

# Soil Organic Matter Quality and Zinc and Lead Sorption as Affected by Sewage Sludge

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Sewage sludge (SS) or sewage sludge compost (SSC) were applied to soil under controlled conditions, at rates of 0 or 200 Mg ha<sup>-1</sup>, to investigate changes in dissolved organic matter (DOM), humic acids (HA), and Pb and Zn sorption in the soil. Infrared spectroscopy, visible spectrophotometry, and sorption isotherms (mono-metal and competitive sorption systems) methods were used to assess the changes. The  $E_4/E_6$  ratio ( $\lambda$  at 465 nm /  $\lambda$  at 665 nm) and the infrared spectra of DOM and HA showed aromatic behaviour in compost-soil (SSC-S); in contrast sewage sludge-soil (SS-S) showed an aliphatic behaviour. Application of either SS or SSC increased the Pb and Zn sorption capacity of soil. The Pb and Zn sorption increased in soil and soil mixtures with a competitive metal system. The metal affinity sequence for soil, SS-S, and SSC-S was compared with the predicted affinity sequences obtained from metal properties. Poor correspondence was observed between the metal affinity sequence and the metal affinity sequence predicted by ionic potential, indicating that metals bonding to soils were not predominantly electrostatic. An affinity sequence based on Pearson's theory agreed with the metal affinity sequences for soils. A statistical analysis showed that the bands assigned to esters (1080 cm<sup>-1</sup>) of DOM, phenolic OH (1420 cm<sup>-1</sup>), amide I (1650 cm<sup>-1</sup>), carboxyl and carbonyl C=O stretches of different nature, C=O stretch of aromatic esters, aliphatic ketone, aldehyde (1720 cm<sup>-1</sup>), ethers and esters (1230 cm<sup>-1</sup>), aliphatic alcohols (1125 cm<sup>-1</sup>), and lignin (1380 cm<sup>-1</sup>) of HA were correlated with Zn constants of Langmuir adsorption isotherm ( $P < 0.05$ ).

## Introduction

Soils are contaminated with metals through a variety of means. One method used commonly to remediate metal-contaminated soil and to promote plant growth is to add organic amendments, some of which are themselves waste materials (Shuman 1999). Organic materials increase the active surface area that can help adsorb metals that would otherwise be toxic to plants and provide specific sorption sites for metals, from which they may be difficult to displace (Shuman 1999; Gao *et al.* 2003). Sewage sludge is often composted prior to application to the soil, to eliminate the risk of disseminating pathogens and to produce an aesthetically acceptable product for agriculture (Bernal *et al.* 1998). Composting transforms organic matter into a uniform and biologically stable product (Sullivan *et al.* 2002). Research has shown also that composting alters the quality of dissolved organic matter (DOM) and humic acids (HA) in organic waste (Baziramakenga and Simard 1998; Chefetz *et al.* 1998; Zhou and Wong 2001). There are few studies on the changes in DOM and HA in sewage sludge after composting.

The phenomena of adsorption – the objective of this research – can be studied through sorption isotherms. Isotherms have been used widely to obtain models of physical adsorption, and in some cases these models also can be applied to chemical sorption (Shuman 1975).

Most studies on the adsorption of metals by soil amendment with organic wastes have investigated the sorption of a single metal single or competitive metal (Lamy *et al.* 1993; Shuman 1999; Illera *et al.* 2000; Zhou and Wong 2001). Relatively few experiments have been conducted to compare both situations. Antoniadis *et al.* (2007) found that metals became more mobile in competition than in single-element systems. Urasa and Macha (1999) mentioned that Pb was retained preferentially when it was in a mixture with other divalent cations such as metallic ions. According with Alloway (1990), antagonistic and synergistic interactions also can occur among heavy metals.

On the other hand, few studies have investigated the competitive metal adsorption and the quality of organic matter in soils amended with sewage sludge or composted sewage sludge, with naturally occurring metal concentrations. In addition, many studies

have evaluated heavy metal mobility, partitioning and sorption behaviour in temperate soils (Dudley *et al.* 1987; McBride and Sauvé 1997; Krishnasamy and Krishnamoorthy 1991; Schwarz *et al.* 1999; Walter *et al.* 2002; Granato *et al.* 2004). Relatively few experiments have been conducted on intertropical soils (Guadalix and Pardo 1995; Appel and Ma 2002).

The objectives of this research were: (i) to study the role of organic matter from sewage sludge or composted sewage sludge on Pb and Zn sorption in the soil, and (ii) to describe the competitive behaviour during metal sorption in soil amended with sewage sludge or composted sewage sludge.

## Materials and Methods

### Solid Samples

The soil samples were obtained from an agricultural area of the valley of Toluca (Mexican High Plateau). This soil was characterized as silty - clayey Haplic Phaeozem soil (CETENAL 1976), and the soil samples were obtained from the Ap horizon (0-20 cm). This soil is distributed widely in the entire Mexican High Plateau, where it has high agronomic value because a great part of the corn that is produced in Mexico is cultivated there.

Sewage sludge was obtained from the municipal wastewater treatment ECOSYS Company from Toluca, Mexico, which has an activated sludge treatment plant. For composting, SS was mixed with corn straw as a source of carbon and with shredded tire chips as a bulking agent (Garrido *et al.* 2005). The composting was carried out at 55°C for 35 days in cone-shaped, 1.5-m diameter static piles with a C/N 30-40 ratio. Sewage sludge-soil (SS-S) and compost-soil (SSC-S) mixtures (200 Mg of sewage sludge or compost dry weight basis) were incubated at 29° ± 2°C for 10 days (Dudley *et al.* 1987). During the incubation period, water was added every two days to the mixtures to obtain a constant value of 100% of its field capacity. Once the incubation period was completed, the mixtures were dried at room temperature.

All the solid samples (soil, sewage sludge, compost and mixtures) were dried, homogenized, sieved <2 mm, ground with an agate mortar, and subsequently kept in plastic bags at room temperature until analysis in the laboratory.

### Chemical Analysis of Solids

The pH was measured in water suspension with a 1:2.5 soil:solution ratio (w:w) after 30 min equilibrium time (McLean 1982). Organic matter content (OM) was

measured by the Walkley and Black (1947) method. Total N was determined by the Kjeldahl digestion-distillation method (Bremner 1996). Cation exchange capacity (CEC) was determined using the NH<sub>4</sub>OAc method (Chapman 1965). Total carbon (TC) was determined by dividing the concentration of OM by 1.724 (Walkley and Black 1947). Total Zn and Pb concentrations were analysed in samples sieved through a 0.149-mm mesh and digested with aqua regia (conc. HNO<sub>3</sub>-conc. HCl) 4:1 v/v on a hot plate; the solutions were analysed by flame atomic absorption spectrophotometry (AAS), (Perkin Elmer mod. 3110, Perkin Elmer, Norwalk, Connecticut) (Hossner 1996). All tests were performed at constant dry weight with three repetitions.

### Extraction and Characterization of Dissolved Organic Matter and Humic Acids

The extraction and characterization of dissolved organic matter (DOM) of Soil, SS-S and SSC-S was reported in Vaca *et al.* (2006).

Humic acids (HA) were obtained from soil and soil mixtures according to the method of Duchaufour and Jacquin (1975). After the extraction of DOM, the residue was extracted with 0.1 M Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> and 0.1 M NaOH. The alkaline supernatant solution was separated from the residue by centrifugation at 15,700g for 45 min, acidified with HCl to pH = 1, and allowed to stand for 24 h to allow coagulation of the HA fraction. The precipitated HA was separated from the supernatant solution by centrifugation at 15,700g for 45 min and dissolved in a minimal volume of 0.5 M NaOH. After removing the suspended solids by centrifugation at 15,700g for 45 min, the clear HA solution was demineralised with 1% HCl-HF and dialyzed versus double-distilled water until there were no salts (this was tested with AgNO<sub>3</sub> 0.1 N) in the distilled water was accomplished. Then, an aliquot was analysed at 465 and 665 nm in the spectrophotometer to determine the E<sub>4</sub>/E<sub>6</sub> ratio (Sato and Kumada 1967). The HA solutions were dried at 40 °C (Schnitzer y Khan 1972; Almendros *et al.* 1990).

Dried DOM and HA samples for the IR analysis were prepared adding 200 mg of anhydrous KBr to 2 mg of dry solid sample; the mixture was homogenized in an agate mortar and analysed in a range of 4000 – 400 cm<sup>-1</sup> by Fourier transform infrared spectra (Almendros *et al.* 1990) using an Infrared Spectrophotometer (Bruker, Tensor 27, Billerica, Massachusetts).

### Resolution-Enhanced Infrared Spectroscopy

The different procedures for resolution enhancement based on mathematical treatments of spectral

data yield valuable information in the case of complex polymer materials, where the broad peaks are due mostly to the overlapping of a series of neighbouring bands (Almendros *et al.* 1990). The method used here is based on subtracting from the raw spectrum a positive multiple of its 2nd derivative.

*Sorption Isotherms*

Metal sorption experiments were carried out under batch conditions on all samples. The dry samples were weighed (0.5 g) into 50 ml polyethylene centrifuge tubes; Zn and Pb were added as Zn(NO<sub>3</sub>)<sub>2</sub> and Pb(NO<sub>3</sub>)<sub>2</sub> in a concentration ranging from 5 to 1200 mg L<sup>-1</sup> in 30 ml of 0.01 M NaNO<sub>3</sub> as background electrolyte, and the mixtures were shaken in a water bath at 27 ± 1 °C for 24 h (Shuman 1999; Zhou and Wong 2001; Adhikari and Singh 2003). These metal concentrations were used to ensure that the Zn and Pb sorbed by the soil were below the maximum amounts allowed for metals in soil according to Kabata-Pendias and Pendias (1992) (Table 1). The experiment was performed on a single-metal sorption and competitive sorption system (Pb-Zn). In the competitive sorption experiment, Zn and Pb ranged from 5 to 300 mg L<sup>-1</sup> (5, 10, 20, 40, 75, 150, 300 mg L<sup>-1</sup> of each metal) because in the single-metal experiment maximum Zn sorption was reached at 300 mg L<sup>-1</sup>. The tubes were centrifuged at 15,700g for 25 min, and the supernatant was filtered with Whatman No. 42 paper. The solutions were analysed for Zn and Pb by AAS. Sorption of Zn or Pb was calculated as the difference between the amounts added initially and the amounts remaining in the solution, following the equation:

$$x/m = V (C_i - C_e) / m$$

where *x/m* is the concentration of Zn<sup>2+</sup> or Pb<sup>2+</sup> sorbed (mg kg<sup>-1</sup>), *C<sub>i</sub>* is the initial metal concentration (mg L<sup>-1</sup>) in solution, *C<sub>e</sub>* is the concentration of Zn<sup>2+</sup> or Pb<sup>2+</sup> in equilibrium solution (mg L<sup>-1</sup>) following sorption, *V* is the volume (L), and *m* is the mass (g).

*Statistical Analysis*

In order to find if the metal sorption capacity of soil and soil mixtures is affected by the quality of the OM added, multiple correlations were developed with 95% probability, using the statistical software Statgraphics Plus 5.0 (Zar 1984).

**Results and Discussion**

According to the maximum permissible amounts of Pb and Zn in sewage sludge and biosolids for their final disposal, as reported by Mexican Regulation (NOM-004-ECOL-2001), the SS and SSC employed in this experiment were classified as excellent amendments for agricultural use (Table 1). Selected chemical properties of soil, SS, and SSC are given in Table 2, the SSC contained less total carbon than SS; this result could be due to microbial decomposition of carbon and its subsequent release as CO<sub>2</sub> (Baziramakenga and Simard 1998). The carbon remaining after the bio-oxidative phase of composting is relatively resistant to microbial degradation (Bernal *et al.* 1998). The addition of SS and SSC to the soil increased the nitrogen percentage 3 times and the OM 1.6 times for SS-S and 2.3 times for SSC-S (Table 2).

TABLE 1. Concentration of Pb and Zn in soil, sewage sludge, and compost and maximum permitted amounts

Metal	Maximum permitted (mg kg <sup>-1</sup> )			Concentration measured(mg kg <sup>-1</sup> )		
	Soil <sup>a</sup>	Good	Excellent	Soil	SS	SSC
Pb	100 - 400	840	300	nq	78.7 ± 1.08	112.4 ± 1.2
Zn	110 - 400	7500	2800	40 ± 1.0	1 094 ± 1.53	1 004.0 ± 1.5

<sup>a</sup>Kabata-Pendias and Pendias (1992). <sup>b</sup>NOM-004-ECOL-2001. SS = sewage sludge; SSC = compost; nq; below quantification limit. Mean ± standard error.

TABLE 2. Chemical properties of soil, sewage sludge, compost, and soil mixtures

	pH	N (%)	OM (%)	CEC (cmol <sup>(+)</sup> kg <sup>-1</sup> )	TC (%)
Soil	6.0 ± 0.2	0.25 ± 0.02	3.2 ± 0.1	13.8 ± 0.4	1.86
SS	6.2 ± 0.1	6.07 ± 0.09	65.2 ± 0.5	42.7 ± 0.5	37.38
SSC	5.5 ± 0.2	3.08 ± 0.05	57.5 ± 0.4	51.9 ± 0.8	33.35
SS-S	7.7 ± 0.1	0.75 ± 0.02	5.1 ± 0.2	19.9 ± 0.4	2.96
SSC-S	7.7 ± 0.1	0.73 ± 0.02	7.5 ± 0.2	22.6 ± 0.3	4.35

SS = sewage sludge; SSC = compost; SS-S = sewage sludge-soil; SSC-S = compost-soil. Tr = trace. Mean ± standard error.

Characterization of Dissolved Organic Matter  
And Humic Acids

The  $E_4/E_6$  ratio is used as a humification index (Stevenson 1982), and its magnitude is related to the degree of condensation of the aromatic carbon network (Chan *et al.* 1977). This ratio is related inversely to the degree of condensation of the aromatic network and high molecular weight hydrophobic fractions (aromatic acids or aromatic phenols). The  $E_4/E_6$  ratio of HA from SSC-S ratio (2.41) reflects a higher degree of molecular condensation than SS-S (2.61) it is due to the humification process during the composting process. In contrast, the higher  $E_4/E_6$  ratio of SS-S infers the presence of relatively large proportions of aliphatic structures.

The infrared spectrum (IR) features of the DOM of the soil ranging between  $4000\text{ cm}^{-1}$  and  $400\text{ cm}^{-1}$  (Figure 1a) can be assigned as follows (Fengel and Wegener 1984; Senesi *et al.* 1989; Almendros *et al.* 1990; Shriner *et al.* 1998): absorptions at  $3400\text{ cm}^{-1}$  (mainly H-bonded OH and NH stretch);  $2930\text{ cm}^{-1}$  (aliphatic C-H stretch);  $1650\text{ cm}^{-1}$  (amide I band, aromatic C=C vibra-

tions);  $1550\text{ cm}^{-1}$  (amide II band, aromatic C vibration);  $1460\text{ cm}^{-1}$  (CH deformation of  $\text{C-CH}_3$  and  $-\text{CH}_2-$ );  $1380\text{ cm}^{-1}$  (symmetrical stretch of  $\text{COO}^-$ );  $1230\text{ cm}^{-1}$  (C=O stretch and OH deformation of carboxyls, phenols and aromatic ethers and esters; amide III band);  $1080\text{ cm}^{-1}$  (aromatic acid esters);  $1030\text{ cm}^{-1}$  (C=O stretch of polysaccharides and possibly Si-O vibrations of silicate impurities).

The IR of SS-S exhibited a peak at  $1550\text{ cm}^{-1}$  (amide II); this band was not detected in SSC-S. There was a decrease in intensity of the peaks of polysaccharides ( $1030\text{ cm}^{-1}$ ), lignin ( $1380\text{ cm}^{-1}$ ,  $1420\text{ cm}^{-1}$ ,  $1460\text{ cm}^{-1}$ ), amide I band ( $1650\text{ cm}^{-1}$ ), aliphatic C-H ( $2930\text{ cm}^{-1}$ ) in SSC-S relative to SS-S (Figure 1b, c). These results suggest that SS-S presented a higher content of polysaccharide, amide, ether, and ester groups than SSC-S.

After obtaining the second derivative of the IR spectra of DOM of S, SS-S, and SSC-S (Figure 2), it

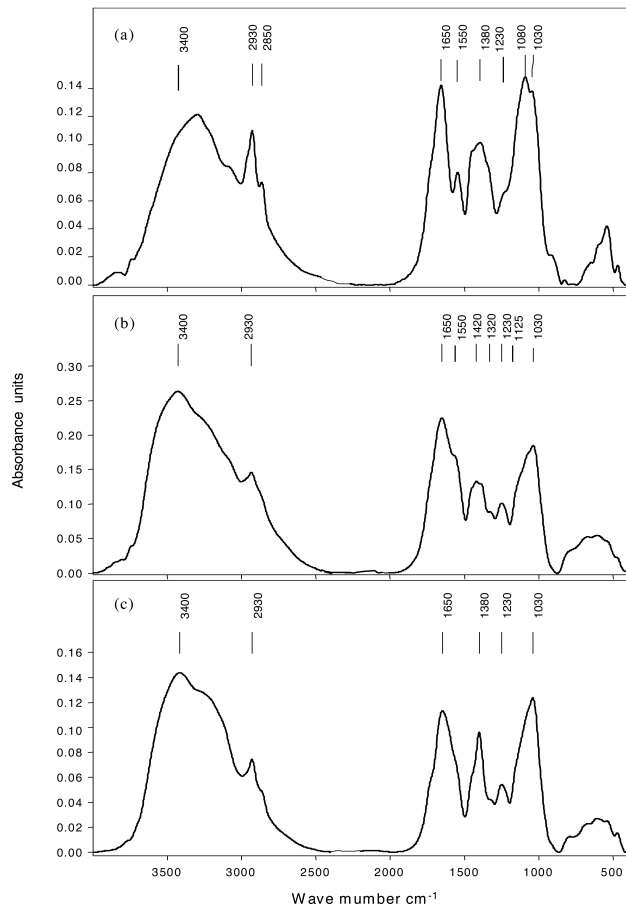


FIGURE 1. Infrared spectra of dissolved organic matter: (a) soil; (b) sewage sludge-soil mixture; (c) compost-soil mixture.

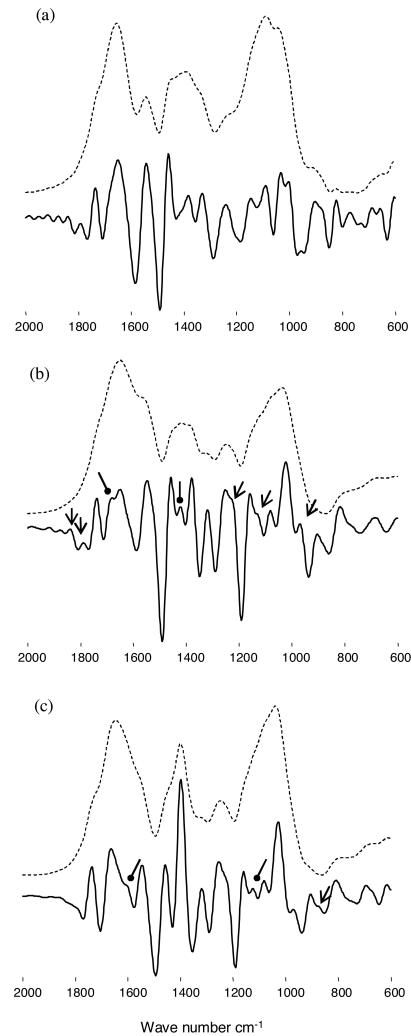


FIGURE 2. Resolution-enhanced infrared spectra (continuous line) of dissolved organic matter: (a) soil; (b) sewage sludge-soil mixture; (c) compost-soil mixture.

was observed that SS-S exhibited a greater number of different peaks than either S and SSC-S (indicated with  $\rightarrow$ ), as well as, SS-S showed different peaks respect to SSC-S (indicated with  $\rightarrow$ ). The differences between SS-S and SSC-S, mentioned previously as small shoulders in the IR, are evident in the spectra of the second derivative; and so, conditioning the soil with sewage sludge added phenolic OH groups ( $1420\text{ cm}^{-1}$ ), as well as, carboxyl and carbonyl CO ( $1720\text{ cm}^{-1}$ ). The IR spectrum of S and SSC-S did not exhibit absorbency in the  $1125\text{ cm}^{-1}$  band (aliphatic alcohols).

The IR of the HA of soil and soil mixtures (Figure 3) were typical of spectra of other humic fractions. The band at  $2600\text{--}2480\text{ cm}^{-1}$  (sulfhydryl SH group) was more conspicuous in SS-S. The IR of S and SSC-S showed a peak at  $1460\text{ cm}^{-1}$  (CH deformation of  $\text{C-CH}_3$  and  $-\text{CH}_2-$ ) not exhibited in the spectrum of SS-S. All bands in the IR of S showed the highest absorption.

Unlike DOM, SSC-S exhibited a larger number of peaks in HA corresponding to different functional

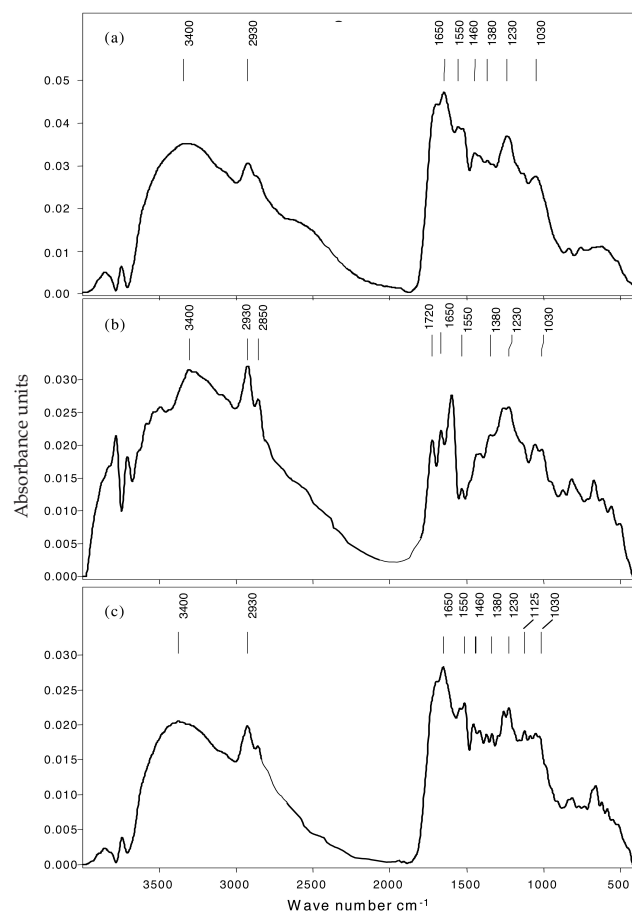


FIGURE 3. Infrared spectra of humic acids: (a) soil; (b) sewage sludge-soil mixture; (c) compost-soil mixture.

(indicated with  $\rightarrow$ ) or in both (indicated with  $\rightarrow$ ), such as esters of aromatic acids ( $1080\text{ cm}^{-1}$ ) (Figure 4).

The intensity of the DOM and HA peaks is influenced by the concentration of organic compounds and their physical properties (Stepanov 1974). The relative optical densities (ROD) calculated with respect to a fixed band allow one to compare the data of different spectra. Table 3 shows the ROD of DOM with respect to  $2930\text{ cm}^{-1}$  (aliphatic CH) and  $1550\text{ cm}^{-1}$  (aromatic CH vibration). The ROD suggests that the DOM of SSC and SSC-S presents the lowest aliphatic character (values higher than 1). The greater aliphatic character of SS (values lower than 1) reflects an aquatic origin (Jackson 1975). The ROD of HA of soil and soil mixtures showed an aliphatic character (Table 4); this behaviour decreased in the order: SS-S > SSC-S > S. The ROD of S and SSC-S with respect to  $1510\text{ cm}^{-1}$  (aromatic CH stretch) suggests an aromatic behaviour (values lower than 1); this is an indicative sign of the humification process.

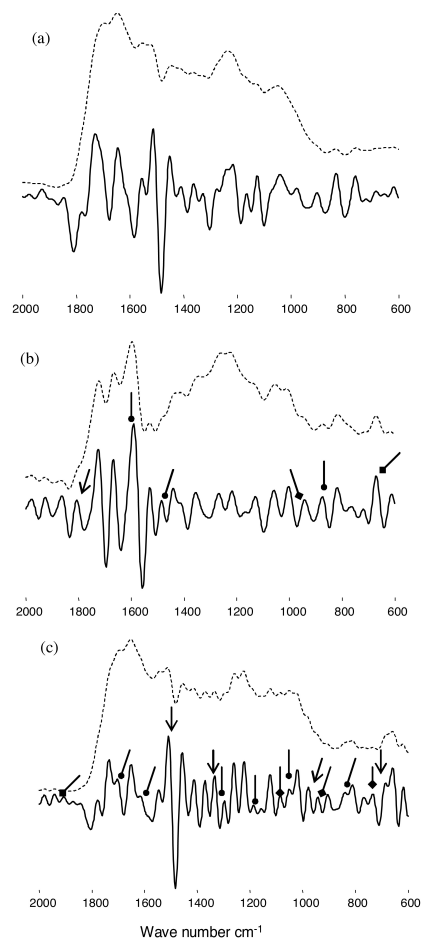


FIGURE 4. Resolution-enhanced infrared spectra (continuous line) of humic acids: (a) soil; (b) sewage sludge-soil mixture; (c) compost-soil mixture.

TABLE 3.  
Relative optical densities of dissolved organic matter of soil, sewage sludge, compost and soil mixtures respect to aliphatic and aromatic C-H

Band (cm <sup>-1</sup> )	Aliphatic C-H stretch (2930 cm <sup>-1</sup> )					Band (cm <sup>-1</sup> )	Aromatic C-H vibration (1550 cm <sup>-1</sup> )				
	Soil	SS	SSC	SS-S	SSC-S		Soil	SS	SSC	SS-S	SSC-S
1030/2930	1.22	1.02	1.91	1.26	1.65	1030/1550	1.71	1.06	1.59	1.08	*
1380/2930	0.89	0.71	1.09	0.88	1.31	1380/1550	1.24	0.74	0.91	0.76	*
1420/2930	0.09	0.75	1.00	0.91	*	1420/1550	0.12	0.78	0.83	0.78	*
1460/2930	0.84	0.70	0.83	0.84	0.80	1460/1550	1.17	0.73	0.69	0.72	*
1550/2930	0.71	0.96	1.20	1.16	*	550/1550	1.00	1.00	1.00	1.00	*
1650/2930	1.25	1.25	2.00	1.58	1.51	1650/1550	1.76	1.30	1.66	1.35	*
1720/2930	0.77	*	*	*	*	1720/1550	1.07	*	*	*	*
3400/2930	1.04	1.21	1.74	1.80	1.92	3400/1550	*	1.26	1.45	1.55	*

SS = sewage sludge; SSC = compost; SS-S = sewage sludge-soil; SSC-S = compost-soil. Values higher than 1 reflects an aliphatic character (2930 cm<sup>-1</sup>) or an aromatic character (1550 cm<sup>-1</sup>), λ not detected.

TABLE 4  
Relative optical densities of humic substances of soil and soil mixtures respect to aliphatic and aromatic C-H

Band (cm <sup>-1</sup> )	Aliphatic C-H stretch (2930 cm <sup>-1</sup> )			Band (cm <sup>-1</sup> )	Aromatic C-H vibration (1550 cm <sup>-1</sup> )		
	Soil	SS-S	SSC-S		Soil	SS-S	SSC-S
1030/2930	0.90	0.64	0.94	1030/1510	0.73	1.62	0.81
1380/2930	1.00	0.68	0.95	1380/1510	0.80	1.70	0.82
1420/2930	1.03	0.60	0.98	1420/1510	0.83	1.51	0.85
1460/2930	1.07	*	1.02	1460/1510	0.86	*	0.89
1550/2930	1.26	0.44	1.00	1550/1510	1.00	1.00	1.00
1650/2930	1.52	0.85	1.45	1650/1510	1.22	2.15	1.26
1720/2930	1.45	0.65	1.35	1720/1510	1.17	1.63	1.17
3400/2930	1.13	0.97	1.05	3400/1510	0.91	2.44	0.91

SS-S = sewage sludge-soil; SSC-S = compost-soil. Values higher than 1 reflects an aliphatic character (2930 cm<sup>-1</sup>) or an aromatic character (1550 cm<sup>-1</sup>), λ not detected.

### Metal Sorption Studies

For the study of sorption relationships, the data were fitted to the following equation:

$$C_e / x/m = 1 / kb + C_e / b \quad \text{Langmuir equation}$$

where  $C_e$  is the equilibrium concentration (mg l<sup>-1</sup>),  $x/m$  is the amount of Zn<sup>2+</sup> or Pb<sup>2+</sup> sorbed (mg kg<sup>-1</sup>) by the sample,  $b$  is the adsorption maxima, and  $k$  is the bonding energy coefficient.  $b$  and  $k$  are constants of Langmuir equation. A plot of  $C_e$  versus  $C_e / x/m$  will yield a straight line of slope  $b$  and intercept of  $k$ .

The amounts of Pb sorbed by SS and SSC were similar. However, the application of compost to soil decreased Pb sorption, and so SSC-S exhibited less sorption capacity than SS-S (Figure 5). In the case of S, when the initial concentration of Pb was low, most of the Pb was sorbed; as the initial metal concentration increased, the slope of the sorption isotherm levelled off (Figure 5), indicating that the sorbate reached its maximum sorption capacity, following a Langmuir model (Figure 6). The amount of Pb sorbed to SS and SSC increased as the initial concentration of the metal increased, following a linear model; SS-S and SSC-S

showed this behaviour in the range of 5-600 and 5-400 mg l<sup>-1</sup>, respectively (Figure 5).

Sewage sludge compost (SSC) and soil mixtures reached their maximum Zn sorption capacity at 400 mg l<sup>-1</sup> of initial concentration, whereas SS reached this capacity at 300 mg l<sup>-1</sup>, so the slope of the sorption isotherms levelled off (Figure 7). The Zn sorption capacity of SSC and SSC-S decreased in relation to SS

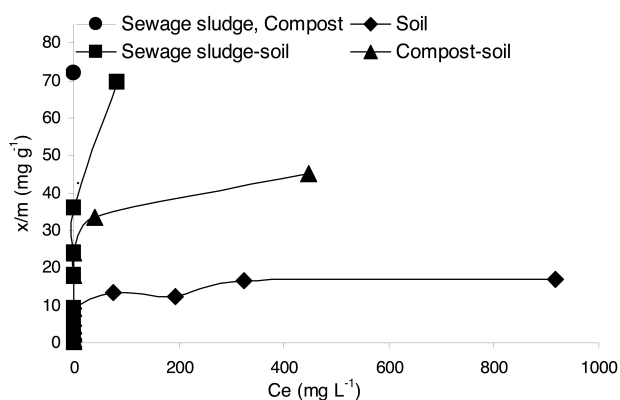


FIGURE 5. Lead sorption on single-metal system by soil, sewage sludge, compost and soil mixtures.

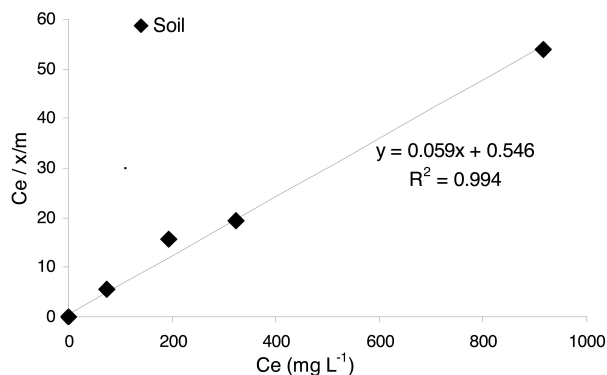


FIGURE 6. Langmuir isotherm for Pb sorption by soil.

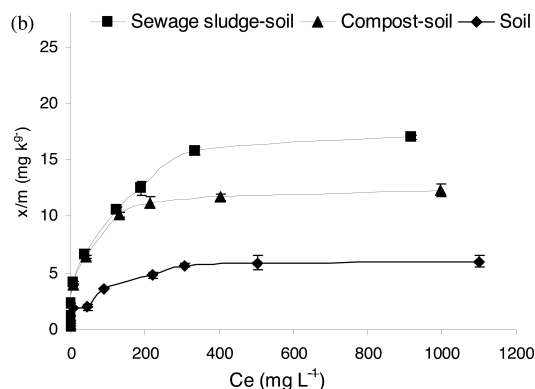
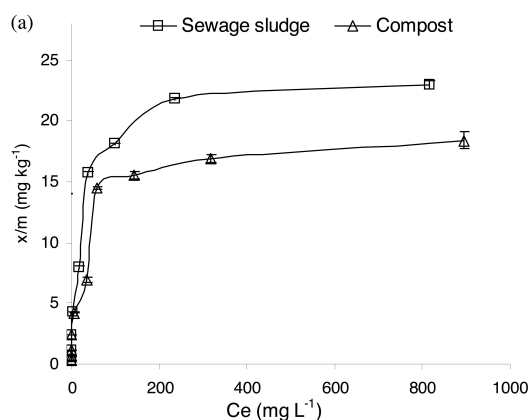


FIGURE 7. Zinc sorption on single-metal system: (a) sewage sludge and compost; (b) soil and soil mixtures.

and SS-S (Figure 7). In all cases, metal sorption followed the Langmuir model (Figure 8).

The constants calculated for Langmuir adsorption isotherm are presented in Table 5. The order of the decreasing sorption intensity constant reflects the trend of decreasing fixation of heavy metals (Jang *et al.* 1998). Significant differences were observed in the intercept and the slope by SS and SSC; thus, the compost

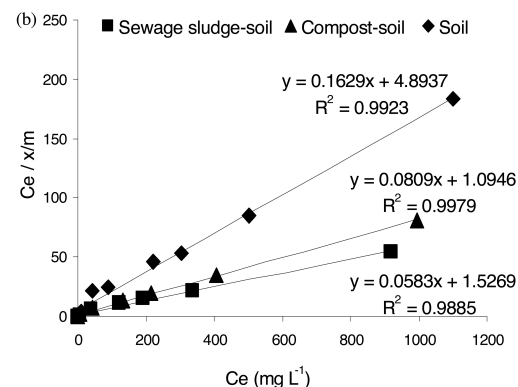
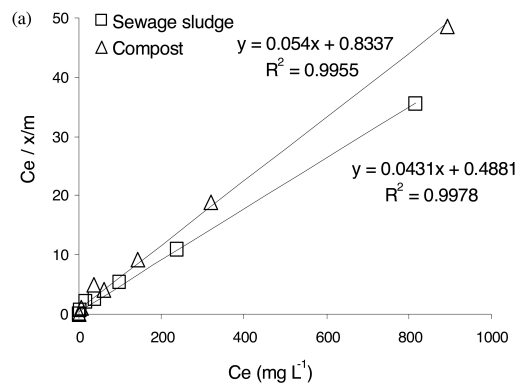


FIGURE 8. Langmuir isotherm for Zn sorption: (a) sewage sludge and compost; (b) soil and soil mixtures.

TABLE 5. Constants of Langmuir equation for Zn

	Zn		
	Langmuir equation		R <sup>2</sup>
	k (X 10 <sup>-2</sup> )	b	
Soil	3.3d	6.14 d	0.992
SS	8.8 a	23.26 a	0.998
SSC	6.5 c	18.52 b	0.996
SS-S	3.8 d	17.15 b	0.989
SSC-S	7.4 b	12.36 c	0.999

\* Numbers within a column followed by the same letter are not significantly different at the 0.05 probability level in accordance with the slopes and intercepts homogeneity test. SS = sewage sludge; SSC = compost; SS-S = sewage sludge-soil; SSC-S = compost-soil; k = bonding energy coefficient; b = adsorption maxima.

process decreased the bonding energy coefficient and adsorption maxima of SS, whereas SSC-S mixtures showed higher bonding energy coefficient and lower adsorption capacity than SS-S.

In both cases, Pb and Zn sorption was higher in soil mixtures than in S; therefore, organic matter added to soil through sewage sludge or compost allowed an increase in the soil metal sorption capacity. In all cases, when the initial concentrations of Pb and Zn were low, most of the metal was sorbed. This phenomenon is char-

acteristic of a strong affinity of the absorbent for the metal. As heavy metal concentration increased, sorption decreased; therefore, there was a limited sorption capacity for cases of Langmuir equations. The sorption capacity of the linear model for tests with soil mixtures did not reach a limit using the concentrations in this study.

Numerous researches have shown that OM is the most important factor in the control of Pb sorption for its significant impact on CEC (Strawn and Spark 2000; Agbenin and Atin 2003). When the content of DOM increases, the rate of Pb sorption decreases (Strawn and Spark 2000); however, this trend was not observed in this work because SSC-S had a lower DOM content ( $0.426 \text{ g kg}^{-1}$ ) than SS-S ( $2.324 \text{ g kg}^{-1}$ ), and therefore, both quantity and quality of OM are important aspects in the sorption phenomena.

Although SSC-S had higher OM levels than SS-S, its Pb sorption capacity was lower (Figure 5), probably due to its lower pH (Table 2). pH affects chelation and humic substance exchange properties and, therefore, the metallic ion mobility (Antoniadis and Alloway 2002). By increasing the pH, the net charge of protons, measured as the difference between proton mass and mass of complexed hydroxyl ions on the surface of functional groups, decreases toward negative values; this tendency gives way to greater electrostatic attraction of the metallic cation toward the surface of the functional groups (Agbenin y Atin 2003). As pH increases, the association of Pb with OM is stronger, and stable complexes with humic acids of high molecular weight are formed, allowing a higher sorption (Ross 1996). In polluted soils, part of the Pb is exhibited as a high-molecular-weight organo-Pb complex, and the proportion represented by this form is greater in soils of higher pH (Strawn and Sparks 2000).

Numerous investigators showed that soil solution pH has a marked influence on adsorption of metals and increases as soil solution pH increases (Cavallaro and McBride 1984; Kiekens 1990; Basta and Tabatabai 1992; Apple and Ma 2002) and that Zn adsorption is lower than Pb adsorption for acid pH (Harter 1983; Pulford 1986; Illera *et al.* 2000). This study showed a correlation between pH and  $k$  constant of Zn (Table 6).

Although Zn sorption behaviour was similar in SSC and SS, as well as in the soil mixtures, presumably

more variable negative charges and sorption sites were formed in SS or SS-S for higher pH (Table 2). The higher pH probably facilitated Zn sorption capacity of SS or SS-S in relation to SSC or SSC-S (Figure 7).

Interactions between Zn and HA are strongly affected by pH. At low pH values, most of the Zn is present in cationic form (soluble), and humate complexes are formed at increasing pH values. Soluble organic ligands from organic wastes (sewage sludge and compost) decrease metal adsorption; these ligands are either low-molecular-weight organic acids or soluble humic or fulvic acids; with increasing fulvic acid concentration in the solution, Zn adsorption decreases at low pH (Kiekens 1990; Shuman 1999). Therefore, it is probably that the low pH of SSC appears to allow the establishment of soluble complexes and chelates between low-molecular-weight organic acids and Zn, thereby decreasing metal sorption. The bonding energy coefficient of Zn was correlated with  $1420 \text{ cm}^{-1}$  (phenolic O-H),  $1650 \text{ cm}^{-1}$  (amide II), and  $1720 \text{ cm}^{-1}$  (carboxyl and carbonyl groups) (Table 6).

Potassium was correlated with the bonding-energy coefficient of Zn (Table 6). Zhu and Alva (1993) reported that K showed weaker negative correlation to sorbed concentrations of Zn than Ca or Mg. This study shows that K actually was correlated positively with sorbed concentrations of Zn.

Lead sorption was greater than Zn sorption at the same solution equilibrium concentrations, in agreement with literature reports (Basta and Tabatabai 1992). The predicted affinity sequences of metals based on their ionic potential, hydrolysis constant and softness are shown in Table 7. For the electrostatic bonding (coulombic) of metals of equal charge ( $Z$ ) on ion-exchange materials, metal affinity should be related inversely to the un-hydrated radii ( $r$ ) (Bohn *et al.* 1993). Therefore, the metal affinity sequence should be proportional to the ionic potential ( $Z^2/r$ ). If metal adsorption were entirely electrostatic, ions of higher ionic potentials should be adsorbed more strongly (Saha *et al.* 2002). The poor agreement of the observed metal affinity sequence (Pb > Zn) of the samples with those predicted by ionic potential (Table 7) shows that bonding of metals by these sorbates is not predominantly electrostatic (coulombic) in nature (Saha *et al.* 2002).

TABLE 6  
Correlation coefficients (R2 value) with Zn Langmuir adsorption isotherms constants

	pH	Mg — ( $\text{cmol kg}^{-1}$ )	K —	HA						
				DOM 1080	1380	1230	1125 ( $\text{cm}^{-1}$ )	1720	1420	1650
$k$	.9972	+	.9987	.9994	+	+	+	.9946	.9946	.9946
$b$		.9980	+	+	.9920	.9972	.9920	+	+	+

$k$  = bonding energy coefficient;  $b$  = adsorption maxima; + = correlation coefficient no significance ( $P > 0.05$ ).



TABLE 7  
Affinity sequences of divalent Zn and Pb on the basis of several metal properties

Metal Property	Metal Affinity Sequence
Ionic radius (nm) <sup>a</sup>	Zn (0.072) > Pb (0.127)
Ionic potential <sup>b</sup>	Zn (5.33) > Pb (3.39)
First hydrolysis constant <sup>c</sup>	Pb (7.8) > Zn (9.0)
Softness <sup>d</sup>	Pb (3.58) > Zn (2.34)

<sup>a</sup>Ionic radius values in parentheses, from Saha et al. (2001). <sup>b</sup>Ionic potential values in parentheses, from Huheey (1972). <sup>c</sup>Hydrolysis constant values in parentheses, from Baes and Mesmer (1976). <sup>d</sup>Softness values in parentheses, from Misono et al. (1967).

Reactions of metallic ions with water-forming, hydrolysis products (i.e., MOH<sup>+</sup>) are common to most metals. The contribution of Lewis acidity and “softness” to stability of metal complexes is responsible for the affinity sequences that are based on the first hydrolysis constants, formation of MOH<sup>+</sup> complexes (Table 7). These complexes are adsorbed more strongly than the divalent free metal cations because they are thermodynamically more stable and easier to adsorb. The metal affinity sequences observed in this study were consistent with those reported in soils (Basta and Tabatabai 1992). According to Pearson (1963), metals with loosely held electrons in outer orbitals, especially d-orbitals, exhibit high polarizability and behave as soft acids (i.e., Zn and Pb); the stability of soft acid-base complexes arise from covalent dative-*pi* bonding between loosely held d-orbitals of the metal and empty orbitals of the ligand. Since dative-*pi* bonding is related directly to the degree of metal “softness” (Pearson 1968), the softness of a metal can be used as a measure of the degree of covalent bonding in metal bonding in soils (Basta and Tabatabai 1992). The softness parameter described by Misono et al (1967) expresses the tendency of a metal to form a dative-*pi* bond (Table 7). It is suggested that the hard and soft acids and bases (HSAB) theory of Pearson (1963) could be used to describe cation selectivity in the soil system, because water is a hard base, and ion-exchange sites are softer bases than water; therefore, softer metals should replace harder metals in ion exchange sites (Basta and Tabatabai 1992). The higher adsorption of Pb in this work is in agreement with earlier work. Therefore, the HSAB model does predict the affinity sequence of results obtained in this work for Pb and Zn. Saha et al. (2002) also reported a good agreement between the observed metal affinity sequence (for Pb and Zn) and that predicted by the HSAB theory.

It appears probable that OM can be used as a major factor to explain retention differences between Pb and Zn sorption. Soil organic matter has a high surface

area and has functional groups that are Lewis bases (e.g., carboxyl and phenol groups) with which metals can form chemical bonds. It has been observed that Pb forms strong complexes with OM and that it can out-compete most metals for adsorption sites (Strawn and Sparks 2000).

## Conclusions

The nature of the functional groups can influence on the forming and characteristics of the organic compounds and contribute to the mechanisms of metal accumulation or metal transport in soils. According to  $E_4/E_6$  ratio of DOM and HA, compost and compost-soil exhibited a higher humification index, and it showed a higher Pb sorption capacity. Composting diminished the polysaccharides, amides, ethers, esters and carboxyl groups contents in sewage sludge. The addition of sewage sludge to soil increased the polysaccharides, lignins, peptides, aliphatic structures and hydroxyl groups contents in the soil organic matter.

The results of the present study indicated that the addition of sewage sludge or compost to soil increased Zn and Pb sorption. In general, metal sorption capacity for Zn was: sewage sludge > compost > sewage sludge-soil > compost-soil >> soil; but Pb sorption capacity was equal for all treatments except for compost-soil and soil, which showed the lowest sorption capacity. Low pH reduces the ability of Zn to be sorbed, whereas organic matter is the major factor to explain Pb sorption.

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