Adsorption of cadmium and copper in representative soils of Eastern Amazonia, Brazil

Adsorção de cádmio e cobre em solos representativos da Amazônia Oriental, Brasil

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Abstract

Studies of heavy metals adsorption in soil play a key role in predicting environmental susceptibility to contamination by toxic elements. The objective of this study was to evaluate cadmium (Cd) and copper (Cu) adsorption in surface and subsurface soil. Samples of six soils: Xanthic Hapludox (XH1 and XH2), Typic Hapludox (TH), Typic Rhodudalf (TR), Typic Fluvaquent (TF), and Amazonian dark earths (ADE) from Eastern Amazonian, Brazil. The soils were selected for chemical, physical and mineralogical characterization and to determine the adsorption by Langmuir and Freundlich isotherms. All soils characterized as kaolinitic, and among them, XH1 and XH2 showed the lowest fertility. The Langmuir and Freundlich isotherms revealed a higher Cu (H curve) than Cd (L curve) adsorption. Parameters of Langmuir and Freundlich isotherms indicate that soils TR, TF and ADE has the greatest capacity and affinity for metal adsorption. Correlation between the curve adsorption parameters and the soil attributes indicates that the pH, CEC, OM and MnO variables had the best influence on metal retention. The Langmuir and Freundlich isotherms satisfactorily described Cu and Cd soil adsorption, where TR, TF and ADE has a lower vulnerability to metal input to the environment. Besides the pH, CEC and OM the MnO had a significant effect on Cu and Cd adsorption in Amazon soils.
Key words: Amazonian dark earths. Environmental management. Heavy metals. Isotherm. Soil pollution.

Resumo

Estudos de adsorção de metais pesados no solo desempenham um papel chave em prever a susceptibilidade à contaminação do ambiente por elementos tóxicos. O objetivo foi avaliar a adsorção de cádmio (Cd) e cobre (Cu) na superfície e subsuperfície de seis solos Amazônicos: Latossolo Amarelo (XH1 e XH2), Latossolo Vermelho (TH), Nitossolo Vermelho (TR), Gleissolo Háplico (TF) e Latossolo Amarelo – Terra Preta de Índio (ADE) da Amazônia Oriental. Os solos foram selecionados para caracterização química, física, mineralógica e determinação da capacidade máxima de adsorção pelas isotermas de Langmuir e Freundlich. Todos os solos foram caracterizados como cauliníticos, e entre eles, XH1 e XH2 apresentaram menor fertilidade. As isotermas de Langmuir e Freundlich revelaram adsorção superior

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de Cu (curva H) em relação ao Cd (L curva). Os parâmetros de Langmuir e Freundlich indicam que os solos TR, TF e ADE tem a maior capacidade e afinidade para adsorção de metais. A correlação entre os parâmetros da curva de adsorção e os atributos do solo indica que o PH, capacidade de troca de cátion (CTC), matéria orgânica (MO) e óxido de manganês (MnO) tiveram influência sobre a retenção dos metais. As isotermas de Langmuir e Freundlich descreveram satisfatoriamente a adsorção de Cu e Cd no solo, onde TR, TF e ADE tem uma menor vulnerabilidade à entrada de metais para o meio ambiente. Além do pH, CTC e MO, o MnO teve um efeito significativo na adsorção de Cu e Cd em solos amazônicos.

Palavras-chave: Isoterma. Manejo ambiental. Metais pesados. Poluição do solo. Terra preta do índio.

Introduction

The Amazon region is the last agricultural frontier and mineral province in Brazil, but most croplands in this region are acidic and have low capacity cation exchange, these attributes contribute to the naturally low fertility of these areas (SILVA et al., 2013), which leads to exposure of their environments to various materials of pollution potential. In this regard, the entry of heavy metals in the soil can occur with the use of fertilizers, liming material, manure, sewage sludge and industrial emissions (SPARKS, 2002), as well as residues of the mining activities (CASSELLA et al., 2006).

The study of adsorption of metals in the soil is an important evaluation tool of the polluting potential of these elements (DÈRE et al., 2006). To describe the metal adsorption forms in the soil, physico-chemistry models are utilized, and several equations are proposed to fit the equilibrium solution data (MOREIRA; ALLEONI, 2010). Among these models are the Langmuir and Freundlich curves, which are simple and provide consistent information about the prediction of soil pollution (ABAT et al., 2012).

In samples of tropical soils, Alleoni et al. (2005) reported that the Langmuir curve fitted well the adsorption of Cu and Cd in Oxisols and Ultisols with different degrees of weathering from Brazilian southeast. In the same region using Langmuir and Freundlich approaches, high coefficients of determination of equations to Cd and Pb in Oxisols and highly weathered Ultisols were observed (LINHARES et al., 2009). The correlation of

chemical, physical and mineralogical attributes with adsorption parameters demonstrates that metal adsorption equations assists in the identification of factors that greatly influence the movement and bioavailability of toxic elements in the soil (HUANG et al., 2014).

Several authors have reported that the soil attributes that are more representative in heavy metals adsorption are the pH, organic matter (OM), cation exchange capacity (CEC) and Fe and Al oxides (BRADL, 2004; VIOLANTE et al., 2010; CERQUEIRA et al., 2011a). Whereas that there is a significant influence of CEC and OM on Cu adsorption (ABAT et al., 2012) and of pH on Cd adsorption (GRAY et al., 1998). In addition to these attributes is MnO, which even at low concentrations in the soil has high reactivity for adsorbing many heavy metals (KÄMPF et al., 2009; BRAZ et al., 2013a, 2013b). Although, several studies converge on the soil chemical properties as the most influential in the adsorption of metals in different regions around the world (ARIAS et al., 2005; CERQUEIRA et al., 2011b), there are few publications with Amazonian soils (BRAZ et al., 2013a).

Total concentrations of Cu above normal highlighting environmental risk have been observed in surrounding soil to a pilot project (Salobo project) of mineral extraction in Carajás – Amazon southeast (CASSELLA et al., 2006). Similarly, soils contaminated with Cd both the mineral activity (MAGALHÃES et al., 2011) and by agriculture (GONÇALVES JÚNIOR et al., 2014) have received extensive attention from environmental agencies in other regions. The existence of very different soil

types in the Amazon region requires more studies evaluating its contrasting differences in chemical and physical attributes, such as high clay content (> 900 g kg^{-1}), rate weathering and influence of oxides (titanium, manganese and silicon) on pollutant retention.

The objective was to evaluate Cu and Cd adsorption and the correlation of the Langmuir and Freundlich equation parameters with contrasting chemical, physical and mineralogical attributes of Amazon soils.

Materials and Methods

Surface (0 – 0.2 m) and subsurface (0.8 – 1.0 m) samples were collected in six regions of the state of Pará in the areas of primary and secondary forest for more than 20 years (SINGH; STEINNES, 1994). To perform soil sampling, a Dutch auger manufactured in stainless steel and plastic basins was used to avoid possible sample contamination (CETESB, 2001). The collection areas were recorded with the GPS (eTrex 30, Garmin, USA). For each area of approximately 20 hectare with similar characteristics in color, soil texture, topography, drainage and vegetation cover, three composite samples were collected at both depths from 10 single samples, as suggested by Embrapa (2009). The following soil classes belong to the sampled areas: Xanthic Hapludox – XH1 (11º 41' 10'' S 48º 132' 24'' W), Xanthic Hapludox – XH2 (21º 59' 45'' S 47º 121' 10'' W), Typic Hapludox – TH (60 00' 03'' S 49º 00' 55'' W), Typic Rhodudalf –TR (31º 17' 41'' S 52º 134' 13'' W), Typic Fluvaquent –TF (1º 27' 54'' S 48º 26' 10'') and Amazonian Dark Earths – ADE (01º 45' 12'' S 48º 131' 00'' W).

The samples were air dried and sieved through a polyethylene mesh opening with a 2.0 mm diameter for the chemical, physical and mineralogical analyses. The pH was determined potentiometrically using a soil:water ratio of 1:2.5. The exchangeable content of calcium (Ca) and magnesium (Mg) extracted with a 1 M solution of potassium chloride (KCl). The content exchangeable Ca and Mg were quantified using atomic absorption spectrophotometry. Potassium (K) extracted using a Mehlich 1 (0.05 M HCl + 0.0125 M H$_2$SO$_4$) solution; the K content was then determined using flame photometry (EMBRAPA, 2011). Using these results, the values of the CEC were calculated. The organic carbon content was determined using the Walkley-Black method, which oxidizes the organic matter in a moist environment with potassium dichromate and then quantifies the organic matter by titration with 0.1 M ammonium iron sulfate (NELSON; SOMMERS, 1982) and the result converted into OM using the factor 1.724 (EMBRAPA, 2011). The particle size was determined using the densitometer method as described by Gee and Or (2002).

The contents of oxides (expressed Al$_2$O$_3$, Fe$_2$O$_3$, TiO$_2$, and MnO) were extracted using a 9 M H$_2$SO$_4$ solution, whereas Si, expressed as SiO$_2$, was extracted using a 1 M NaOH solution (EMBRAPA, 2011). The Fe, Mn and Al contents were determined using atomic absorption spectrophotometry (AAS); those of Ti were determined using colorimetry, and those of Si were determined using gravimetry. The levels of SiO$_2$, Fe$_2$O$_3$, Al$_2$O$_3$, MnO and TiO$_2$, as well as the Ki and Kr weathering index, were measured according to the molar relation method that were described by the Brazilian Agricultural Research Corporation (EMBRAPA, 2011).

For interpretation of soil chemical properties were used the values originally proposed by Alvarez Venegas et al. (1999) and adapted by Moreira and Fageria (2009) for the state of Amazonas soils, to sort the attributes in five quantitative categories: very low, low, medium, high and very high.

For the curves of Cd and Cu adsorption, 2 g of ADFE (air-dried fine earth) in triplicate was added to 20 mL of 0.0025 M CaCl$_2$ solution (supporting electrolyte) containing concentrations of Cd (0.0; 3.99; 7.8; 19; 37.5; 67.3; 101.1; and 120.0 mg/L) and Cu concentrations (0.0; 5.0; 10.0; 18.7; 38.4; 86.6; 135.4; and 171.8 mg/L). The suspensions were

stirred for 24 h, centrifuged for 3 min at 3040 r/min and filtered through qualitative paper. In the extracts, the Cd and Cu concentrations were determined by atomic absorption spectrophotometry.

The concentrations of Cd and Cu as adsorbed to the soil were calculated according to the following expression: $C_{ads} = (C_0 - C_{eq})$ DF, where C_{ads} is the amount of the metal that is retained in the solid phase, C_0 is the concentration of heavy metals in solution after shaking, and DF is the dilution factor, which considers the solution:soil ratio according to equation (1):

$$DF = \frac{20 \, ml \, of \, Solution}{2 \, gADFE} \quad (1)$$

The Langmuir and Freundlich equations were applied to fit the data from the isotherm studies, equations (2) and (3):

$$qe = \frac{K_L q_m C_e}{1} + K_L C_e \quad (2)$$

$$qe = K_F C_e^{\frac{1}{n}} \quad (3)$$

where q_e is the amount of adsorbed metal concentration at equilibrium (mg kg^{-1}); C_e is the concentration of the metal in solution at equilibrium (mg L^{-1}); q_m is the maximum adsorption amount of metal onto the soil (mg kg^{-1}); K_L (L kg^{-1}) is the affinity constant for the Langmuir isotherm; K_F (L kg^{-1}) is the adsorption coefficient; and n is a dimensionless parameter that is related to the slope of the curve and that indicates the affinity of the solute in the ground by the Freundlich isotherm.

The maximum adsorption capacity and affinity for Cu and Cd among different soils were submitted to analysis of variance and when significant the F test compared by Tukey test at 5% probability. In addition, we carried out a Pearson correlation analysis between the soil properties and the parameters of the adsorption curves.

Results and Discussion

The soils presented a very low or low pH (MOREIRA; FAGERIA, 2009) (Table 1). In surficial layer, cation exchange capacity (CEC) of TR and both depths of Typic Fluvaquent (TF) were classified as very high, whereas in other soils, values range from very low to high. The organic matter (OM) was very high in all samples regardless of the depth, according to Moreira and Fageria (2009). Soils presented large textural variation (Table 1). The surface layer ranged from 128 (XH1) – 729 g kg^{-1} (XH2) and was characterized as clayey to very clayey, respectively. The subsurface layer ranged from sandy clay loam (189 g kg^{-1}) in ADE to very clayey (931 g kg^{-1}) in XH2. The TF presented a silt-clay-loam texture with a predominance of silt. The Ki values indicate the degree of alteration of the soils, demonstrating weathering by the proportion between kaolinite and gibbsite, whereas Kr indicates the degree of alteration of minerals in soils by the ratio of Fe to Al.

Amazonian soils those are naturally acidic, mainly due to the rapid mineralization of organic matter (SILVA JUNIOR et al., 2012). Very high CEC observed in TF are due to the large sediment deposition, typical in this type of soil (ABREU et al., 2007). Higher concentration of organic matter on the surface related to the addition of biomass of plant cover of sampling sites and the accelerated process of decomposition of this material. The TR, TH and XH2 samples showed the largest levels of oxides, especially TR, with very superior quantities of TiO_2 and MnO. This latter mineral, although found in small amounts in soils, has a significant influence on soil reactivity, and among the metals, the Cu^{2+} is the second most absorbed by manganese oxides (KÄMPF et al., 2009).

Table 1. Chemistry, granulometry and mineralogy attributes of Amazonian soils.

Soil[a]	Depth	pH H$_2$O	CEC	OM	Clay	Silt	Sand	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	TiO$_2$	MnO	Ki	Kr
			mmol$_c$ dm^{-3}					g kg^{-1}						
XH1	Surf.	3.8	16.3	22.6	128	120	752	32	42.3	91.0	42.6	0.08	1.29	1.13
	Sub.	4.1	8.8	11.5	202	141	657	68	85.0	13.7	67.9	0.09	1.36	1.23
XH2	Surf.	4.4	21.9	27.3	729	195	76	247	284.7	35.3	125.5	0.24	1.47	1.37
	Sub.	4.5	9.1	11.2	931	41	28	268	313.3	40.8	123.6	0.15	1.45	1.34
ADE	Surf.	4.8	55.9	28.5	139	79	782	45	47.7	25.8	29.9	0.27	1.60	1.19
	Sub.	4.9	27.9	11.8	189	70	741	59	66.4	32.6	46.4	0.23	1.51	1.15
TH	Surf.	4.4	25.2	28.5	642	62	296	146	185.9	172.7	127.4	0.29	1.34	0.84
	Sub.	4.4	3.0	12.7	747	18	235	166	207.1	202.0	132.5	0.27	1.36	0.84
TR	Surf.	5.1	72.4	19.8	539	177	284	156	143.4	139.0	388.2	3.46	1.85	1.14
	Sub.	4.9	45.8	9.3	737	96	167	198	191.2	152.3	280.6	2.19	1.76	1.17
TF	Surf.	3.9	88.2	25.1	301	679	20	119	71.7	30.1	42.6	0.44	2.82	2.22
	Sub.	4.3	97.6	9.9	299	654	47	177	95.6	50.3	57.1	1.26	3.15	2.35

Surf. – Surface; Sub. – Subsurface; [a] USDA Soil Taxonomy (Soil Survey Staff, 1999); XH1 and XH2 – Xanthic Hapuludox; TH – Typic Hapludox, TR – Typic Rhodudalf, TF – Typic Fluvaquent and Amazonian Dark Earths – ADE.

All of the soils were kaolinitic (Ki and Kr > 0.75) (IBGE, 2007). In the samples of XH1, XH2 and TH, the values of Ki were lower and accompanied by high Kr values, indicating the oxidic and weathering state of the samples, which was confirmed by the poor fertility of soils (BRAZ et al., 2013a), which may result in a lower adsorption of pollutant metals. In contrast, the greatest value of Ki and the fertility to TF were observed, demonstrating less-intense weathering, which is justified because this soil is formed from the deposition of sediments due to flooding (ABREU et al., 2007).

Values of metal adsorption fitted well with the Langmuir and Freundlich models (Figures 1 and 2), as evidenced by satisfactory correlation coefficients (Table 2). The metal adsorption increased with the increasing rates of addition (PETRUZZELLI et al., 1985; ROSS, 1994), where the Cu^{2+} was more adsorbed than Cd^{2+} considering the individual adsorption system. The surface layer adsorption was larger than that of the subsurface, as evidenced by higher levels of OM, CEC and pH attributes.

For Cu^{2+} in all soils and Cd^{2+} in the surficial samples of TR, the isotherms were of H type (High), according the classification proposed by Giles et al. (1974), which refers to a convex shape. The isotherm H type assigned to a high-affinity metal-adsorbent surface. Another factor is that the high Cu adsorption in the low equilibrium solution concentrations followed by an adsorption attenuation in major concentrations indicates the probability that the adsorption process of this metal has two steps that can linked to the occupation of different sites (MOREIRA; ALLEONI, 2010). For Cd^{2+}, in most of the soils, the isotherms were of L type (Langmuir), which characterizes the minor energy of adsorption as expressed by the low slope of the curves due to the decreased adsorption sites when the adsorbent surface coverage increases.

Figure 1. Adsorption isotherms of Cu and Cd in Xanthic Hapludox 1 (A, B); Xanthic Hapludox 2 (C, D) and Amazonian Dark Earths (E, F).
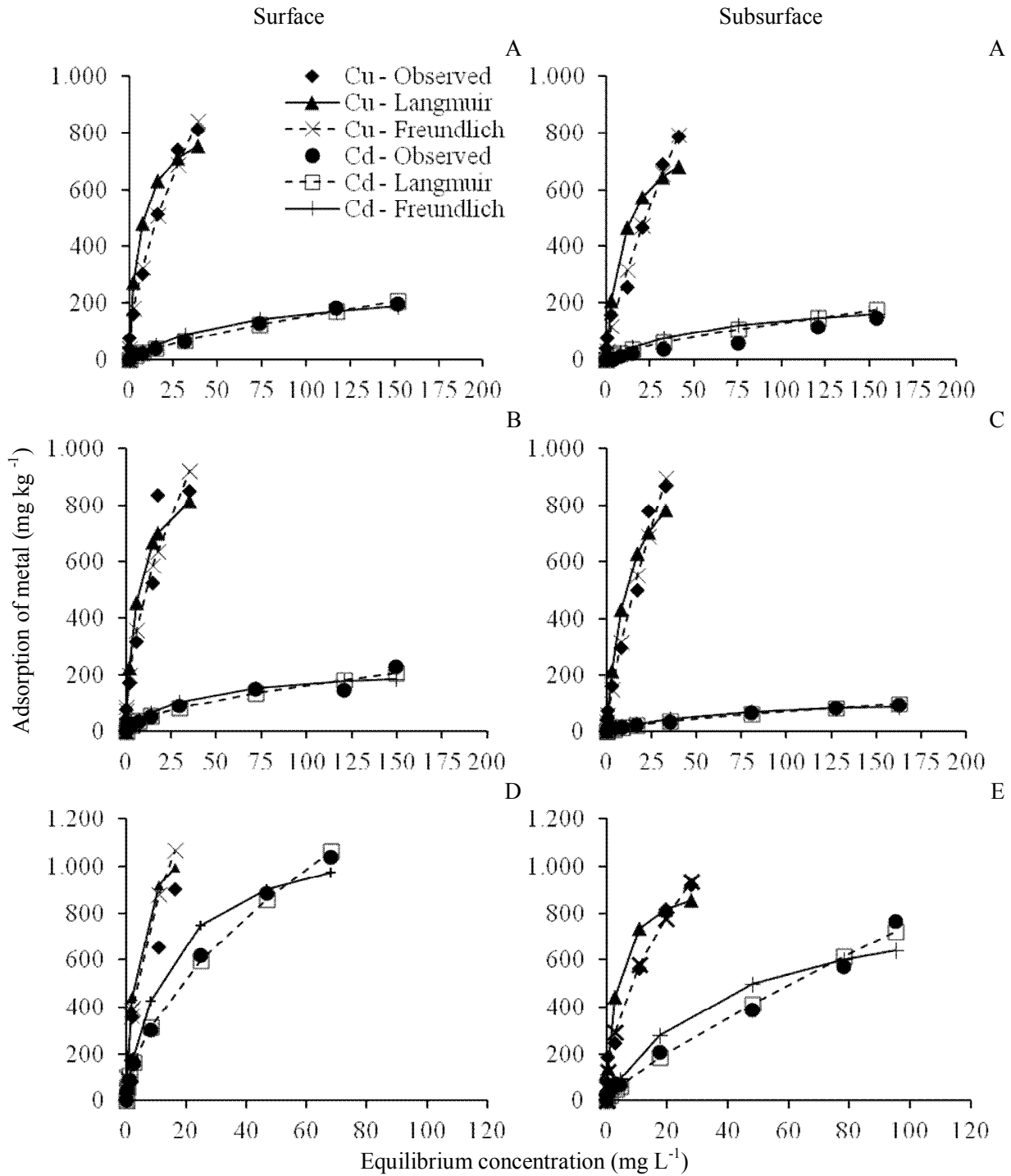
Figure 2. Adsorption isotherms of Cu and Cd in Typic Hapludox (A, B); Typic Rhodudalf (C, D) and Typic Fluvaquent (E, F).
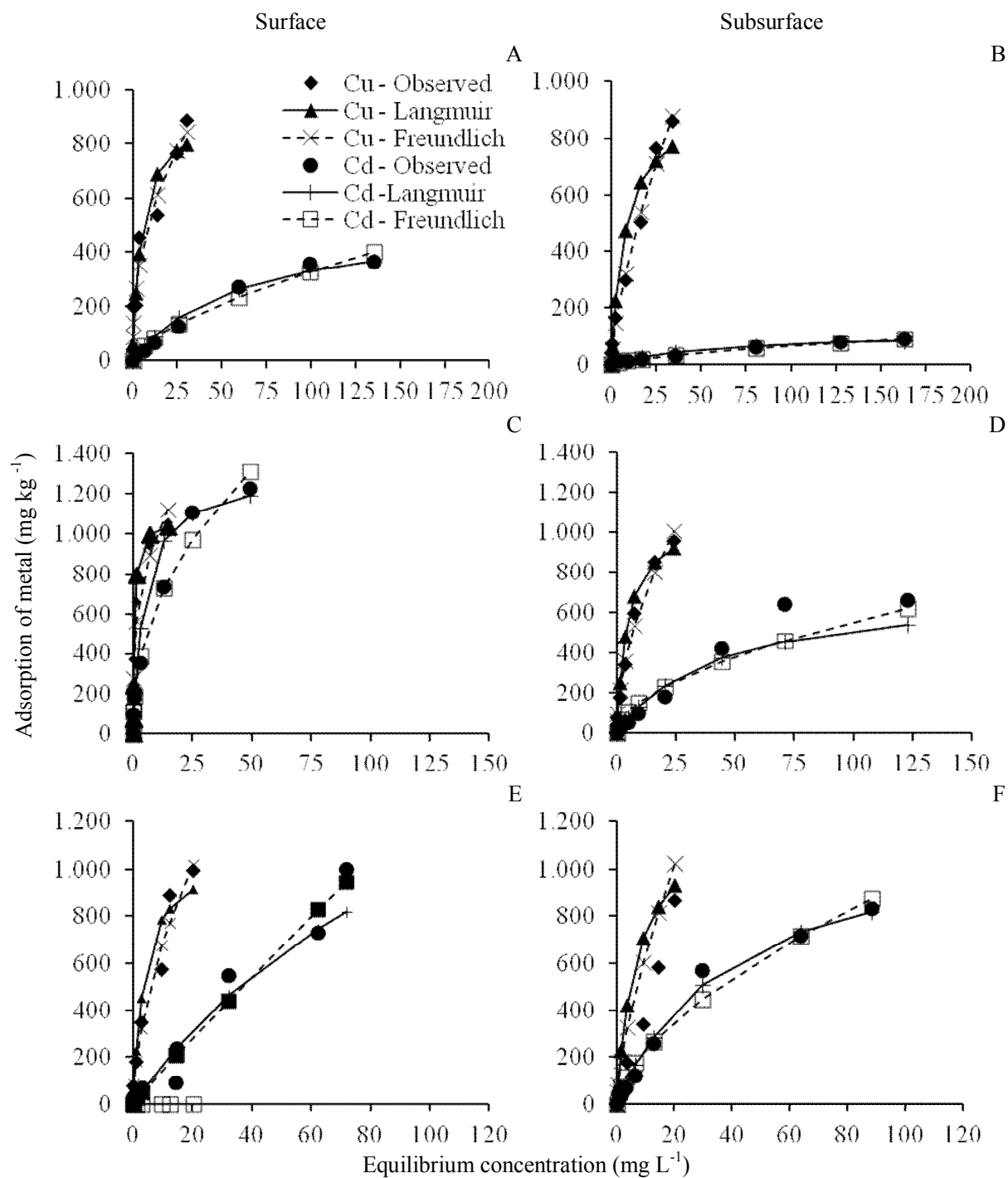
The low adsorption of Cd^{2+} in the Amazon soils, excepting TR surface, indicates that a great migration of this metal through the soil profile may occur when Cd^{2+} is added to the environment. The Cd^{2+} migration was observed by Dère et al. (2006) in irrigated sand Luvisol in North-West Paris. Soils with the greater adsorption of Cu^{2+} and Cd^{2+} in the Langmuir and Freundlich models were TF, ADE and TR, highlighting the TF in Langmuir equation at both depths and the TR in the Freundlich equation in surficial layer. TR and ADE showed elevated pH and CEC compared to those of the other soils (Table 1), which can contribute to the greater adsorption of metallic cations. The increase in the dependent charges in the soil promotes the competitive decrease of H^+ in complexation sites of organic matter favoring metal adsorption (ALLOWAY, 1995).

Table 2. Adsorption parameters of Cu and Cd curves in the soils of eastern Amazonia.

Soil[a]	Depth	Langmuir										
		Cu						Cd				
		qm		K_L		R²		qm		K_L		R²
XH1	Surface	825.1	f	0.17	def	0.89	*	268.7	e	0.015	de	0.99 **
	Subsurface	864.2	ef	0.11	ef	0.92	**	274.7	e	0.013	e	0.96 **
XH2	Surface	964.1	d	0.15	def	0.89	*	231.4	e	0.027	cd	0.93 **
	Subsurface	1064.8	c	0.08	f	0.95	**	120.2	e	0.015	de	0.96 **
ADE	Surface	1165.5	b	0.33	ab	0.91	*	1180.3	b	0.069	b	0.92 **
	Subsurface	933.4	de	0.38	b	0.90	*	822.9	c	0.034	c	0.96 **
TH	Surface	919.1	de	0.23	cdef	0.91	*	544.8	d	0.015	de	0.98 **
	Subsurface	947.1	d	0.13	def	0.96	**	115.6	e	0.015	de	0.98 **
TR	Surface	1072.5	c	1.82	a	0.82	*	1283.6	b	0.246	a	0.95 **
	Subsurface	1076.4	c	0.23	bcde	0.90	*	724.6	c	0.025	cde	0.93 **
TF	Surface	1106.5	bc	0.26	bcd	0.92	**	1505.9	a	0.018	de	0.99 **
	Subsurface	1260.1	a	0.14	def	0.95	**	1190.1	b	0.024	cde	0.96 **
		Freundlich										
		Cu						Cd				
		K_F		n		R²		K_F		n		R²
XH1	Surface	107.2	def	0.58	bc	0.97	**	6.12	fg	0.701	abc	0.96 **
	Subsurface	55.2	f	0.75	a	0.99	**	5.21	g	0.697	bc	0.99 **
XH2	Surface	138.1	cde	0.54	cd	0.96	**	11.34	fg	0.681	bcd	0.97 **
	Subsurface	69.7	ef	0.73	a	0.99	**	2.89	b	0.579	de	0.99 **
ADE	Surface	291.9	b	0.45	d	0.95	**	93.49	b	0.576	de	0.98 **
	Subsurface	200.3	c	0.46	d	0.97	**	26.77	e	0.724	a	0.99 **
TH	Surface	142.2	cde	0.53	cd	0.95	**	15.84	f	0.658	bcde	0.99 **
	Subsurface	80.2	ef	0.68	ab	0.99	**	2.71	b	0.703	abc	0.99 **
TR	Surface	458.6	a	0.30	e	0.92	**	243.11	a	0.431	f	0.85 **
	Subsurface	177.9	cd	0.53	cd	0.97	**	44.88	d	0.547	e	0.97 **
TF	Surface	199.6	c	0.54	cd	0.97	**	29.29	e	0.809	a	0.99 **
	Subsurface	138.1	cde	0.63	abc	0.98	**	56.40	c	0.610	cde	0.98 **

qm (mg kg⁻¹); [a]USDA Soil Taxonomy (Soil Survey Staff, 1999); XH1 and XH2 – Xanthic Hapludox; TH – Typic Hapludox, TR – Typic Rhodudalf, TF – Typic Fluvaquent and Amazonian Dark Earths – ADE.

Similar to maximum adsorption, the constants K_L of Langmuir and n of Freundlich showed a greater affinity in TR, ADE and TF to the studied metals to the detriment of XH1, XH2 and TF. The n parameter, in turn, is interpreted in the reverse way of K_L, in that a greater n means a smaller affinity of adsorbent to the adsorbate. This low retention of metal of Amazon Oxisols concerns the agricultural sector because these soils constitute 41% of total areas of this region. Langmuir maximum adsorption and the Freundlich Kf parameter of Cu ranged from 825 to 1260 mg kg^{-1} and from 55.3 to 458.6 mg kg^{-1}, respectively. These same variables of Cd ranged from 115.6 to 1506 and 2.7 to 243.1, respectively (Table 2). The results are similar to the values that were reported by Alleoni et al. (2005) in five Oxisols, two Alfisols and one Ultisol in relation to the Cu^{2+} in Southeast Brazil and, in this same region and similar to that observed by Linhares et al. (2009), to the Cd^{2+} in four Oxisols and one highly weathered Ultisol.

Linear correlation coefficients between the soil properties and the parameters of the adsorption isotherms (Table 3) indicate that the pH, OM, CEC, MnO, Ki and Kr are mainly responsible for the maximum adsorption of and Cd^{2+}. The Cu^{2+} adsorption was 58 times higher in limed soils than in non-limed soils in Malaysia (ABAT et al., 2012). This fact was related to the CEC elevation in soils that received lime, mainly to CEC-dependent pH (organic matter), which increases the negative charge to metal adsorption. The Cd^{2+} adsorption is significantly influenced by pH, fact that overcomes even mineralogical properties: while at higher pH values, it increases the amount of high-affinity sites that are occupied by the metal in the adsorption-specific mechanism (GRAY et al., 1998). The bond of Cd^{2+} and metal oxides also depends on the pH determining the adsorption to be specific, non-specific and electrostatic mechanisms (ALLEONI et al., 2005).

Table 3. Correlation coefficient between the soil attributes and parameters of adsorption isotherms Langmuir and Freundlich for copper (Cu) and cadmium (Cd).

Soil attributes	Langmuir				Freundlich			
	Cu		Cd		Cu		Cd	
	qm	K_L	qm	K_L	K_F	n	K_F	n
pH $_{H2O}$	0.41	0.38	0.54	-0.61	0,65 *	0.38	0,69 *	-0.68 *
CEC	0.91 **	0.19	0.32	-0.34	0.17	0.22	0.18	-0.18
OM	0.83 *	0.31	0.58	-0.54	0.94 **	0.33	0.50	-0.34
Clay	0.07	-0.02	-0.12	0.12	-0.42	-0.02	-0.09	-0.10
Silt	0.51	-0.05	0.06	0.02	0.44	-0.04	0.09	0.07
Sand	-0.52	0.06	0.07	-0.12	-0.08	0.05	0.02	0.04
SiO$_2$	0.35	-0.06	-0.11	0.13	-0.24	-0.02	-0.04	-0.19
Al$_2$O$_3$	0.02	-0.12	-0.23	0.23	-0.54	-0.09	-0.18	-0.09
Fe$_2$O$_3$	-0.01	0.27	0.19	-0.19	-0.07	0.21	0.20	-0.13
TiO$_2$	0.09	0.12	0.23	-0.55	0.13	0.39	0.45	-0.33
MnO	0.39	0.80 *	0.77 *	-0.70 *	0.51	0.78 *	0.83 *	-0.72 *
Ki	0.79 *	0.05	0.20	-0.12	0.74 *	0.07	0.23	-0.06
Kr	0.68 *	-0.15	-0.02	0.09	0.56	-0.12	0.02	0.06

CEC – Cation exchange capacity; OM – Organic matter; qm (mg kg^{-1}); ** and *, significant at 1 and 5%, respectively.

Entisols and Alfisols are 6.0% and 0.4% of Amazon soils, respectively. Entisols have high natural fertility, due mainly to sediments that are deposited on riverbanks during successive cycles of flooding (ABREU et al., 2007). A significant proportion of the rural population of the Amazonia (riverine) occupy these areas, which despite its high potential for adsorption of metals, these soils are at high risk for environmental pollution because the Amazonian cities still dump the majority of their waste in rivers. The Alfisols, in turn, have a small representation, although their high fertility supports important grazing areas in eastern Amazonia.

The correlation coefficient of the present study (Table 3) corroborate those that were obtained by Arias et al. (2005), who observed a positive correlation between the pH and the maximum adsorption and affinity coefficients of Cu^{2+} in 27 acid soils from Spain. According to Bradl (2004), the pH is the most important soil attribute that influences metal adsorption. These authors observed that a sediment compound of iron and aluminum oxide adsorbed 50% of the Cu^{2+} at pH 4.1 and the increasing of pH tends to promote the maximum adsorption of Cu^{2+} faster than Zn^{2+} and Cd^{2+}. In relation to organic matter, its positive correlation with adsorption parameters of Cu is a function of the strong binding between the elements with humic substances (STEVENSON, 1994). While the correlation between soil constant of affinity to Cu^{2+} and MnO is due to the role of this oxide as primary sink of heavy metals in its inner layers region that have high reactivity (VIOLANTE et al., 2010).

Soil attributes with significant coefficients to maximum adsorption and affinity of Cd was MnO in the Langmuir isotherm and pH and MnO in the Freundlich isotherm (Table 3). In highly weathered tropical Oxisols and Ultisols from southeastern Brazil, there was the highest correlation of pH with the maximum adsorption and binding energy of Cd (LINHARES et al., 2009, 2010), as well as a Humic Umbrisol, an Umbric Cambisol, an Endoleptic

Luvisol and an Humic Cambisol from Spain (CERQUEIRA et al., 2011a). According to Bradl (2004), the soil ability to adsorb Cd can increase three-fold with an increase of one unit in pH; this parameter significantly influences the mobility of Cd in the soil, and at low values of this attribute, high metal leaching can occur (ALLOWAY, 1995; ADRIANO, 2001).

Conclusions

The Langmuir and Freundlich isotherms adequately described the Cu and Cd adsorption in soils. The surface layer of soil adsorbed more than the subsurface due to the higher content of organic matter. The Cu showed a greater maximum adsorption and affinity to the soils than Cd due to the high influence of pH and CEC on its retention. The Typic Rhodudalf, Typic Fluvaquent and Amazonian Dark Earths, due to their higher values of pH, CEC, OM and prominently MnO, adsorbed more heavy metals than the Xanthic Hapludox and Typic Hapludox according to the parameters qm and K_L of Langmuir and K_F of Freundlich.

Acknowledgments

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