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Cadmium sorption and extractability in tropical soils with variable charge

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Abstract The availability of cadmium (Cd) for plants and its impact in the environment depends on Cd sorption in soil colloids. The study of Cd sorption in soil and its fractionation is an interesting tool for the evaluation of Cd affinity with soil pools. The objective with this study was to evaluate Cd sorption and desorption in tropical soils with variable charge (three Oxisols), in a Mollisol and in two Entisols with diverse physical, chemical, and mineralogical attributes. We used a thermodynamic approach to evaluate Cd sorption and performed a chemical fractionation of Cd in the six soils. Data from Cd sorption fit the Langmuir model ($r >$ 0.94), and the sorption capacity ranged from 0.33 to 11.5 mmol kg^{-1}. The Gibbs standard free energy was positively correlated to Cd sorption capacity ($r = 0.74$, except for the Quartzipsamments), and it was more favorable in soils with great sorption capacity. Distribution of Cd among fractions was not affected (t test, $\alpha =$ 0.05) by initial concentration, and there was a predominance of Cd extractable in 0.1 mol L^{-1} $CaCl_2$.

Keywords Cd availability · Cd sorption in soil · Cd extractability · Sorption affinity · Soil pollution · Soil contamination

Introduction

The interaction between soil and cadmium (Cd) is dependent on chemical, physical, and mineralogical attributes of the soil. The evaluation of the reactivity and mobility of Cd in soils is important for environmental studies as well as food safety. Cadmium is highly toxic, has no beneficial biological function, and can contaminate the environment and food (Kabata-Pendias 2011). It is used mainly in batteries (86%) and pigments (9%) (Adriano 2001; Alloway 1995; Devesa and Vélez 2016; Tolcin 2015). Cadmium mining produced 22,000 t in 2013, with 200 t produced in Brazil (Tolcin 2015). The background concentration in soil is typically ≤ 9 μmol kg^{-1}, and anthropogenic activities may increase this concentration to up to 89 μmol kg^{-1} (Adriano 2001). The Brazilian environmental agency established the following investigation values at the most restrictive limits applicable to inorganic substances: 27 μmol kg^{-1} for agricultural soils, 71 μmol kg^{-1} for residential soils, and 178 μmol kg^{-1} for industrial soils (Brazilian National Environmental Concil 2009).

Sorption experiments are often employed to assess quantitatively the affinity of Cd with soil in environmental studies (He et al. 2005b). These results are evaluated based mainly on isotherms such as the mathematical models of Langmuir and Freundlich (Sen Gupta and Bhattacharyya 2014). The equilibrium constants derived from isotherms have been used for calculations of changes in Gibbs free energy (ΔG^0), and a unity conversion is required for appropriate use of isotherm data. The ΔG^0 indicates the degree of spontaneity

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of the sorption process, and a higher negative value reflects a more energetically favorable sorption process (Liu 2009; Milonjic 2007; Tran et al. 2016).

The extension and spontaneity of the sorption process of a metal in the soil depends on the soil type, the chemical species, the contact time, and the environmental conditions. The highly weathered soils from humid tropical region have a predominance of functional groups in organic matter and in the surfaces of Fe and Al hydroxides with pH-dependent charges (He et al. 2005a; Loganathan et al. 2012; Naidu et al. 1997). As the amount and origin of the negative charges differ from the less weathered soils, the interaction of Cd with soil colloids and its release or stabilization may vary.

The amount of metal sorbed that is released in selective extractors is used to distinguish sorption stability, providing information regarding availability and environmental risk. Although there is a limitation in providing information of original species since the extraction may produce artifacts (Bacon and Davidson 2008; Rapin et al. 1986; Tipping et al. 1985; Wallmann et al. 1993), chemical fractionation is sensitive, direct and widely used for comparing extractability and metal pools. Many procedures, extractants, and target pools have been developed for soil fractionation (Table 1). In soils from temperate regions, 2:1 minerals prevail in the clay fraction; conversely, there are greater amounts of 1:1 minerals (e.g., kaolinite) and Fe, Al, and Mn hydroxides in soils from humid tropical regions. Therefore, the chemical reactivity of metals with soil surfaces differs. The main difference in the procedures is that carbonate is not expected to be a significant pool in humid tropical soils due to soil acidity. Besides that, the separation of oxides may be infeasible, due to low concentrations of metals in those pools, so those fractions are often grouped.

The evaluation of the fractionation after adsorption allows the assessment of parameters such as mobility and distribution of the metals in soil fractions. Although similar studies have been described previously (Garrido et al. 2001), there has been no report concerning the application of this technique in tropical soils with predominance of pH-variable charges.

The aim of the authors in this study was to investigate Cd sorption followed by desorption in Brazilian variable charge soils evaluated through isotherms, thermodynamic evaluation, and chemical fractionation. The set of six soil samples included three Oxisols that are highly weathered, abundant in humid tropical regions, and the predominant soil class in Brazil (around 60% of the total area).

Material and methods

Soil samples

The set of Brazilian soil samples was compound by three Oxisols — Anionic Acrudox (Acrudox), Rhodic Hapludox (R. Hapludox), and Typic Hapludox (T. Hapludox); a Mollisol — Typic Argiudoll (Argiudoll); and two Entisols — Mollic Epiaquent (Epiaquent) and Typic Quartzipsamment (Quartzipsamment) (USDA 1999) (Table 2). Epiaquent, Argiudoll, and Quartzipsamment present mineralogical and parent material characteristics different from those of Oxisols and were selected to compare the adsorption and desorption of Cd under diverse soil conditions. Once these soil samples were characterized previously, the methods for characterization were summarized in this section. For further detail, refer to Colzato et al. (2017).

Soil samples were collected from 0 to 20 cm under the forest surface or with minimal anthropic intervention, except by Acrudux, that was collected in the Bw horizon (80 to 100 cm). Organic carbon (C_{org} in g kg^{-1}) was determined by titration of dichromate remaining after oxidation of organic matter (Nelson and Sommers 1996). Point of zero salt effect (PZSE) was obtained as the intersection of pH titration curves taken at three ionic strengths of KCl (Sparks 1995). The pH in 1 mol L^{-1} KCl (pH_{KCl}) and pH in water (pH_{water}) was measured with glass electrode with a soil/solution ratio of 1:2.5. Percentages of sand and silt were measured by the hydrometer method and clay by the pipette method (Gee and Bauder 2002). Cationic and anionic exchange capacities (CEC and AEC, mmol$_c$ kg^{-1}) were obtained by compulsory exchange of Mg^{2+} and Cl^- with Ba^{2+} at constant electrical conductivity (Gillman 1979). Aluminum and iron contents (g kg^{-1}) were extracted with 9 mol L^{-1} sulfuric acid, sodium dithionite citrate and bicarbonate (DCB), and pH 3 ammonium oxalate (oxalate) (Camargo et al. 2009). Silicon contents (g kg^{-1}) were extracted with 1 mol L^{-1} NaOH and gravimetry (Camargo et al. 2009). The weathering index (Ki) was calculated as $(\%SiO_2/60)/(\%Al_2O_3/102)$ (Embrapa 1997) (Table 2).

X-ray diffraction analysis (XRD) was performed on the clay fraction using a Rigaku Miniflex II Desktop X-

Table 1 Selected procedures for chemical fractionation of metal in soil for 1 g sample. Note the lack of standardization between pools and extractants

Reference	Accessed pools	Extractants
Silveira et al. (2006)	Soluble and exchangeable	15 mL 0.1 mol L^{-1} $CaCl_2$
	Sorbed in surfaces, hydroxides and carbonates	30 mL 1 mol L^{-1} NaOAc pH 5
	Organic matter	5 mL NaOCl at pH 8.5
	Manganese oxides	30 mL 0.05 mol L^{-1} $NH_2OH{\cdot}HCl$ at pH 2
	Poorly crystalline iron oxides	30 mL 0.2 mol L^{-1} oxalic acid + 0.2 mol L^{-1} ammonium oxalate at pH 3
	Crystalline iron oxides	40 mL 6 mol L^{-1} HCl
	Residual	Digestion with HNO_3 and HCl – 3050b (USEPA 1996a)
Nogueirol et al. (2010)	Exchangeable	15 mL 0.1 mol L^{-1} $Sr(NO_3)_2$
	Organic matter	5 mL 5% NaOCl at pH 8,5
	Oxides	0.2 mol L^{-1} ammonium oxalate + 0.2 mol L^{-1} oxalic acid + 0.1 mol L^{-1} ascorbic acid at pH 3
	Residual	Digestion with HNO_3 and HF – 3052 (USEPA 1996b)
Hall et al. (1996)	Sorbed, exchangeable and carbonate	20 mL 1 mol L^{-1} NaOAc at pH 5
	Amorphous iron oxides	20 mL 0.25 mol L^{-1} $NH_2OH{\cdot}HCl$ in 0.25 mol L^{-1} HCl
	Crystalline iron oxides	30 mL 1 mol L^{-1} $NH_2OH{\cdot}HCl$ in 25% NaOAc
	Sulfide and organic	750 mg $KClO_3$ and 5 mL 12 mol L^{-1} HCl
	Residual	Digestion with HNO_3, HCl, $HClO_4$, and HF.
Ahnstrom and Parker (1999)	Soluble and exchangeable	15 mL 0.1 mol L^{-1} $Sr(NO_3)_2$
	Carbonate	30 mL 1 mol L^{-1} NaOAC at pH 5
	Oxidizable	5 mL NaOCl at pH 8.5
	Reducible	20 mL 0.2 mol L^{-1} oxalic acid + 0.2 mol L^{-1} ammonium oxalate + 0.1 mol L^{-1} ascorbic acid at pH 3
	Residual	Digestion with HNO_3 and HCl – 3050b (USEPA 1996a)
Tessier et al. (1979)	Exchangeable	8 mL 1 mol L^{-1} $MgCl_2$ at pH 7
	Carbonate	8 mL 1 mol L^{-1} NaOAc at pH 5
	Iron and manganese oxides	20 mL 0.04 mol L^{-1} $NH_2OH{\cdot}HCl$ in 25% HOAc
	Organic matter	3 mL 0.02 mol L^{-1} HNO_3 + 5 mL 30% H_2O_2 at pH 2/5 mL 3.2 mol L^{-1} NH_4OAC in HNO_3 20%
Du et al. (2012)	Water soluble, sorbed, and exchangeable	20 mL 1 mol L^{-1} NaOAc at pH 5
	Organic matter	40 mL 1 mol L^{-1} $Na_4P_2O_7$
	Amorphous iron oxides	20 mL 0.25 mol L^{-1} $NH_2OH{\cdot}HCl$ in 0.25 mol L^{-1} HCl
	Crystalline iron oxides	30 mL 1 mol L^{-1} $NH_2OH{\cdot}HCl$ in 25% HOAc
	Residual	Fusion with lithium metaborate/tetraborate. Ressuspension with 10% HCl
Rauret et al. (1999)	Soluble and exchangeable	40 mL 0.11 mol L^{-1} acetic acid
	Oxidizable	40 mL 0.5 mol L^{-1} $NH_2OH{\cdot}HCl$
	Organic matter	20 mL H_2O_2/50 mL 1 mol L^{-1} ammonium acetate

Ray Diffractometer with Cu-Kα radiation (λ = 1.541 Å). Clays were treated with hydrogen peroxide and DCB to eliminate organic matter and Fe oxides, respectively, to enhance the analytical sensitivity to phyllosilicates and gibbsite by eliminating organic matter and Fe oxides (Jackson 1979) — XRD data not shown. Diffraction patterns of the Argiudoll sample had a signal indicative of poorly crystalline,

Table 2 Soil characterization data (Colzato et al. 2017)

	Soil class					
Property	Oxisols			Mollisol		Entisol
Soils	Anionic Acrudox	Rhodic Hapludox	Typic Hapludox	Typic Argiudoll	Mollic Epiaquent	Typic Quartzipsamment
C_{org} (g kg^{-1})	9	30	18	27	35	6
PZSE	6	4.6	3.6	4.5	3.3	3.4
pH_{water}	5.6	5.8	5.9	6.2	3.9	5.3
$pH_{1\ mol/L\ KCl}$	5.9	6	5.3	5	3.4	4.2
CEC (mmol$_c$ kg^{-1})	20	145	48	320	85	44
AEC (mmol$_c$ kg^{-1})	15	–	–	–	–	–
Sand–silt–clay (%)	20–20–60	10–25–65	83–4–13	60–8–32	18–31–51	95–2–3
Si_{alkali} (g kg^{-1})	43.0	59.4	10.8	98.2	78.1	9.8
$Al_{sulfuric}$ (g kg^{-1})	142.4	129.1	23.3	77.8	63.0	22.8
Al_{DCB} (g kg^{-1})	15.0	17.2	2.1	9.8	6.7	1.4
$Al_{oxalate}$ (g kg^{-1})	2.9	5.7	0.8	3.0	1.9	0.6
$Fe_{sulfuric}$ (g kg^{-1})	183.9	223.1	11.9	152.5	19.6	9.1
Fe_{DCB} (g kg^{-1})	132.9	182.5	5.7	61.5	9.0	3.1
$Fe_{oxalate}$ (g kg^{-1})	3.1	4.4	3.6	8.0	2.0	0.3
Ki	0.6	0.9	0.9	2.4	2.4	0.8

C_{org} organic carbon, PZSE points of zero salt effect, *CEC* cationic exchange capacity, *AEC* anionic exchange capacity, Si_{alkali} 1 mol L^{-1} NaOH extractable Si, $Al_{sulfuric}$ 9 mol L^{-1} sulfuric acid-extractable Al, Al_{DCB} sodium dithionite citrate and bicarbonate-extractable Al, $Al_{oxalate}$ acidic solution of ammonium oxalate-extractable Al, $Fe_{sulfuric}$ 9 mol L^{-1} sulfuric acid-extractable Fe, Fe_{DCB} sodium dithionite citrate and bicarbonate-extractable Fe, $Fe_{oxalate}$ acidic solution of ammonium oxalate-extractable Fe; *Ki* weathering index

interstratified kaolinite with a 2:1 layer of silicate mineral, attributed to smectite.

Cadmium sorption

Cadmium sorption was evaluated with 2 g of soil ground and sieved (particle diameter < 150 μm) and 20 mL of Cd solutions prepared from $Cd(NO_3)_2{\cdot}4H_2O$ at 89 to 889 μmol L^{-1} and 0.01 mol L^{-1} $NaNO_3$ (Harter and Naidu 2001). The added Cd ranged from 0.89 to 89 μmol L^{-1} for the Quartzipsamment due to its lower sorption capacity. After horizontal agitation for 24 h at 150 rpm and room temperature, 25 °C in the average, the vials were centrifuged for 30 min at 1844×*g*. All samples were analyzed in triplicate, and Cd sorption was calculated as loss from solution. The pH after equilibration was measured with glass electrode and decreased up to 0.6 pH unit of the initial native soil pH.

The Cd concentration in solution data were used for modeling the isotherms using the Langmuir equation (Eq. 1). The amount sorbed (q_m) was calculated by using Eq. 2, and Eq. 3 gave the linearized Langmuir equation, directly employed in the calculations to obtain q_m and K_L.

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \tag{1}$$

$$q_e = \frac{V(C_0\text{-}C_e)}{m} \tag{2}$$

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \tag{3}$$

where C_e is the remaining concentration (mmol L^{-1}), C_0 is the initial concentrations (mmol L^{-1}), q_e is the amount sorbed (mmol kg^{-1}), K_L is the Langmuir constant related to energy of sorption (L mmol^{-1}), q_m is the maximum adsorption capacity (mmol kg^{-1}), *V* is the volume added (20 mL), and *m* is the mass of soil (2 g) (Sparks 1995). Standard Gibbs free energy (ΔG^o) was calculated from the Langmuir constant according to Eq. 4 (Milonjic 2007; Tran et al. 2016; Zhou and Zhou 2014a).

$$\Delta G^0 = -RT\ln(55.5\cdot 1000\cdot K_L) \quad (4)$$

where R is the universal gas constant (8.314 J K^{-1} mol^{-1}) and $T = 298$ K, assuming constant pressure. The constant 55.5 is the number of moles of water per liter of solution, and the constant 1000 was employed to unit conversion.

Chemical fractionation

After centrifugation performed in the sorption test, the supernatant was referred for Cd determination and soils from each of the replicates were transferred to a porcelain crucible and dried at 50 °C for 24 h. Two initial concentrations and the corresponding replicates were selected: (i) the lowest concentration added in the sorption test, and (ii) a concentration below the maximum adsorption capacity (q_m), obtained from the Langmuir model. After that, sequential extraction was carried out with 1 g of soil and extractant solutions suitable for accessing the target pools (Table 3).

The poorly crystalline and the crystallized Fe oxides are released in separate fractions in the procedure proposed for highly weathered soils, which can lead to low concentrations (Silveira et al. 2006). So, the fractions bound to crystalline, poorly crystalline, and amorphous oxides were extracted with a single extractant (Nogueirol et al. 2010). After each fraction, the flasks were subjected to centrifugation at 1844×*g* for 15 min, and Cd in the supernatant was quantified.

Cadmium quantification

The determination of Cd in sorption test and chemical fractionation extracts was performed by atomic absorption spectrometry with flame atomization (AAnalyst 400, Perkin Elmer). Coefficients of correlation in the calibration solutions were greater than 0.995. Blanks of analysis followed all analytical steps to verify the absence of contamination. The limit of quantification (LOQ) was 0.11 μmol L^{-1} (Skoog et al. 2005).

Results

Cadmium sorption

Data of Cd sorption fit to Langmuir model ($r > 0.94$) and provided sorption capacities (q_m) and Langmuir constants (K_L) for the set of six soil samples (Fig. 1). The pH after equilibration decreased by up to 0.6 unit of the native soil pH of 3.9 to 6.2, and the greater decrease was in Quartzipsamment. Sorption capacities (q_m) ranged from 0.33 to 11.5 mmol kg^{-1}. The Quartzipsamment had low contents of C_{org} (6 g kg^{-1}) and clay (3%), and then the lowest q_m of this set of soil samples (0.33 mmol kg^{-1}).

The Acrudox represents the extreme in degree of weathering, resulting in a positive balance of charges in the Bw horizon. This soil has a PZSE (6.0) higher than its pH_{water} (5.6) and values of cationic exchange capacity (CEC) low and close to anionic exchange capacity (AEC) values. Acrudox had q_m value of 6.42 mmol kg^{-1}, lower than the values of the two other Oxisols (9.53 and 10.3 mmol kg^{-1}), attributed to the low CEC, 20 $mmol_c$ kg^{-1}. The PZSE for Acrudox is 0.4 unit higher than pH_{water}; thus, the number of positive charges is greater than negatives, so sorption sites were com-

Table 3 Fractions, solutions, and conditions applied to sequential extraction (Nogueirol et al. 2010; Silveira et al. 2006)

Target pool	Extractant	Condition
1. Soluble or weakly exchangable	15 mL 0.1 mol L^{-1} $CaCl_2$	2 h at 180 rpm and 25 °C
2. Soluble in acid / specifically exchangeable	30 mL 1 mol L^{-1} CH_3COONa at pH 5.0	5 h at 180 rpm and 25 °C
3. Bound to organic matter	5 mL NaOCl at pH 8.5	30 min at 90 °C
4. Bound to oxides	40 mL 0.2 mol L^{-1} ammonium oxalate, 0.2 mol L^{-1} oxalic acid and 0.1 mol L^{-1} ascorbic acid at pH 3.0	30 min at 90 °C, dark
5. Residual (microwave-assisted acid digestion) (USEPA 2007)	9 mL HNO_3 and 3 mL HCl	5.5 min until reach 175 °C and remain for 4.5 min in 175 °C.

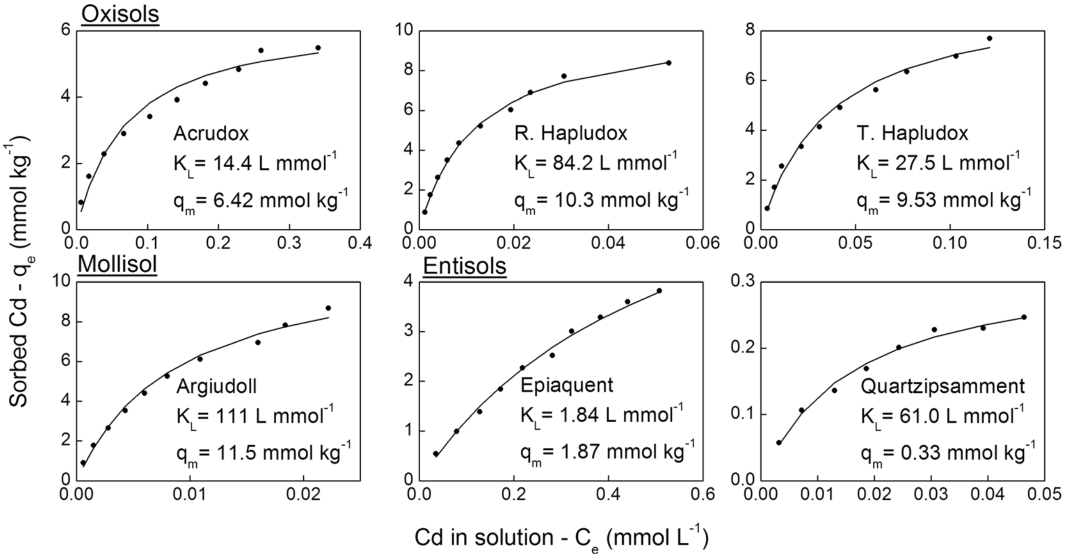

Fig. 1 Langmuir sorption isotherms. Points are empirical results, and the lines were obtained by the Langmuir isotherm model. K_L is the Langmuir constant (L mmol) and q_m corresponds to the estimate of the sorption capacity (mmol kg^{-1})

posed mainly by negative charges from dissociated organic groups.

The q_m value for Epiaquent was 1.87 mmol kg^{-1}, which had 35 g kg^{-1} of C_{org}, the largest of this set. Although potentially in pronounced amount, the adsorption sites were not available in their entirety due to $pH_{water} = 3.9$. The T. Hapludox had q_m value of 9.53 mmol kg^{-1}, and the pH_{water} was 2.3 units higher than the PZSE, the greatest difference among this set of soil samples, revealing the arising of negative charges, even with a lower content of C_{org} and clay, when compared to the other soils. The q_m value of R. Hapludox was 10.3 mmol kg^{-1}, attributed to the high contents of C_{org} (30 g kg^{-1}) and clay (65%). The Argiudoll, that had the largest value of q_m (11.5 mmol kg^{-1}), stands out due to not only the high proportion of clay and organic matter, but also mainly to the content of 2:1 phyllosilicates in the clay fraction, indicated by XRD—data not shown.

Langmuir constant (K_L) ranged from 1.84 to 111 L mmol^{-1}. The low value of the Langmuir constant for Epiaquent was probably due to the sandy texture and $pH_{water} = 3.9$, the lowest among the tested samples. Another key point is the difference between pH_{water} and the PZSE, of only 0.6 pH unit, which reflects a lower number of active sites with negative charge (Sparks 1995).

The K_L value for the Oxisols were 14.4 L mmol^{-1} for Acrudox, 84.2 L mmol^{-1} for R. Hapludox, and 27.5 L mmol^{-1} for T. Hapludox. The largest value of K_L for R. Hapludox is mainly due to higher organic carbon content and the negative balance of charge, as expressed by the difference between the pH_{water} and the PZSE. The Quartzipsamment presented an intermediate K_L (61 L mmol^{-1}) despite low C_{org} and clay contents. Argiudoll had a $K_L = 111$ L mmol^{-1}, the highest among the studied soils, favored by soil organic matter, clay, and 2:1 phyllosilicates in the clay fraction.

Standard Gibbs free energy obtained by Eq. 4 (Table 4) for the six soils ranged from − 38.7 to − 28.6 kJ mol^{-1}. The ΔG^0 was negative, and the lowest ΔG^0 was for Argiudoll (− 38.7 kJ mol^{-1}), that had also the larger sorption capacity of the set of soil samples (11.5 mmol kg^{-1}). Among the soil samples that were

Table 4 Standard Gibbs free energy for the interaction between soil-Cd

Soil sample	ΔG^0 (kJ mol^{-1})
Acrudox	− 33.7
R. Hapludox	− 38.1
T. Hapludox	− 35.3
Argiudoll	− 38.8
Epiaquent	− 28.6
Quartzipsamment	− 37.3

evaluated under the same concentrations (89 to 889 μmol L^{-1}), thus excluding Quartipsamment (evaluated from 0.89 to 89 μmol L^{-1}), the thermodynamic results were related to Cd sorption capacity ($r = 0.74$).

Chemical fractionation

Two concentrations of each soil were used to evaluate the interaction of Cd with soil: the lowest concentration and a high concentration though below the value of q_m. Amounts of Cd released in each extractant were calculated as a percentage to adjust for differences in the initial concentration, or the Cd sorbed (Fig. 2). Recoveries ranged from 70 to 129%, which comprised the propagated error, since the relative standard deviation of single fractions were lower than 10%.

Initial concentration did not affect consistently (*t* test, $\alpha = 0.05$) Cd relative concentrations in extractants of chemical fractionation (Fig. 2), and similar results were reported by Luo et al. (2011). From 87 to 98% of Cd remained as extractable in 0.1 mol L^{-1} $CaCl_2$ (F1) or 1 mol L^{-1} CH_3COONa at pH 5.0 (F2), of which 51% of Cd were 0.1 mol L^{-1} $CaCl_2$ extractable, indicating sorption with low energy. From 2 to 9% of Cd was released with oxidation with NaOCl (F3). The evaluation of Cd extracted with reduction (F4) and residual (F5) were impaired because some results were below the limit of quantification, indicating that the portion sorbed to those soil pool was effectively low (below 4%).

Discussion

The sorption capacity results were consistent with soil attributes, primarily pH, and organic carbon and clay contents, and may have accounted a combination of sorption processes and origins of negative charges, from organic and inorganic soil compounds or soil pools. Phyllosilicates sorbs Cd electrostatically as an outer sphere complex in permanent negative charges at the surface of the silicon layer, and specifically, as an inner sphere complex to the variable charges at aluminum layers and edges (Loganathan et al. 2012). In variable charge from oxides, Cd is sorbed by ion exchange in hydroxyl groups or at superficial negative charges. The organic matter sorbs Cd in carboxylic, phenolic and amine groups, forming complexes. Furthermore, precipitation as carbonates, hydroxides, sulfates, and phosphates may also occur (Naidu et al. 1997).

Cadmium sorption capacities ranged from 0.33 to 11.5 mmol L^{-1} for our set of Brazilian soil samples. In tropical Indian soil samples, the range was reported as 6.8 to 38 mmol kg^{-1} (Ramachandran and Souza 1999), and values between 1.27 and 17 mmol kg^{-1} were reported for Spanish soils (Serrano et al. 2005). Those intervals indicated that our values were similar in magnitude and had a wide range between soils as well.

Langmuir constant values have been related to the sorption energy and dissociation constants, and higher represent specific sorption at high energy surfaces and low dissociation constants. Alternatively, lower K_L values relate to sorption at low energy surfaces with

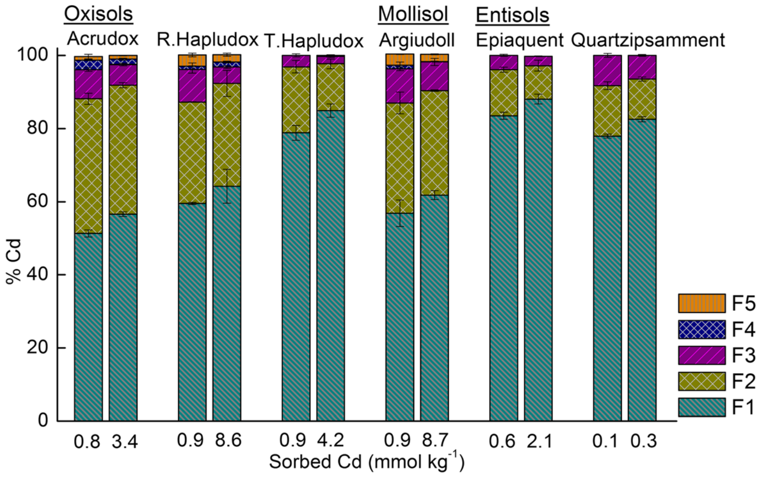

Fig. 2 Relative contribution of each fraction of chemical fractionation in Cd extraction with two initial concentrations each soil. Fractions corresponds to Cd extractable in F1, 0.1 mol L^{-1} $CaCl_2$; F2, 1 mol L^{-1} CH_3COONa at pH 5.0; F3, NaOCl at pH 8.5; F4, 0.2 mol L^{-1} ammonium oxalate, 0.2 mol L^{-1} oxalic acid, and 0.1 mol L^{-1} ascorbic acid at pH 3.0; and F5, microwave-assisted acid digestion with HNO_3 and HCl

high dissociation constants (Adhikari and Singh 2003; Ma and Rao 1997). In highly weathered soils, such as the Oxisols, variable charge oxides are predominant in the clay fraction; thus, the difference between the PZSE and pH_{water} is an important parameter for explaining our data. The pH_{water} higher than the PZSE indicates the predominance of negative charges, and the greater the difference, the higher the number of charges. In extreme degrees of soil weathering, such as in the subsuperficial sample of the Acrudox, the opposite may occur, and the pH_{water} can be lower than the PZSE (Naidu et al. 1997; Sparks 1995).

Thermodynamically favorable interactions and low level of interaction energy are represented by negative values for standard Gibbs free energy, thus characterizing that Cd sorption in our soil samples were mostly due to physical processes (Atkins 1994; Sheikhhosseini et al. 2014). These physical processes of sorption are reversible, with rapid kinetics and composed especially of electrostatic interactions without exchange or sharing electrons (Atkins 1994). Negative values of ΔG^0 in the same magnitude as ours, between −21 and −24 kJ mol^{-1}, were reported to French (Roth et al. 2012), and Chinese soils (Xue et al. 2009), and these had values close to −20 kJ mol^{-1} also for zinc (Xue et al. 2009).

The ΔG^0 in an Anionic Acrudox was reported to be positive, from 3 to 11 kJ mol^{-1} (Dias et al. 2003). Unfortunately, the use of Langmuir parameters for calculating ΔG^0 have been questioned due to suitability of parameters and units (Milonjic 2007; Tran et al. 2016; Zhou and Zhou 2014b). Equation 4 considered that the unit of K_L was L $mmol^{-1}$; thus, the conversion was necessary for obtaining ΔG^0 in kJ mol^{-1}.

Sorption followed by chemical fractionation procedure for Cd aimed to access releasing and contribution of pools for sorption. This composition of procedures was a suitable approach for evaluating the retention of Pb and Cd in natural surface coatings, indicating that Cd sorption is less stable than Pb. Morera et al. (2001) assessed the sorption and the distribution of Cd, Cu, Ni, Pb, and Zn in soils from temperate region and reported significant sorption in carbonates compounds.

Relating availability and chemical fractionation, the elements with a extractant targeting soluble compounds (F1) are easily available (Kabata-Pendias 2011). Yet, the availability is moderate if elements are released in extractants targeting exchangeable or acid soluble (F2). Thus, these two fractions or pools have potential of releasing to soil solution and comprise available pools. Organic matter (F3) and oxide (F4) pools represent low and residual (F5) very low availability (Kabata-Pendias 2011). He et al. (2005a) evaluated Cd desorption after sorption for the same 24 h in variable charge soils and observed that approximately half of the adsorbed Cd was removed with a 0.01 mol L^{-1} $NaNO_3$ solution, equivalent to F1 in this study, that extracted 51% of the adsorbed Cd.

The six soil samples had results in the same order of magnitude, and highly weathered soil samples (Acrudox, R. Hapludox, and T. Hapludox) had sorption and desorption parameters interspersed with less weathered (Epiaquent, Argiudoll, and Quartzipsamment). Yet, the results were consistent and suitably explained with soil attributes.

The available species were defined as those that are easily assimilated by living organisms (International Union of Pure and Applied Chemistry 2002). The majority (87%) of Cd sorbed in our set of soil samples was available. These results were consistent with the values of ΔG^0 that indicated the prevalence of low energy sorption. The predominance of available species of Cd and low energy sorption characterized the potential of environmental risk regarding Cd in soil, since the release showed up to be likely in natural conditions.

The sorption in different sites, in accordance with soil class and attributes, did not present clear distinction in releasing potential. Thus, the sorption sites from variable charges in Oxisols had similar characteristics for Cd sorption as the sorption sites from diverse origin. The Cd sorption in the six soil samples was consistent showing high availability and low energy of sorption.

Conclusions

The Langmuir model fits the sorption data, and estimated sorption capacity ranged from 0.33 to 11.5 mmol kg^{-1} in our set of soils. The standard Gibbs free energy calculated from Langmuir constants were negative/thermodynamically favorable and ranged from −38.7 to −28.6 kJ mol^{-1}. Chemical fractionation showed that up to 90% of sorbed cadmium was weak and reversible, comprising available species. Cadmium in soil could be a potential environmental risk, since most of sorbed Cd could be released and absorbed by living organisms or be transported, regardless of soil class or attributes.

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