qual 30:1222–1230

Basta NT, Ryan J, Chaney R (2005) Trace element chemistry in residual-treated soil: key concepts and metal bioavailability. J Environ Qual 34:49–63

Bolan N, Adriano D, de-la Luz M (2004) Dynamics and environmental significance of dissolved organic matter in soil. SuperSoil 2004: 3rd Australian New Zealand Soils Conference, 5–9 December 2004, University of Sydney, Australia

Bolster CH, Hornberger GM (2007) On the use of linearized Langmuir equations. Soil Sci Soc Am J 71:1796–1806

Chaturvedi P, Chandra S, Virendra M (2006) Sorption kinetics and leachability of heavy metal from the contaminated soil amended with immobilizing agent (humus soil and hydroxyapatite). Chemosphere 64:1109–1114

Chefetz B, Hadar Y, Chen Y (1988) Dissolved organic carbon fractions formed during composting of municipal solid waste: properties and significance. Acta Hydrochim Hydrobiol 26:172–179

Chen Y, Inbar Y, Barak P (1991) Soil testing methods (in Hebrew). Hebrew University of Jerusalem, Rehovot

Christensen T (1983) Cadmium soil sorption at low concentrations: 1. Effect of time, cadmium load, pH, and calcium. Water Air Soil Pollut 21:105–114

Dho N, Lee SR (2003) Effect of temperature on single and competitive adsorptions of Cu(II) and Zn(II) onto natural clays. Environ Monit Assess 83:177–203

Dube A, Zbytniewski R, Kowalkowski T, Cukrowska E, Buszewski B (2001) Adsorption and migration of heavy metals in soil. Pol J Environ Stud 10:1–10

Dudal Y, Sevenier G, Dupont L, Guillon E (2005) Fate of the metal-binding soluble organic matter throughout a soil profile. Soil Sci 170:707–715

Echeverria J, Morera M, Mazkiaran C, Garrido J (1998) Competitive sorption of heavy metal by soils. Isotherms and fractional factorial experiments. Environ Pollut 101:275–284

EPA Method 6010c (2007) Inductively coupled plasma–atomic emission spectrometry. https://www.epa.gov/sites/production/files/2015-07/documents/epa-6010c.pdf. Accessed 10 April 2017

Filgueiras A, Lavilla I, Bendicho C (2002) Chemical sequential extraction for metal partitioning in environmental solid samples. J Environ Monit 4:823–857

Fine P, Hass A, Prost R, Atzmon N (2002) Organic carbon leaching from effluent irrigated lysimeters as affected by residence time. Soil Sci Soc Am J 66:1531–1539

Fontaine S, Mariotti A, Ababdie L (2003) The priming effect of organic matter: a question of microbial competition? Soil Biol Biochem 35:837–843

Fontes M (2013) Behavior of heavy metals in soils: individual and multiple competitive adsorption. In: Selim H (ed) Competitive sorption and transport of heavy metals in soils and geological media. CRC Press, Boca Raton, pp 77–119

Gat P (2006) The effect of dissolved organic matter (DOM) originaing from biosolid on metal binding, solubilization and uptake by plants. Dissertation, The Hebrew University of Jerusalem

Gomes PC, Fontes MPF, da Silva AG, Mendonca E de S, Netto A (2001) Selectivity sequence and competitive adsorption of heavy metals by Brazilian soils. Soil Sci Soc Am J 65:1115–1121

Guggenberger G, Kaiser K (2003) Dissolved organic matter in soil: challenging the paradigm of sorptive preservation. Geoderma 113:293–310

Han F, Banin A (2001) Fractional loading isotherm of heavy metals in an arid-zone soil. Commun Soil Sci Plant Anal 32(17&18):2691–2708

He X, Logan T, Traina S (1995) Physical and chemical characteristics of selected U.S. municipal solid waste composts. J Environ Qual 24:543–552

Jueschke E, Marschner B, Tarchitzky J, Chen Y (2008) Effects of treated wastewater irrigation on the dissolved and soil organic carbon in Israeli soils. Water Sci Technol 57:727–733

Kabata-Pendias A, Pendias H (2001) Trace elements in soils and plants. CRC Press LLC, London

Langmuir I (1918) The adsorption of gases on plane surfaces of glass, mica and platinum. J Am Chem Soc 40:1361–1403

Madrid F, Lopez R, Cabrera F (2007) Metal accumulation in soil after application of municipal solid waste compost under intensive farming conditions. Agric Ecosyst Environ 119(3–4):249–256

Martinez-Villegas N, Flores-Velez L, Domnguez O (2004) Sorption of lead in soil as a function of pH: a study case in Mexico. Chemosphere 57:1537–1542

McLean JE, Bledsoe BE (1992) Behavior of metals in soils. EPA ground water issue EPA/540/S-92/018

Minkina T, Motusova G, Mandzhieva S, Nazarenko O, Simunic I (2011) Transformation of heavy metal compounds during the remediation of contaminated soils. Agric Conspec Sci 76(1):19–25

Pueyo M, Rauret G, Luck D, Yli-Halla M, Muntau H, Quevauviller P, Lopez-Sanchez J (2001) Certification of the extractable contents of Cd, Cr, Cu, Ni, Pb and Zn in a freshwater sediment following a collaboratively tested and optimised three-step sequential extraction procedure. J Environ Monit 3:243–250

Rosen V, Chen Y (2014) The influence of compost addition on heavy metal distribution between operationally defined geochemical fractions and on metal accumulation in plant. J Soils Sediments 14:713–720

Salim IA, Miller C, Howard J (1996) Sorption isotherm-sequential extraction analysis of heavy metal retention in landfill liners. Soil Sci Soc Am J 60:107–114

Selim H (2013) Competitive sorption of heavy metals in soils: experimental evidence. In: Selim H (ed) Competitive sorption and transport of heavy metals in soils and geological media. CRC Press, Boca Raton, pp 1–49

Shlosberg A (2010) Syndromes of ill-health associated with copper. Isr J Vet Med 65:170–171

Smith R (2009) A critical review of the bioavailability and impacts of heavy metals in municipal solid waste composts compared to sewage sludge. Environ Int 35(1):142–156

Stevenson FJ (1994) Humus chemistry: genesis, composition, reactions. Wiley, New York

Tandy S, Healey J, Nason M, Williamson J, Jones D (2009) Remediation of metal polluted mine soil with compost: co-composting versus incorporation. Environ Pollut 157:690–697

Vaca-Paulin R, Esteller-Alberich M, Lugo-de la Fuente J, Zavaleta-Mancera H (2006) Effect of sewage sludge or compost on the sorption and distribution of copper and cadmium in soil. Waste Manag 26:71–81

Vega FA, Covelo E, Andrade M (2011) Applying Freundlich, Langmuir and Temkim models in Cu and Pb soil sorption experiments. Spanish J Soil Sci 1(1):20–37

Vidal M, Santos M, Abrao T, Rodriguez J, Rigol A (2009) Modeling competitive metal sorption in a mineral soil. Geoderma 149:189–198

Weng L, Temminghoff EJM, Lofts S, Tipping E, van Riemsdijk WH (2002) Complexation with dissolved organic matter and solubility control of heavy metals in a sandy soil. Environ Sci Technol 36:4804–4810

Wong J, Zhou L (2003) Behavior of heavy metals in soil: effect of dissolved organic matter. In: Selim H, Kingery W (eds) Geochemical and hydrology reactivity of heavy metals in soils. Lewis Publishers, Boca Raton, pp 245–269

Zheng G, Chen T, Gao D, Luo W (2004) Dynamic of lead speciation in sewage sludge composting. Water Sci Technol 50:75–82

Zmora-Nahum S, Hadar Y, Chen Y (2007) Physico-chemical properties of commercial composts varying in their source materials and country of origin. Soil Biol Biochem 39:1263–1276