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## Effect of sewage sludge or compost on the sorption and distribution of copper and cadmium in soil

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### Abstract

The application of biosolids such as sewage sludge is a concern, because of the potential release of toxic metals after decomposition of the organic matter. The effect of application of sewage sludge (Sw) and compost (C) to the soil (S) on the Cu and Cd sorption, distribution and the quality of the dissolved organic matter (DOM) in the soil, was investigated under controlled conditions. Visible spectrophotometry, infrared spectroscopy, sorption isotherms (simple and competitive sorption systems), and sequential extraction methods were used. The  $E_4/E_6$  ( $\lambda$  at 465 and 665 nm) ratio and the infrared spectra (IR) of DOM showed an aromatic behaviour in compost–soil (C–S); in contrast sewage sludge–soil (Sw–S) showed an aliphatic behaviour. Application of either Sw or C increased the Cu sorption capacity of soil. The Cd sorption decreased only in soil with a competitive metal system. The availability of Cu was low due to its occurrence in the acid soluble fraction (F3). The Cu concentration varied in accordance with the amounts of Cu added. The highest Cd concentration was found in the exchangeable fraction (F2). The Sw and C applications did not increase the Cd availability in the soil.

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### 1. Introduction

Biosolids are a valuable source of organic matter, N and P at low cost in agricultural soils. However, one of the main concerns regarding their application to the soil is the presence of potentially toxic elements (PTE) (Ross, 1996). There are still some uncertainties about the final destination of PTE in the soil where sewage sludge is applied. For instance, metals introduced with sewage sludge can be released and become available to organisms, but the organic matter can also immobilise them. There is controversy about the changes of the me-

tal availability after the application to the soil, and about the adsorption capacity of the soil with time (Stacey et al., 2001).

Because of the recent environmental regulations in Mexico regarding of the treatment of wastewater, it is expected that the volume of sewage sludge produced from wastewater treatment will increase in upcoming years, and new alternatives for reducing the risk of pollution need to be found (SEMARNAT, 2003).

To restore metal-contaminated soil, it is commonly recommended to add organic matter, which itself may contain waste materials (Shuman, 1999). Organic materials provide a large number of non-specific and specific sorption sites for metals from which they may be difficult to displace (Shuman, 1999). In fact, some researchers have shown that the application of organic acids

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reduced the bioavailability of heavy metals in polluted soil (Gao et al., 2003). Sewage sludge is often composted prior to application to the soil, in order to reduce metal availability, to eliminate pathogens and to produce an adequate product for agriculture (Bernal et al., 1998). Composting transforms organic matter into a drier, more uniform and biologically stable product that could act as a good source of plant nutrients (Sullivan et al., 2002). Research has also shown that the composting process changes greatly the composition of the dissolved organic matter (DOM) from organic waste (Basiramakenga and Simard, 1998; Zhou and Wong, 2001). The behaviour of DOM in the soil and its effect on pollutant chemistry is of particular interest to researchers, since the DOM plays a fundamental role in immobilisation and transport of pollutants (Kaiser and Zech, 1997; Naidu and Harter, 1998). Hydrophilic and hydrophobic DOM fractions can be adsorbed by soil minerals and adsorption surfaces, but there is still a lack of information about the effect of DOM from sewage sludge and of composted sewage sludge on metal sorption to the soil. There are few studies on the changes in DOM in sewage sludge after composting.

Metal adsorption to soil after the application of organic wastes has been studied in single metal systems (Shuman, 1999; Illera et al., 2000; Zhou and Wong, 2001) on the other hand, few studies have investigated the competitive metal adsorption in terms of the quality of organic matter (OM) in soils amended with sewage sludge or composted sewage sludge, with naturally occurring metal concentrations. Moreover, the research efforts have focused on the evaluation of heavy metal mobility, partitioning and sorption in temperate soils (McBride et al., 1997; Krishnasamy and Krishnamoorthy, 1991; Schwarz et al., 1999; Walter et al., 2002). Relatively few experiments have been conducted in inter-tropical soils (Guadalix and Pardo, 1995; Appel and Ma, 2002).

Fractionation techniques using different reagents (salts, bases and in some cases, acids) are used to assess how elements change their chemical state in response to changing soil conditions, and to identify the chemical species present in the solid phase (Shuman, 1979; Chang et al., 1994). Such information is necessary to predict the environmental impact of heavy metals from anthropogenic sources, as well as to propose suitable regulatory guides for application to the soil of wastes containing heavy metals.

The objectives of this research were: (i) to study the role of organic matter from sewage sludge and composted sewage sludge in soil sorption of Cu and Cd by sorption isotherms, (ii) to describe the competitive behaviour during metal sorption in soils amended with sewage sludge and composted sewage sludge, and (iii) to determine the soil fraction in which Cu and Cd are adsorbed in a competitive metal system.

## 2. Materials and methods

### 2.1. Solid samples

The soil sample was collected from the Toluca Valley (Central México) characterized as clay loam Haplic Phaeozem (CETENAL, 1976); this is a locally important agronomic soil from Central Mexico. Samples were collected from the Ap horizon (0–20 cm).

Sewage sludge (Sw) was obtained from the urban wastewater treatment ECOSYS Company from Toluca, México. For composting, Sw was mixed with corn (*Zea mays* L.) fragments of stalks and it was allowed to ferment at 55 °C for 35 d to kill pathogens and to decompose phytotoxic substances. Sewage sludge–soil (Sw–S) and compost–soil (C–S) mixtures (200 Mg ha<sup>-1</sup> of sewage sludge or compost dry weight basis) were incubated at 29° ± 2 °C for 10 d (Dudley et al., 1987). Every second day, moisture content was restored to 100% field capacity. At the end of the incubation period, the mixtures were dried at room temperature.

All samples (soil, sewage sludge, compost and soil mixtures) were air-dried; ground in an agate mortar, homogenised and sieved to <2 mm prior to be stored in plastic bags at room temperature until analysis.

### 2.2. Chemical analysis of solids

All tests were performed at constant dry weight. 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. Cation exchange capacity (CEC) was determined using a sodium acetate method (Chapman, 1965). Total N was determined by the Kjeldahl digestion-distillation procedure (Bremner, 1996). Total carbon (TC) was determined by dividing the concentration of OM by 1.724 (Walkley and Black, 1947), and exchange cations (K, Ca, Mg, Na) were determined by ethylenediamine tetraacetic acid (EDTA) method (Jackson, 1982). Total heavy metal concentration was 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 for Cu and Cd by flame atomic absorption spectrophotometry (AAS), Perkin–Elmer mod. 3110 (Perkin–Elmer, Norwalk, CT, USA).

### 2.3. Extraction and characterization of dissolved organic matter

Infrared spectroscopy (IRS) permits qualitative identification of the atomic groups in the studied material. The use of IRS in the study of organomineral soil systems allows establishment of the occurrence, nature, and relative amounts of the main functional groups

involved in the interaction of humic substances with soil (Stepanov, 1974).

The DOM was extracted from the samples with double-distilled water using a solid-to-water ratio of 1:4 (w/v; dw) on a reciprocal shaker at 300 rpm at room temperature for 4 h. After centrifugation at 15,700g for 35 min, the supernatant solution was filtered through Whatman No. 40 paper. The filtrates were washed with distilled water until complete removal of the salts (this was tested with  $\text{AgNO}_3$ ) in the distilled water was accomplished. Then, an aliquot was analysed at 465 and 665 nm in the spectrophotometer to determine the  $E_4/E_6$  ratio (Sato and Kumada, 1967). The  $E_4/E_6$  ratio has been widely used by soil scientists for the characterization of organic materials; this ratio is related to the degree of condensation of the aromatic carbon network, carbon content, and molecular weight of humic substances (Chen et al., 1977). The dialysed solutions were dried at 40 °C. The solid residue obtained was taken as DOM.

The dried DOM samples were prepared adding 200 mg of dry anhydrous KBr to 2 mg of dry solid sample, the mixture was homogenized in an agate mortar, and analysed by Fourier transform infrared spectra (Almendros et al., 1990) using an IRS (Bruker, Tensor 27, Billerica, MA, USA).

#### 2.4. Sorption isotherms

Sorption isotherms have been used to investigate the nature of various types of sorption phenomena. They provide useful models for physical adsorption, and some

of the equations are well suited to chemisorption (Shuman, 1975).

Metal sorption experiments were carried out in batch conditions on the soil (S), Sw, C, Sw–S and C–S. Copper and Cd were added as  $\text{Cu}(\text{NO}_3)_2$  and  $\text{Cd}(\text{NO}_3)_2$  to 0.5 g dry organic waste, soil, and soil mixtures in 30 ml of 0.01 M  $\text{NaNO}_3$  as background electrolyte, and the mixtures were shaken in a water bath at  $27 \pm 1$  °C for 24 h (Shuman, 1999; Zhou and Wong, 2001; Adhikari and Singh, 2003). Copper concentrations in the solution ranged from 2 to 400  $\text{mg l}^{-1}$ , and Cd concentrations ranged from 0.5 to 24  $\text{mg l}^{-1}$ . These metal concentrations were used to ensure that the Cu and Cd sorbed by soil were below the maximum amounts allowed for the 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 (Cu–Cd). In the competitive sorption experiment, Cu ranged from 2 to 100  $\text{mg l}^{-1}$  and Cd from 1.0 to 24  $\text{mg l}^{-1}$ . For the sequential extraction, a competitive sorption process was performed, with high (100  $\text{mg l}^{-1}$  Cu and 24  $\text{mg l}^{-1}$  Cd) and low (24  $\text{mg l}^{-1}$  Cu and 6  $\text{mg l}^{-1}$  Cd) concentrations. The tubes were centrifuged at 15,700g for 25 min, and the supernatant was filtered with No. 42 Whatman paper. The solutions were analysed for Cu and Cd using AAS.

#### 2.5. Chemical fractionation procedure

The metal distribution in S, Sw–S and C–S was evaluated by using the sequential extraction developed by Tessier et al. (1979). The following fractions were

Table 1  
Maximum permitted amounts in soils and sewage sludge and concentration of Cu and Cd in soil, sewage sludge and compost

Metal	Maximum permitted ( $\text{mg kg}^{-1}$ )			Concentration measured ( $\text{mg kg}^{-1}$ )		
	Soil <sup>a</sup>	Sewage sludge <sup>b</sup>		S	SW	C
		Good	Excellent			
Cu	60–125	4300	1500	11.1	352.2	382.3
Cd	3–8	85	39	nd	31.7	nd

<sup>a</sup> Kabata-Pendias and Pendias (1992).

<sup>b</sup> (PROY-NOM-004-ECOL-2001.). S, soil; SW, sewage sludge; C, compost; nd, below detected limit.

Table 2  
Chemical properties of soil, sewage sludge, compost and soil mixtures

	pH	DOM ( $\text{mg g}^{-1}$ )	OM (%)	TC (%)	N (%)	CEC ( $\text{cmol kg}^{-1}$ )	K ( $\text{cmol kg}^{-1}$ )	Ca ( $\text{cmol kg}^{-1}$ )	Mg ( $\text{cmol kg}^{-1}$ )	Na ( $\text{cmol kg}^{-1}$ )
S	5.97	0.15	3.20	1.86	0.25	13.8	0.3	6.7	3.6	Tr
SW	6.18	4.04	65.21	37.38	6.07	42.7	0.3	16.1	6.2	0.1
C	5.48	1.34	57.50	33.35	3.08	51.9	9.9	42.7	14.5	1.0
SW–S	7.70	2.32	5.10	2.96	0.75	22.6	1.9	13.7	5.0	0.2
C–S	7.66	0.43	7.50	4.35	0.73	19.9	2.0	5.6	5.2	0.6

S, soil; SW, sewage sludge; C, compost; SW–S, sewage sludge–soil; C–S, compost–soil; Tr, trace.

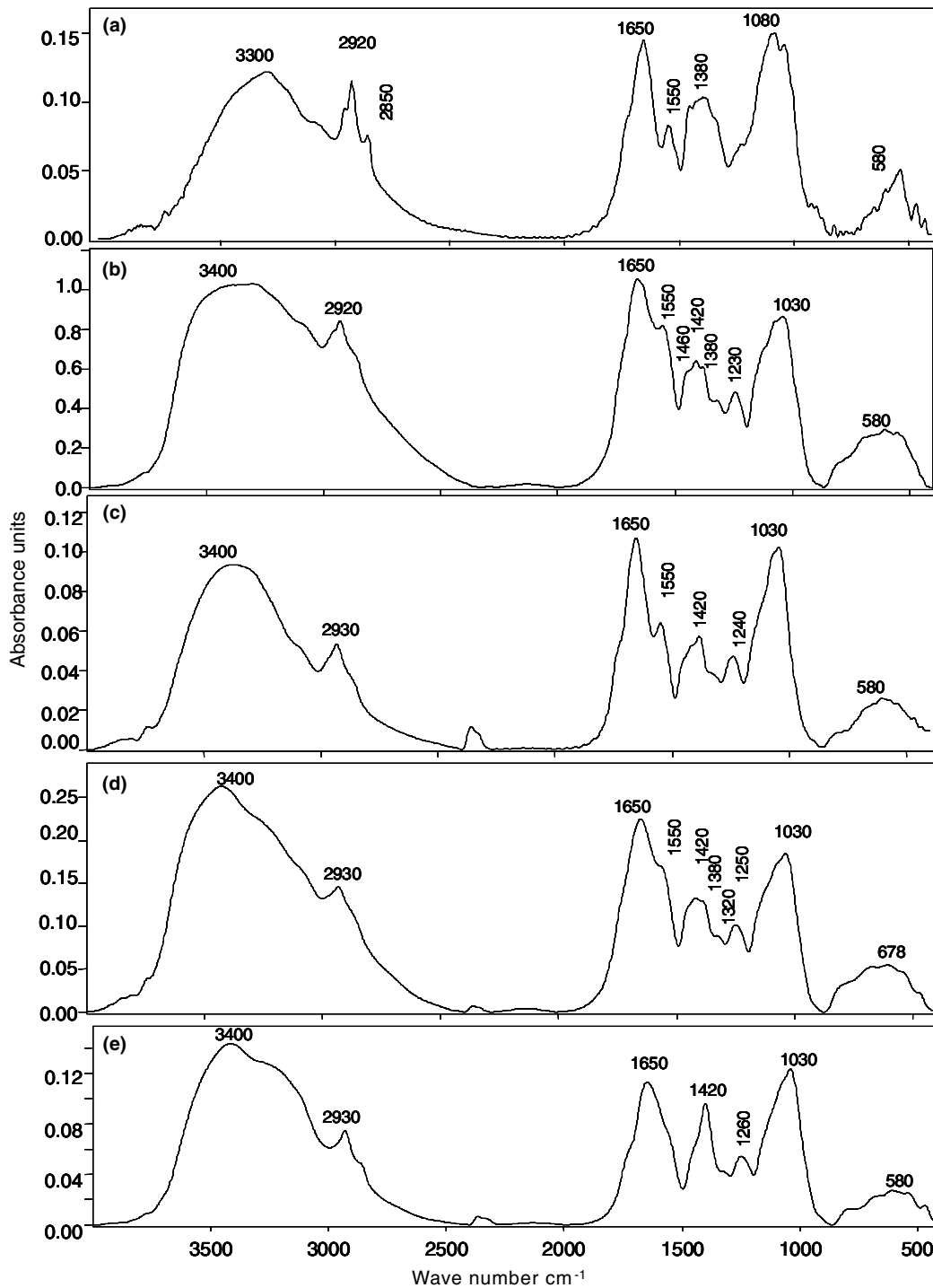


Fig. 1. Infrared spectra of dissolved organic matter: (a) soil; (b) sewage sludge; (c) compost; (d) sewage sludge–soil mixture; and (e) compost–soil mixture.

obtained: Fraction 1, water soluble (16 ml distilled water, 25 °C, 1 h); Fraction 2, exchangeable-weakly sorbed (16 ml of 1 M MgCl<sub>2</sub>, pH 7.0, 25 °C, 1 h); Fraction 3, acid soluble fraction (16 ml of 1 M NaOAc, pH 5/HOAc, 5 h); Fraction 4, strongly bound to easily reducible manganese oxides and amorphous iron oxides, and strongly sorbed to organic matter (40 ml of 1.0 M

NH<sub>2</sub>OH · HCl/HOAc 25%, pH 2, 85 °C, 5 h); Fraction 5, very strongly bound or incorporated into organic matter or other oxidizable species (6 ml of 0.02 M HNO<sub>3</sub>, +16 ml of 30% H<sub>2</sub>O<sub>2</sub>, pH 2, +10 ml of 1 M NH<sub>4</sub>OAc in 6% HNO<sub>3</sub>, 85 °C, 5 h); Fraction 6, incorporated within resistant minerals (8 ml HNO<sub>3</sub> + 2 ml HCl near boiling point, 45 min). Sequential extractions were

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 (2920 cm <sup>-1</sup> )					Band (cm <sup>-1</sup> )	Aromatic C–H vibration (1550 cm <sup>-1</sup> )				
	S	SW	C	SW–S	C–S		S	SW	C	SW–S	C–S
1030/2920	1.22	1.02	1.91	1.26	1.65	1030/1550	1.71	1.06	1.59	1.08	–
1380/2920	0.89	0.71	1.09	0.88	1.31	1380/1550	1.24	0.74	0.91	0.76	–
1420/2920	0.09	0.75	1.00	0.91	–	1420/1550	0.12	0.78	0.83	0.78	–
1460/2920	0.84	0.70	0.83	0.84	0.80	1460/1550	1.17	0.73	0.69	0.72	–
1550/2920	0.71	0.96	1.20	1.16	–	1550/1550	1.00	1.00	1.00	1.00	–
1650/2920	1.25	1.25	2.00	1.58	1.51	1650/1550	1.76	1.30	1.66	1.35	–
1720/2920	0.77	–	–	–	–	1720/1550	1.07	–	–	–	–
3400/2920	1.04	1.21	1.74	1.80	1.92	3400/1550	–	1.26	1.45	1.55	–

S, soil; SW, sewage sludge; C, compost; SW–S, sewage sludge–soil; C–S, compost–soil.

carried out on triplicate subsamples. To minimize the risk of contamination and losses through handling, successive extractions were performed in the same centrifuge tube. Suspensions were centrifuged at 15,700g for 15 min (Alva et al., 2000). Aliquots from the supernatants were removed with a pipette. Standards for both trace metals were analyzed in the same matrix as the extractant. Metal concentrations were determined by AAS.

### 2.6. Statistical analysis

Statistical analysis was performed using Statgraphics Plus ver. 5.0 software. Multiple correlations of S, SW–S and C–S were calculated with 95% probability.

## 3. Results and discussion

Selected chemical properties of S, Sw, C, SW–S, and C–S are given in Tables 1 and 2. According to the maximum permitted amounts of heavy metals in sewage sludge and biosolids for their final disposal, as reported by Mexican regulation (PROY-NOM-004-ECOL-2001.), the Sw and C employed in this experiment were classified as excellent amendments for agricultural use

(Table 1), because the Cd and Cu concentrations were lower than the maximum permitted. Compost contained less TC than Sw (Table 2); this could be due to microbial decomposition of carbon and its subsequent release as CO<sub>2</sub> (Basiramakenga 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 Sw and C to the soil increased the nitrogen percentage 3 times, and OM 3.8 times for SW–S and 5.3 times for C–S (Table 2).

### 3.1. Characterization of dissolved organic matter

The magnitude of the  $E_4/E_6$  ratio is related to the degree of condensation of the aromatic carbon network (Chen et al., 1977). The DOM from C had the lowest  $E_4/E_6$  ratio (1.95). This ratio is inversely related to the degree of condensation of the aromatic network and high molecular weight hydrophobic fractions (aromatic acids or aromatic phenols). Conversely, the highest  $E_4/E_6$  ratio of Sw (2.17) reflects a low degree of aromatic condensation (Kononova, 1966) indicating the presence of low-molecular-weight organic acids. Because the ratio can be used as a humification index (Stevenson, 1982), the low values may reflect a low degree of humification.

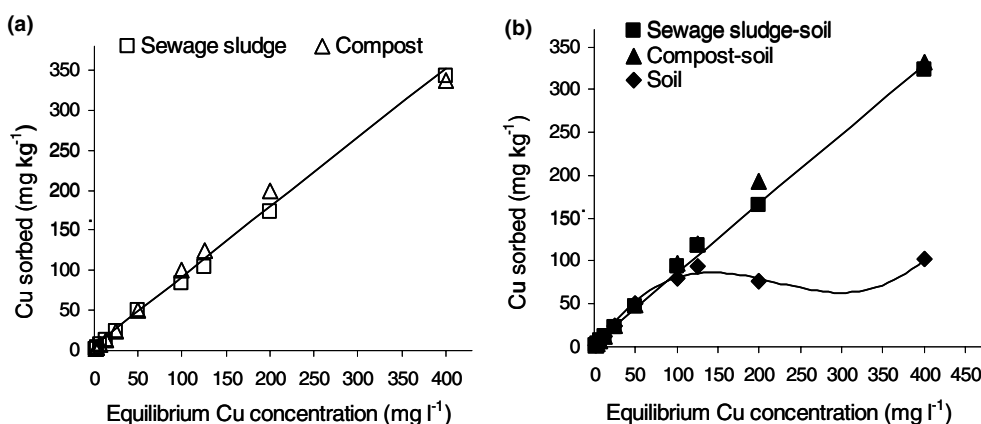


Fig. 2. Cu sorption on single-metal system by soil, sewage sludge, compost and soil mixtures.

It has been suggested that most of the DOM consists of extracellular polymers (mainly polysaccharides) released by anaerobic bacteria, and also metabolic products of their decomposition. Aliphatic acids and other simple molecules may also be present (Fletcher and Beckett, 1987). The IR of the DOM of Sw, C, C–S, and Sw–S samples were qualitatively similar to one another, although some important differences in peak intensities were observed (Fig. 1). The Sw spectrum exhibited a slightly higher intensity of the bands at  $3400\text{ cm}^{-1}$  (–OH groups of carboxyl and hydroxyl groups),  $2920\text{ cm}^{-1}$  (aliphatic C–H stretching),  $1650\text{ cm}^{-1}$  (amides I),  $1550\text{ cm}^{-1}$  (amides II), 1230 and  $1260\text{ cm}^{-1}$  (C–O stretch and O–H bending of carboxyls, phenols and aromatic ethers and esters; amides III band), and  $1080$  and  $1030\text{ cm}^{-1}$  (polysaccharides) with respect to the C spectrum. These results suggest that the Sw sample showed a higher content of polysaccharides, amides, ethers and esters groups than C, as reported by Stacey et al. (2001).

The IR of C–S showed a band at  $2900$ – $2700\text{ cm}^{-1}$  (shoulder; group hydroxy-nitrogen), which was not detected in Sw–S. The IR of Sw–S exhibited bands at  $1550\text{ cm}^{-1}$  (amide II),  $1420\text{ cm}^{-1}$  (phenolic O–H), and  $1125\text{ cm}^{-1}$  (shoulder; aliphatic alcohols), which were not detected in C–S.

After an application of Sw to the soil, Sw–S showed an increase in the intensity of the peaks of polysaccharides ( $1030\text{ cm}^{-1}$ ), lignin ( $1380$ ,  $1420$ ,  $1460\text{ cm}^{-1}$  pattern), amide II band ( $1550\text{ cm}^{-1}$ ), amide I band ( $1650\text{ cm}^{-1}$ ), and aliphatic C–H ( $2920$ – $2930\text{ cm}^{-1}$ ), with respect to S. The IR of S sample did not exhibit bands at  $3400$  and  $1125\text{ cm}^{-1}$ .

The relative optical densities (ROD) calculated for specific bands allows one to compare the data between different spectra. Table 3 shows the ROD of DOM with respect to  $2920\text{ cm}^{-1}$  (aliphatic C–H) and  $1550\text{ cm}^{-1}$  (aromatic C–H vibration). The ROD suggests that the DOM of C and C–S presents the lowest aliphatic character (values higher than 1). The greater aliphatic character of Sw (values lower than 1) probably reflects an aquatic origin (Jackson, 1975).

### 3.2. Metal sorption studies

The amount of Cu sorbed to C, Sw, Sw–S and C–S increased as the equilibrium metal concentrations increased, following a linear model (Fig. 2). In the case of S, when the initial concentration of Cu was low, most of the Cu was sorbed; as the initial concentration of the metal increased, the slope of the sorption isotherm leveled off (Fig. 2(b)), indicating that the sorbate reached its maximum sorption capacity, following a Freundlich model (Fig. 3). The Cu sorption was higher in soil mixtures; therefore, the OM added to soil through Sw and C allowed an increase in the Cu sorption capacity of S. No

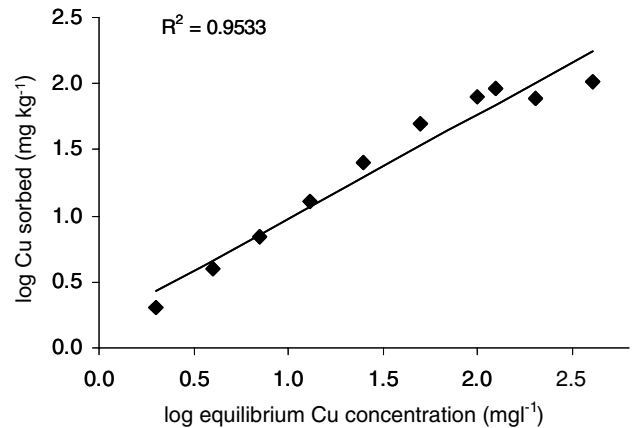


Fig. 3. Freundlich isotherm for Cu sorption by soil.

significant differences were observed in the Cu sorption by C and Sw. In all cases, when the initial concentrations of Cd and Cu were low, most of the metal was sorbed by the sorbate. This represents a strong affinity of the sorbate for the metal. The results obtained were similar to those of Jang et al. (1998). The form of the Freundlich isotherm equation used in this study was:

$$C_s = K_F C_e^{1/n}, \quad (1)$$

where  $C_s$  is the adsorbed heavy metal per unit soil ( $\text{mg kg}^{-1}$ ),  $C_e$  is the equilibrium concentration ( $\text{mg l}^{-1}$ ),  $K_F$  is the sorption coefficient and  $1/n$  is the sorption intensity.  $K_F$  and  $1/n$  are constants of Freundlich. A plot of  $\log C_s$  versus  $\log C_e$  will yield a straight line of slope  $1/n$  and intercept of  $\log K_F$ .

The calculated constants for either the Freundlich adsorption isotherm and the linear model are presented in Table 4.

The trends of Cu sorption, indicated by the slope of the curves, in C and Sw were very similar whereas in C–S this sorption intensity was higher than Sw–S (Table 4). The explanation of this behaviour could be due to the

Table 4  
Constants of Freundlich equation and linear model for Cu

	Cu					
	Freundlich equation			Linear model		
	$K_F$	$1/n$	$R^2$	$K_D$	$a$	$R^2$
S	6.17	0.790	0.953			
SW	*			0.85 <sup>a</sup>	3.31 <sup>a</sup>	0.998
C	*			0.87 <sup>a</sup>	6.13 <sup>a</sup>	0.992
SW–S	*			0.81 <sup>b</sup>	4.57 <sup>a</sup>	0.997
C–S	*			0.85 <sup>a</sup>	5.57 <sup>a</sup>	0.993

† 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.

\* Cu sorption obeys the linear isotherm model. S, soil; SW, sewage sludge; C, compost; SW–S, sewage sludge–soil; C–S, compost–soil;  $K_D$ , slope; a, intercept.

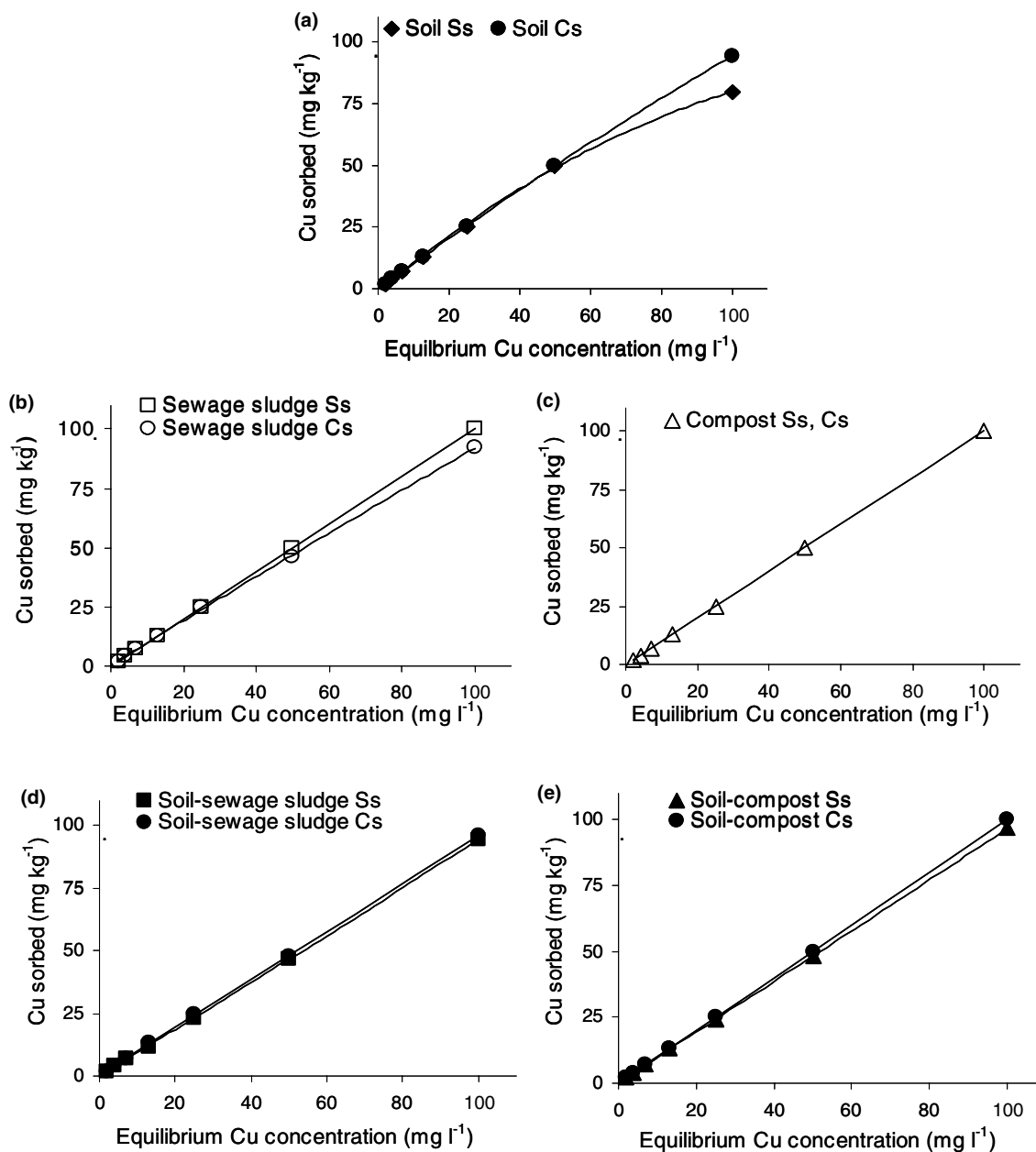


Fig. 4. Cu sorption on single metal system (Ss) and competitive metal sorption (Cs) by soil, sewage sludge, compost and soil mixtures.

high content and stability of the OM in C-S (Table 2). The Cu could interact, forming stable complexes with high or low molecular weight organic substances (Naidu et al., 1997; Calace et al., 2001). Sewage sludge showed the highest DOM concentration (Table 2). This condition has probably decreased the Cu sorption capacity for Sw or Sw-S. The DOM derived from C had a smaller effect in reducing the Cu sorption capacity of soil than that from Sw (Zhou and Wong, 2001). This effect could be due to the fact that C contained a relatively greater amount of high-molecular-weight hydrophobic fractions (aromatic acids or aromatic phenols), visualized by the magnitude of  $E_4/E_6$  ratio, which allows the formation of a Cu-DOM soluble complexes. The  $E_4/E_6$

ratio was important for the Cu sorption ( $r = -0.997$ ). The greatest values of this ratio suggest a low degree of molecular complexity and are in general associated with a high content in oxygen-containing functional groups (Chen et al., 1977), which could be reflected in the formation of high solubility adducts and therefore a lower binding energy of Cu. The sorption intensity of Cu was correlated with the intensity of the polysaccharide band ( $1080\text{ cm}^{-1}$ ) ( $r = -0.985$ ).

All samples exhibited a high Cd sorption capacity following a linear model ( $r^2 = 1.0$ ). In fact, the soil surface is dominated by permanent negative charge and therefore has the capacity to sorb relatively large amounts of metal ion. Another factor that influences Cd sorption

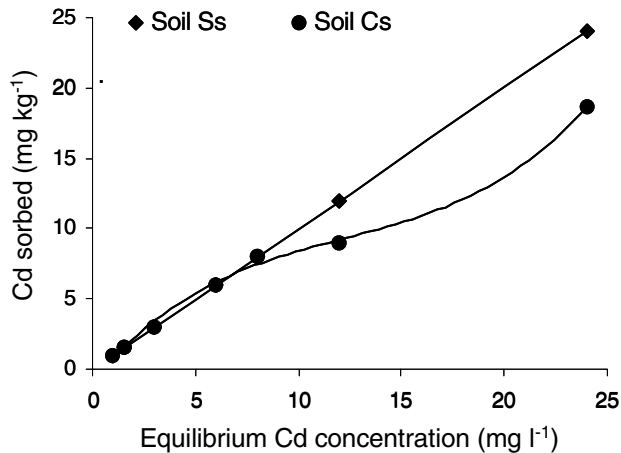


Fig. 5. Cd sorption on single metal system (Ss) and competitive metal sorption (Cs) by soil.

Table 5  
Affinity sequences of divalent Cu and Cd on the basis of several metal properties

Metal property	Metal affinity sequence
Ionic radius (nm) <sup>a</sup>	Cu (0.074) > Cd (0.075)
Ionic potential <sup>b</sup>	Cu (5.48) > Cd (4.21)
First hydrolysis constant <sup>c</sup>	Cu (8.0) > Cd (10.1)
Softness <sup>d</sup>	Cd (3.04) > Cu (2.89)

<sup>a</sup> Ionic radius values in parentheses, from Sposito (1989).

<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).

was the pH. It is known that soils with a pH between 6 and 7 have the capacity to sorb large amounts of Cd (Naidu et al., 1997), which is the pH range measured in this experiment (Table 2).

The Cu sorption behaviour in single metal and competitive metal sorption systems was very similar, in the range from 2 to 100 mg l<sup>-1</sup>. Copper sorption in a competitive metal sorption system was not affected by the presence of Cd (Fig. 4); on the contrary, Cd sorption

by soil was affected by the Cu, which reduced Cd sorption by soil components (Fig. 5). The sorption affinity of Cu was greater than that of Cd. This affinity could be related to some metal properties discussed below. The predicted affinity sequences of metals based on their ionic potential, hydrolysis constant, and softness are shown in Table 5. For electrostatic adsorption of metals with equal charge ( $Z$ ) on ion-exchange materials, metal affinity should be inversely related to un-hydrated radii ( $r$ ). If the metal adsorption nature were entirely electrostatic, ions of higher ionic potential ( $Z^2/r$ ) should be adsorbed more strongly (Saha et al., 2002). It is believed that the ionic potential predicts the metal affinity of Cu and Cd for soil in the present study. A softness parameter that numerically expresses the tendency of a metal to form covalent bonds has been proposed (Misono et al., 1967). This parameter is presented in Table 5. The sorption affinity of Cu showed that the softness parameter did not predict the metal affinity observed in the present study. There are discrepancies in the literature about the application of the softness concept, particularly in relation to the trace metal cations (Saha et al., 2002). Different affinity sequences could occur due to the influence of several factors, including type of adsorbate and experimental conditions. Agreement between the affinity sequence obtained in this study and hydrolysis constants for Cu and Cd (Table 5) suggests that adsorption of  $\text{CuOH}^+$  could explain the high affinity of this metal for soil.

### 3.3. Sequential extraction

Organic matter plays an important role in Cu sorption; in particular humic substances have a large effect on its retention (Flores et al., 1997; Zemberyová et al., 1988). However, substantial amounts of Cu were not in the organic matter fraction. A significant amount of Cu was associated in tightly bonded forms (F6), presumably corresponding to copper held to minerals lattices or sorbed to the clays (Fig. 6). This behaviour has also been reported by others (Gibson and Farmer, 1986; Lena and

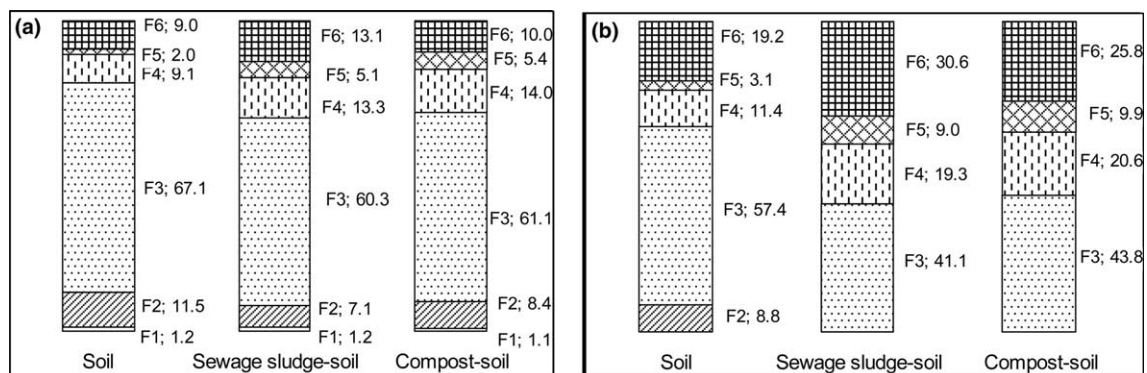


Fig. 6. Percentage of Cu in soil, sewage sludge-soil and compost-soil fractions: (a) high Cu concentration added; (b) low Cu concentration added.



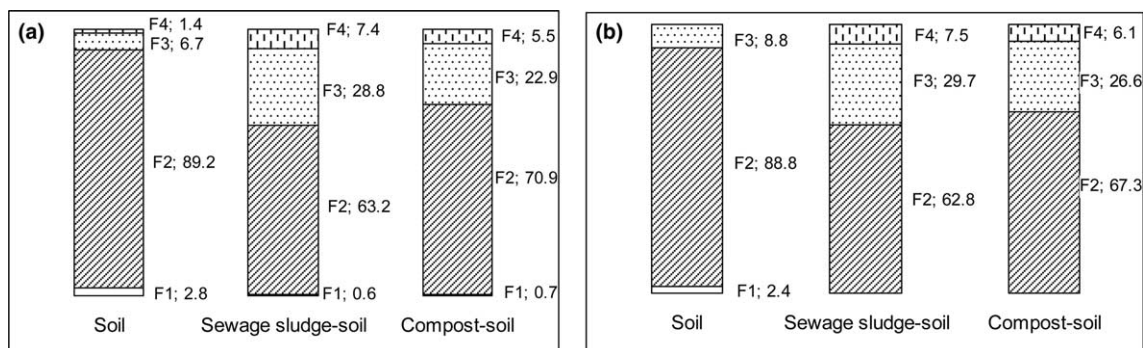


Fig. 7. Percentage of Cd in soil, sewage sludge–soil and compost–soil fractions: (a) high Cd concentration added; (b) low Cd concentration added.

Gade, 1997), who concluded that more than 75% of total metal was associated to lattices of primary minerals, Fe–Mn oxides, organic matter, and sulphides (Miller et al., 1986), so the formation of Cu-organic adducts is not necessarily high in all cases.

In either high or low Cu concentrations, a low level of Cu in soil was present in an exchangeable form (F2) and associated with organic matter (F5), suggesting extremely low levels of Cu availability. Application of sewage sludge and compost to soil decreased Cu sorbed on fraction F2. The distribution pattern of Cu changed according to the concentration used. For instance, with the application of high Cu levels ( $100 \text{ mg l}^{-1}$ ), the percentage sorbed to F3 was higher whereas that sorbed to F5 and F6 was lower than that sorbed with the application of low levels ( $24 \text{ mg l}^{-1}$ ) (Fig. 6).

The F2 was by far the most important fraction of Cd in the soil and soil mixtures, suggesting a high bioavailability (Fig. 7). Cadmium can be retained by precipitation and adsorption reactions; precipitation appears to be the predominant process in the presence of anions such as  $\text{S}^{2-}$ ,  $\text{CO}_3^{2-}$ , and  $\text{PO}_4^{3-}$ . In this study, Cd was found only in three fractions, F2, F3 and F4 (Fig. 7), in agreement with the findings of Gibson and Farmer (1986). A previous report indicated that Cd concentration must be above  $50 \text{ mg kg}^{-1}$  in order to be present in all fractions (Lena and Gade, 1997). Some authors mention that exchangeable forms of Cd increase significantly under sludge application (Kabata-Pendias and Pendias, 1992); however this tendency was not observed in the present study because the percentage of Cd in F2 decreased with the application of sewage sludge and compost, increasing the Cd sorbed on F3 (Fig. 7). Similar Cd distributions were found among the different fractions, from high or low concentration added to soil or soil mixtures (Fig. 7). Copper has been shown to have a greater affinity for F3 than Cd, whereas Cd has a greater affinity for F2 than Cu. Oxides of Fe–Mn (F4), organic matter (F5) and residual (F6) fractions showed a preferential sorption of Cu over Cd regardless of the heavy metal levels. These affinities would be related to the softness concept, which is derived from the hard-soft

acid base (HSAB) theory of Pearson (1968), where hard acids tend to associate with hard bases and soft acids with soft bases. Water is a hard base; therefore ion-exchange sites can be considered as softer bases than water. Likewise Cd is a softer acid than Cu (Ross, 1996), and therefore Cd (a soft acid) is associated primarily to F2.

#### 4. Conclusions

The structural characteristics of the DOM with special emphasis in the molecular size and related concentration of functional groups can contribute to the mechanisms of metal accumulation or metal transport in the soil under study. In agreement with the  $E_4/E_6$  ratio of DOM, compost and compost–soil exhibited a higher humification index, and it showed a higher Cu sorption capacity and intensity. The concentration of Cu is an important factor for its distribution in the various fractions of soil, but this behaviour is not as clear for Cd. The results of the present study indicated that addition of sewage sludge or compost to soil increased sorption of Cu and Cd, suggesting that the bioavailability of Cd added to soils as a contaminant, or as biosolids fertilizer did not increase under these conditions, but that it can be modified by the pH.

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