University of São Paulo
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Background concentrations and adsorption of selenium in tropical soils

Mariana Bassetto Gabos

Thesis presented to obtain the degree of Doctor in Science. Area: Soils and Plant Nutrition

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versão revisada de acordo com a resolução CoPGr 6018 de 2011

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“Imagination is more important than knowledge. Knowledge is limited.
Imagination encircles the world.”
Albert Einstein

CONTENTS

RESUMO

Valores de referência e adsorção de selênio em solos tropicais

O selênio (Se) é um elemento traço essencial a nutrição animal. Por outro lado, o limiar de concentração entre suficiente e tóxico é estreito. A presença de Se nos alimentos está relacionada à sua concentração no solo. Deste modo, conhecer a quantidade e o comportamento do Se no solo é muito importante para um correto manejo ambiental, previnindo problemas toxicológicos e deficiência em humanos. Os objetivos deste estudo foram: (i) quantificar os conteúdos naturais de Se em solos brasileiros e correlacioná-los com seus atributos; (ii) avaliar a adsorção de selenito e selenato em função da variação do pH e da concentração de Se em solos tropicais; (iii) ajustar o modelo de capacitancia constante para descrever a adsorção de Se em solos tropicais comparado a modelos empíricos. As concentrações de Se variaram de <0,08 - 1,61 mg kg^{-1}, com média de 0,19 mg kg^{-1}. As concentrações de Se nas amostras coletadas nas camadas superficiais do solo foram positivamente correlacionadas com a capacidade de troca catiônica, bem como os teores de argila, matéria orgânica e óxidos de Fe e Al do solos. Nas amostras subsuperficiais, apenas pH e teor de óxido de alumínio foram correlacionadas com as concentrações de Se. A maioria das amostras com maiores concentrações de selênio foram provenientes de material de origem sedimentar. A adsorção de Se(IV) foi elevada para todos os solos, diminuiu com o aumento do pH e foi fortemente correlacionada com teores de matéria orgânica e de óxidos de Fe e de Al. Por outro lado, a adsorção de Se(VI) foi muito baixa em valores de pH normalmente encontrados em solos agrícolas, excepto para o Latossolo Vermelho acriférrico, que foi positivamente correlacionada com o teor de gibbsita dos solos. O modelo de capacitância constante ajustou-se bem aos resultados de adsorção Se(IV) e Se(VI), com ajuste similar aos modelos empíricos de Langmuir e de Freundlich. Para os resultados de adsorção de Se(IV) foram utilizadas otimizações das constantes de complexação mono e bidentadas e da constante de protonação de superfície. Para Se(VI), foram empregadas otimizações para as duas espécies de monodentadas.

Palavras-chave: Selenito; Selenato; Valor de referência de qualidade de solo; Modelo de capacitância constante; Isoterma

ABSTRACT

Background concentrations and adsorption of selenium in tropical soils

Selenium (Se) is a trace element essential to the nutrition of animals. On the other hand, in a narrow concentration range, Se can cause toxicity. The presence of Se in food is related to the concentration of the element in soil. Thus, the knowledge of the Se amount and its behavior in soil are very important to the better manage the environment and to prevent toxicological problems and human deficiency. The objectives of this study were: (i) to quantify the natural content of Se in some Brazilian soils and correlates them with soil attributes; (ii) to evaluate the adsorption of selenite and selenate as a function of pH and Se concentration in tropical soils; (iii) to adjust the constant capacitance model to describe the Se adsorption in tropical soil as compared to empiric models. Se concentrations ranged from <0.08 to 1.61 mg kg^{-1}, with a mean of 0.19 mg kg^{-1}. Concentrations of Se in the samples collected in the superficial layers were positively correlated to cationic exchange capacity, as well as to clay, organic matter and oxide contents of the soils. In the subsurface samples, only pH and aluminum oxide content were correlated with Se concentrations. Most samples with the highest Se concentrations were derived from sedimentary parent material. Se(IV) adsorption was high for all soils, decreased with increasing pH and was strongly correlated to organic matter and Fe and Al oxides' contents. On the other hand, Se(VI) adsorption was very low at pH values commonly found in agricultural soils, except for the highly weathered Rhodic Acrudox which was positively correlated with the gibbsite content. The constant capacitance model fit the Se(IV) and Se(VI) adsorption data well, and was similar to Langmuir and Freundlich empirical models. Optimizations of mono and bidentate complexation and surface protonation constant were used for the Se(IV) adsorption data. For Se(VI), optimizations for the two monodentate species were employed.

Keywords: Selenite; Selenate; Soil quality reference; Constant capacitance model; Isotherm

1 INTRODUCTION

Selenium (Se) is used as a raw material in the electronics industry, in glass, as a pigment, and in pharmaceutical products and pesticides. It is a trace element essential to animal life. Se is present in many metabolic pathways, such as hormone metabolism, antioxidant defense systems, immune function, and growth modulation (FAIRWEATHER-TAIT et al., 2011).

Insufficient ingestion of Se by humans may cause health problems such as cardiomyopathy (Keshan disease) and muscular dystrophy, as has been reported in China and southeastern Siberia (FAO, 2001; TAN et al., 2002). On the other hand, too much Se can be toxic for animals and humans. Symptoms of Se deficiency and toxicity in adults can be observed at ingestion rates of less than 40 or more than 400 µg per day, respectively (WINKEL et al., 2012). Se is also indicated to be essential for metabolic functions in plants, but this affirmation is not conclusive (HAWKESFORD; ZHAO, 2007). Se is incorporated into proteins in the place of sulfur, for example, forming selenocysteine, a compound that is easily absorbed by the human body (HIMENO; IMURA, 2002). High concentrations of Se in soils can cause toxic symptoms in plants, like chlorosis in leaves and pink coloration in roots (ALLOWAY, 1990).

Se contents in normal adult humans can vary widely, and this reflects the influence of the natural environment on the Se contents of soils, crops, and human tissues (FAO, 2001). The concentration of Se in plants is positively correlated to the natural occurrence of the element in soils where the plants grow (KABATA-PENDIAS, 2000). A large-scale example of the public health consequences occurred in the United Kingdom during the mid-1970s, when there was a decrease of 40% in the mean amount of Se consumed by people, following the reduction of wheat (*Triticum aestivum* L.) imports from North America. The decrease was attributed to the lower Se concentrations in European soils, which led to lower Se levels in the wheat grains produced in Europe (ZHAO et al., 2007). The presence of Se in crops is dependent on Se bioavailability in soils, which is usually between 1 and 6% of the total Se concentration, depending on soil attributes (GERLA; SHARIF; KOROM, 2011).

Total Se content in soil usually ranges between < 0.1 and 2 mg kg^{-1}, with some records of up to 2,018 mg kg^{-1} (PEZZAROSSA; PETRUZZELLI, 2001; ZHU et al., 2008). Se deficiencies have been described in countries such as Australia, New

Zealand, Mexico, India, and China (OLDFIELD, 1992). Elevated Se contents can be a consequence of natural sources or of anthropogenic activity. In some regions of China, natural levels of Se are toxic, because the soils are derived from Se-rich parent materials with 10 to 40 mg kg^{-1} of Se, such as pyritic, black carbonaceous slate and volcanic tuff (KUNLI et al. 2004). In the San Joaquin valley (California, USA) Se-rich groundwater has been used for irrigation, causing Se accumulation in the upper layer of soils (OHLENDORT et al., 1986).

Se compounds are widespread in the terrestrial environment (rocks, soil, water and air) (FERNÁNDEZ-MARTÍNEZ; CHARLET, 2009). The natural occurrence of Se in soils is dependent on the degree of weathering and parent material. Igneous and metamorphic rocks contain less than 1 mg kg^{-1}, while levels in sedimentary rocks generally vary between 1 and 100 mg kg^{-1} (KABATA-PENDIAS, 2000). In rocks, high concentrations of Se are associated with a reducing environment for a period of time, since the reduced species of Se precipitates. Elemental Se and the metal selenide are insoluble under reduced conditions (ZAWISLANSKI; ZAVARIN, 1996). Due to chemical similarities between Se and S, partial substitutions may occur, and the S:Se ratio is 1:6,000 in sulfide deposits (ALLOWAY, 1990).

To correct Se deficiency, some countries are allowing Se fertilization with the objective of food fortification, also known as agronomic biofortification. Broadley et al. (2010), for example, showed 20–35% of total recovery (wheat grain and straw) of applied Se in soil. However, despite these promising results, a better understanding of the interactions of Se in soil is required to prevent public health and environmental problems in the future. In Finland, the addition of Se in fertilizer formulas was implemented in 1984. As a result, the content of Se in food has since improved, although the destination of the annual increment of selenate that is not absorbed by crops has not been totally explained. It is assumed that residual Se is reduced from selenate to insoluble species, thus accumulating in soil (KESKINEN et al., 2009).

The main forms of Se in soil are: selenite (SeO_3^{2-}), selenate (SeO_4^{2-}), selenides (Se^{2-}), and elemental Se (Se^0). Selenite and selenate are thermodynamically stable at typical values of pH and redox potential (E_H) in soils. Selenite is slightly mobile in neutral and acidic soils, and easily adsorbed by iron (Fe), aluminum (Al) and manganese (Mn) oxides and organic matter. For this reason Se (IV) is considered less toxic than Se (VI) (COBO-FERNANDEZ et al. 1993). By contrast, selenate is mobile in alkaline soils, and its adsorption on hydrated oxides is

low. In deep soil layers, Se mobility is controlled by biogeochemical processes such as adsorption and desorption; oxidation and reduction; precipitation and complexation with others minerals (KABATA-PENDIA, 1998).

Variation in E_H is directly related to Se behavior in soils and to its availability to plants. In *Carex* sp. the bioavailability of Se decreased with decreasing E_H (MINCHER et al., 2007). The Se species present in soil influence its absorption by plants and its toxicity. Selenite and selenate are the most frequent forms in soils and both are absorbed by plants. Selenate is the predominant form translocated inside the plant, while selenite is previously converted to selenate or organic compounds (MINORSKY, 2003).

Adsorption studies of ions in soils are important to delineate ion accumulation in the solid-liquid interface. Ion adsorption is correlated with electrochemical reactions on colloid surfaces, which are influenced by soil attributes such as content and type of organic matter, texture, structure, content and type of clay minerals, and the nature and transformation of parent materials (ALLEONI et al., 2009). From an environmental perspective, adsorption studies help explain soil processes such as the behavior, mobility, and bioaccessibility of ions in soil.

Se adsorption in soils has been studied by several researchers (HAYES et al., 1987; GOH; LIM, 2004; GOLDBERG et al., 2007), but studies of soils from wet tropical regions are scarce (MOURA et al. 2008; ABREU et al. 2011). Moura et al. (2008) quantified the adsorption of total Se in Brazilian Oxisols, and reported maximum Se adsorption ranging from 135 to 2,245 mg kg^{-1}. The soil with the highest adsorption was a Rhodic Acrudox. Evaluating the adsorption of the two main Se species in soil (Se(IV) and Se(VI)), Barrow and Whelan (1989) found that selenite is more strongly sorbed than selenate. When compared to others anions, Se bonds are weaker than phosphate and fluoride sorptions. Barrow and Whelan (1989) also observed a decrease in Se sorption with increasing pH, and this trend was more pronounced for selenite than for selenate. Hayes et al. (1987) employed extended X-ray absorption fine structure (EXAFS) and described selenate adsorption in goethite as outer-sphere complexes. Conversely, inner-sphere complexes were formed with selenite.

Chemical modeling of ion adsorption in soils comes in direction to global concerns about soil and environmental quality. Such models address the need for a better understanding of how chemical species are distributed in the environment and

which mechanisms regulate its concentration in soil solution. The empirical models offer a simple description of results, but have limitations in its prognostic. Because of their robustness, semi-empirical, theoretical, mechanistic, or chemical models take into account other parameters obeying thermodynamic proprieties and reactions of equilibrium linked to the mass balance of charges. However, due to their apparent complexity, these models have been little used by the Brazilian scientific community (CASAGRANDE; SOARES, 2009).

In the capacitance constant model, protons, hydroxyl, and specifically adsorbed ions such as phosphate are adsorbed in a unique plan, with a constant value of capacitance for each electrolyte, but varying with its concentration. This chemical model represents an advance on approximations of isotherm equations of adsorptions, which contain two adjustable empirical parameters (GOLDBERG, 1992).

The objectives of this study were (i) to quantify natural levels of Se in soils from São Paulo state, Brazil, and to correlate those levels with the chemical, physical, and mineralogical attributes of soils; (ii) to evaluate the adsorption of selenite and selenate as a function of pH and Se concentration ranges in tropical soils; and (iii) to adjust the constant capacitance model to describe Se adsorption in tropical soils as compared to empirical models.

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2 BACKGROUND LEVELS OF SELENIUM IN SELECTED TROPICAL SOILS

Abstract

Selenium (Se) is an essential trace element required in low amounts by humans and animals, but it can be toxic when ingested at high concentrations. Information regarding Se background levels in soils is important to prevent Se deficiency, to optimize human nutrition and to prevent toxicological effects. Background Se levels in Brazilian soils were evaluated and correlated with other soil attributes. Se concentrations were quantified in samples from the superficial layer (0-0.2 m) and from the subsurface layer (the highest portion of the B horizon) for 58 soils. Soils were selected across a wide range of soil types and parent materials. Se concentrations ranged from <0.08 to 1.61 mg kg^{-1}, with a mean of 0.19 mg kg^{-1}. Concentrations of Se in the samples collected in the superficial layers were positively correlated with cation exchange capacity, as well as to clay, organic matter and oxide contents of the soils. In the subsurface samples, only pH and aluminum oxide content were correlated with Se concentrations. Most samples with the highest Se concentrations were derived from sedimentary parent material. The amount of Se present in these soils seems to be insufficient to supply plants with the Se required by the local resident's nutrition.

Keywords: Se; Tropical soil; Aqua regia; Organic matter; Oxides

2.1 Introduction

Selenium (Se) is a trace element that is widespread in different biogeochemical environments. Low quantities of Se are essential for animal and human nutrition, and play a role in important processes like the antioxidant function in organisms. Studies have identified Se deficiency as a cause of cardiomyopathy in some areas in China where Keshan disease is endemic (TAN et al., 2002). The Institute of Medicine of the National Academy of Science of the United States recommends that adults ingest 55 µg of Se per day (BOYD, 2011). Above a very narrow content range, Se can be toxic for animals, and daily intake by humans should not exceed 400 µg (FERNANDEZ-MARTÍNEZ; CHARLES, 2009).

The amount of Se in soils is closely correlated with soil mineralogical composition (WINKEL et al., 2011). Se concentrations in soil result either from parent material or from human activities, and some soil attributes play an important role in maintaining Se in the soil phase.

Because the range between essential and toxic Se concentrations in soils is very narrow, it is important to quantify background Se concentrations in soils and therefore the amount of Se that may enter the food chain. Worldwide, the total

amount of Se in soils is typically between 0.1 and 2 mg kg^{-1} (PEZZAROSSA; PETRUZZELLI, 2001). Researchers have observed Se deficiency in soils of various countries, such as 0.03 to 1.42 mg kg^{-1} in China (ZHANG et al., 2008); 0.11 to 0.88 mg kg^{-1} in Scotland (FORDYCE et al., 2010); 0.05 to 2.80 mg kg^{-1} in Japan (YAMADA et al., 2009); and 0.01 to 2.7 mg kg^{-1} in Spain (PEREZ-SIRVENT et al., 2010). Se concentration in other soils can be extremely toxic. For example, in China's Yutangba region, 11 samples had concentrations ranging from 346 to 2,018 mg kg^{-1}, which represent serious risks to local residents (ZHU, 2008).

The predominant forms of Se in soils are selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}). As a consequence, adsorption is dependent on the presence of colloids with net positive balance of charge. It is well known that soils in the wet tropics have a large amount of pH-dependent charges (GOH; LIM, 2004; FONTES; ALLEONI, 2006).

The amount of Se in food is directly related to its concentration in agricultural soils. Generally, crop concentrations lower than 0.1 mg kg^{-1} for grass and 0.05 mg kg^{-1} for grains are considered low. Low Se concentrations in UK soils yield bread-making wheat (*Triticum aestivum* L.) with Se concentrations ten times lower (0.025 to 0.033 mg kg^{-1}) than the UK recommended human intake (ADAMS et al., 2002). In Brazil there is evidence of high Se content in some soils from the Amazon region (LEMIRE et al., 2010). This large area, however, is occupied by only 8% of the Brazilian population (BRASIL, 2011). Because some animals fed in natural pastures have shown Se deficiency, it is assumed that soils from Brazil's central-southern region are deficient in Se (OLIVEIRA et al., 2007). As consequence, there is a risk of insufficient intake of Se in the diet of people who live in the area. Brazil nut (*Bertholletia excelsa*), a food with high Se concentrations (PAREKH et al., 2008 LEMIRE et al., 2010), and have been reported as an important source of Se in Amazonian areas of northern Brazil. However Brazil is a huge country, however, and São Paulo state is located in the southeastern region, where Brazil nut trees are not cultivated. As a consequence, Brazil nuts are not present in the diet of most São Paulo residents, and they are too expensive to be accessible for most people.

The state of São Paulo is the most populated in Brazil. With more than 40 million inhabitants living in 250,000 km^2, it contributes 31% of Brazilian gross national product. In 2005 the São Paulo Environmental Agency published Guideline Values for soils and groundwater, including the "Quality Reference Value" obtained from the

background levels of Se in soils from the state (CETESB, 2005). For some elements, like Se, most samples presented values lower than the detection limit, and in such cases the background value was considered to be the detection limit (0.25 mg kg^{-1} of Se). However, equipment with higher analytical precision and a larger number of soil samples representing variation across the entire state would allow a more accurate determination of the background Se levels naturally occurring in soils. This study was carried out to determine Se background levels in soils of the state of São Paulo and to test for correlations with soil attributes.

2.2 Materials and Methods

2.2.1 Soil selection

The experiment was carried out with samples from 58 soils from São Paulo state, collected separately in the topsoil (0-0.2 m) and subsoil (the highest expression of the B horizon) layers, under native vegetation. Samples were chosen to reflect a broad range of different soil types and parent materials, which localizations are showed in the Table 1.

2.2.2 Sample characterization

Samples were air dried, crushed, and passed through a 0.150-mm (100 mesh) sieve. The pH values were potentiometrically determined in water (pH_{water}), with a 1:2.5 soil/water ratio, and in a 0.01 M $CaCl_2$ suspension, with a 1:2.5 soil/solution ratio (CAMPBELL et al., 1986). Total soil organic carbon (OC) content was obtained by the Walkley-Black method (NELSON; SOMMER, 1982): OC contents were quantified after oxidation of soil organic matter with a 0.167 M potassium dichromate ($K_2Cr_2O_7$) solution, in the presence of 5 M H_2SO_4. The excess $K_2Cr_2O_7$ was titrated with Fe^{2+} ions from a standardized solution of ferrous ammonium sulfate. Phosphorus, K, Ca, and Mg contents were extracted by an ion exchange resin and determined by colorimetry (P), flame emission photometry (K), and atomic absorption spectrometry (AAS) – (Ca and Mg) (RAIJ et al., 1986). Exchangeable aluminum was extracted by a 1 M KCl solution and determined by titration with 0.025 M ammonium hydroxide. Total acidity (H+Al) was extracted by a 1 M calcium acetate solution and determined by titration with 0.025 M ammonium hydroxide. The following parameters were calculated: total cation exchange capacity

at pH 7.0 (CEC_T = SB + (H + Al)) and base saturation (V% = (SB x 100) / CEC_T). The densimeter method was used for particle-size analysis (GEE; OR, 2002).

Sodium citrate-bicarbonate-dithionite (CBD) solution was used to extract the "free" iron oxides of the mineralogical fraction (MEHRA; JACKSON, 1960). Contents of "amorphous" oxides (Ox-Al and Ox-Fe) were extracted by oxalate solution (LOEPPERT; INSKEEP, 1996). A 9 M H_2SO_4 solution was employed to solubilize contents of Fe and Al present in secondary minerals. The same process was performed for Si, which was extracted with a 30% NaOH solution. Contents of Fe and Al were determined by AAS, and Si was quantified by gravimetry (CAMARGO et al., 1986).

2.2.3 Selenium contents

The "Total" (reactive fraction or pseudo total) contents of Se in soil samples were extracted with aqua regia (ISO 11466:1995). In a Teflon vessel 0.5 g of soil was weighed, and then mixed with 3 mL of HNO_3 (65%) and 9 ml of HCl and allowed to digest overnight at room temperature. Subsequently, the vessels were sealed and accommodated in a microwave oven. After digestion, the extracts were filtered, and the volume filled up to 25 mL with ultrapure water. For Se determination, the extracts were reduced to Se (IV) using 5 ml of the digests, 2.5 ml of hydrochloric acid, and 2.5 ml of ultrapure water, heated in a water bath for 1 h at 70° C, and the volume completed to 25 mL in volumetric flasks (ISO 20280:2007). The amount of Se was determined by hydride generation in a flow injection analysis system coupled to an atomic absorption spectrometer (HG-AAS) using 0.2% borohydride and 10% hydrochloric acid (USEPA 7010, 2007). A certified soil sample of San Joaquin soil (SRM 2709a) from the National Institute of Standards and Technology (NIST) with 1.5 mg kg^{-1} of Se was included in each digestion series to ensure a quality analysis control (recovery rate between 76-82%). Data were obtained in triplicates, and means submitted to a Pearson covariance analysis using Statistical Analysis System software (SAS Institute, 1993).

2.3 Results and discussion

2.3.1 Selenium in soil

The amounts of Se in the soils we studied varied from <0.089 and 1.612 mg kg^{-1} (Table 1), and the average was 0.191 mg kg^{-1}. Half of the soils had less Se

then the quantification limit (0.089 mg kg^{-1}), and 75% of the soil samples showed values lower than 0.223 mg kg^{-1}. In China, TAN et al. (2002) studied the relationships between soil Se and endemic human diseases, and they considered 0.123 - 0.175 mg kg^{-1} as the reference threshold values for the risk assessment of potential selenium deficiency in soils. The concern related to Se in tropical soils from São Paulo state was initially motivated by interest in establishing reference levels for soil quality. Background levels are required to prevent environmental damage, and São Paulo's status as the most populated and industrialized state in Brazil makes it vulnerable to pollution risks. However, the results made it clear that the focus of the study of Se in soil should not be restricted to environmental safety. Se-deficient soils are a health concern, and especially for people whose diet is based on food produced in this area, because people with a more diversified diet have higher chance of obtaining Se from other sources. São Paulo State concentrates 22% of the Brazilian population (BRASIL, 2010), and it has 20 million hectares of productive agricultural lands (CATI, 2008).

Table 1 - Geographic coordinates, soil order, parent material and some chemical characteristics of each soil. Superficial and subsurface samples are denoted by A and B respectively.

(continue)

Coordinate (Lat., Long.)	Soil Order	Parent Material	Depth		$pH_{(water)}$		OC		Clay		Fe CBD		Se	
			A	B	A	B	A	B	A	B	A	B	A	B
			m				g kg^{-1}		g kg^{-1}		g kg^{-1}		mg kg^{-1}	
-46.70, -21.93	Alfisol	Tinguaite	0.0-0.2	1.0-1.5	5.7	6	12.2	7.0	45	61	86.3	92.9	0.2	0.17
-47.04, -22.48	Alfisol	Claystone	0.0-0.3	1.6-2.0	5.3	6.1	4.1	1.2	29	34	17.9	28.6	0.14	0.18
-48.53, -20.20	Alfisol	Fluvic Sediments	0.0-0.2	0.7-1.0	5.4	5.8	7.0	0.6	24	61	1.0	6.0	0.06	0.05
-51.15, -21.66	Alfisol	Sandstone	0.0-0.2	0.6-0.8	5.9	6.3	3.5	2.3	10	28	6.9	15.9	0.09	0.11
-48.55, -22.25	Alfisol	Basalt	0.0-0.1	0.7-1.1	6.2	6.4	20.3	2.9	34	55	68.8	85.6	0.15	0.16
-48.55, -22.23	Alfisol	Sedimentary	0.0-0.3	1.1-1.5	5.6	7	14.0	4.7	23	58	26.0	4.3	0.13	0.04
-47.85, -23.33	Alfisol	Siltstone (Permian)	0.0-0.1	0.4-0.7	5.9	5.1	18.0	6.4	14	40	2.1	9.4	0.05	0.05
-47.90, -23.10	Alfisol	Claystone (Permian)	0.0-0.1	0.6-0.9	5.6	5.5	8.7	2.9	35	70	29.6	65.9	0.4	0.47
-42.92, -23.13	Entisol	Schist	0.0-0.1	0.5-0.9	5.7	5.5	16.3	1.7	20	29	9.2	13.9	0.06	0.06
-42.92, -23.13	Entisol	Sedimentary	0.0-0.3	0.7-0.8	5.3	5.1	2.9	1.7	28	36	13.1	7.1	0.09	0.1
-46.42, -23.13	Entisol	Granite	0.0-0.2	0.2-0.4	5	4.9	18.0	6.4	28	35	25.9	24.4	0.23	0.37
-46.36, -22.43	Entisol	Sand sediments	0.0-0.2	0.4-0.6	5	5.7	16.3	4.7	27	18	25.9	12.9	0.08	0.14
-46.57, -23.11	Entisol	Sedimentary	0.0-0.1	0.7-1.1	5.4	5.5	17.4	12.2	78	67	6.3	26.6	0.31	0.41
-47.88, -24.65	Entisol	Fluvic Sediments	0.0-0.2	0.4-0.7	5	5.4	10.5	0.0	28	13	33.3	13.5	0.45	0.06
-47.67, -22.21	Entisol	Sandstone	0.0-0.4	1.2-2.4	5	4.8	2.3	1.2	4	7	2.9	4.8	0.04	0.04
-47.54, -21.49	Entisol	Sandstone (Triassic)	0.0-0.2	0.8-1.0	5.2	4.8	2.9	1.2	6	6	6.7	8.1	0.04	0.06
-47.09, -22.86	Entisol	Sedimentary	0.0-0.1	0.9-1.1	4.2	4.9	13.4	6.4	23	48	1.5	0.3	0.05	0.12
-47.87, -23.30	Entisol	Claystone (Permian)	0.0-0.1	0.6-0.8	4.9	5	2.9	1.7	57	26	42.3	1.5	0.32	0.05
-47.88, -24.65	Histosol	Organic Matter	0.0-0.1	0.3-0.4	4.7	3.7	15.1	19.8	19	24	5.3	14.1	1.19	0.44
-46.37, -22.43	Inceptisol	Amphibolite	0.0-0.1	0.3-0.6	6	6.5	18.6	5.2	24	44	37.3	65.0	0.22	0.21
-46.34, -22.42	Inceptisol	Gneiss	0.0-0.1	0.1-0.2	5.3	5.5	22.1	8.1	14	14	10.5	10.0	0.03	0.03
-49.13, -24.16	Inceptisol	Sandstone (Devonian)	0.0-0.3	0.5-0.7	4.8	4.8	11.0	4.7	22	27	10.3	18.6	0.21	0.44
-47.57, -24.70	Inceptisol	Sandstone (Pleistocene)	0.0-0.2	0.6-0.7	4.2	4.6	3.5	4.7	0	5	0.4	4.6	0.07	0.37
-47.88, -24.70	Inceptisol	Conglomerate	0.0-0.2	0.5-1.0	4.7	4.3	17.4	2.9	44	48	76.6	39.1	1.37	1.63
-47.79, -22.73	Inceptisol	Sandstone (Triassic)	0.0-0.2	0.5-0.8	4.9	5.4	7.0	9.3	10	12	1.2	1.4	0.04	0.05
-50.45, -22.67	Inceptisol	Sandstone	0.0-0.1	1.2-1.6	5	4.6	3.5	1.2	4	12	5.5	9.5	0.05	0.08
-48.55, -21.18	Oxisol	Basalt	0.0-0.2	1.2-1.5	5.5	6.6	9.9	1.7	53	55	128.2	135.0	0.11	0.05
-49.12, -24.18	Oxisol	Sandstone (Devonian)	0.0-0.3	1.4-1.7	4.6	4.8	14.0	4.1	28	43	18.1	48.6	0.37	0.68

Table 1 - Geographic coordinates, soil order, parent material and some chemical characteristics of each soil. Superficial and subsurface samples are denoted by A and B respectively.

(continuation)

Coordinate (Lat., Long.)	Soil Order	Parent Material	Depth		$pH_{(water)}$		OC		Clay		Fe DBC		Se	
			A	B	A	B	A	B	A	B	A	B	A	B
			m				g kg^{-1}		g kg^{-1}		g kg^{-1}		mg kg^{-1}	
-47.05, -22.90	Oxisol	Sandstone	0.0-0.2	1.1-1.5	4.7	4.8	5.2	1.7	11	19	8.6	11.1	0.04	0.08
-47.76, -22.09	Oxisol	Claystone	0.0-0.1	0.5-0.7	4.3	4.5	27.9	4.1	59	73	34.7	47.7	0.18	0.26
-47.79, -22.45	Oxisol	Basalt	0.0-0.3	0.5-0.9	4.4	4.6	16.9	5.8	70	76	75.0	63.3	0.37	0.34
-47.92, -21.42	Oxisol	Basalt	0.0-0.2	1.3-1.7	5.6	6	9.3	2.9	50	57	25.7	14.8	0.05	0.03
-47.80, -21.06	Oxisol	Diabase	0.0-0.2	1.0-1.5	6.3	5.5	8.1	4.7	49	51	85.1	81.9	0.16	0.1
-46.66, -22.16	Oxisol	Migmatite	0.0-0.2	0.9-1.3	4.6	4.9	11.0	4.1	43	53	44.2	29.8	0.2	0.22
-46.92, -22.08	Oxisol	Sandstone	0.0-0.2	1.3-2.0	5.6	5.2	4.1	1.2	14	24	9.4	12.1	0.05	0.08
-46.73, -22.28	Oxisol	Granite	0.0-0.1	0.5-1.3	5.8	6.2	16.3	1.7	30	57	24.3	44.1	0.13	0.19
-48.37, -20.17	Oxisol	Basalt	0.0-0.2	0.6-0.9	5.8	5.4	18.0	5.2	56	70	98.4	102.6	0.19	0.13
-48.08, -21.59	Oxisol	Basalt	0.0-0.3	0.7-1.0	5.2	5.3	12.2	4.1	58	64	123.7	121.0	0.09	0.07
-45.15, -21.68	Oxisol	Sandstone	0.0-0.3	0.8-1.1	6	5.2	0.2	0.1	14	23	10.4	13.0	0.05	0.09
-50.45, -23.25	Oxisol	Sandstone	0.0-0.2	1.0-1.4	4.8	4.6	3.5	1.2	16	18	10.8	14.9	0.05	0.05
-46.62, -22.72	Ultisol	Gneiss	0.0-0.1	0.4-0.6	5.5	5	8.7	2.9	18	26	4.6	6.5	0.04	0.07
-42.42, -23.13	Ultisol	Schist	0.0-0.1	0.6-0.8	4.9	4.7	16.9	3.5	28	32	16.5	34.3	0.1	0.11
-46.37, -22.44	Ultisol	Amphibolite	0.0-0.1	0.4-0.7	5.5	5.6	7.0	2.9	22	54	12.1	44.8	0.1	0.27
-46.56, -23.11	Ultisol	Granite/Gneiss	0.0-0.1	0.5-0.7	5.7	4.9	7.6	2.3	21	43	9.5	34.2	0.09	0.19
-46.56, -23.05	Ultisol	Granite/Gneiss	0.0-0.1	2.1-2.6	5.2	4.5	18.0	5.8	47	66	46.5	65.3	0.24	0.25
-48.92, -21.22	Ultisol	Sandstone (Cretaceous)	0.0-0.2	0.5-0.8	5.2	5	4.7	2.3	8	30	7.4	27.9	0.04	0.1
-49.22, -24.27	Ultisol	Sandstone (Devonian)	0.0-0.1	0.8-0.9	4.8	4.9	15.1	5.2	31	41	40.6	54.1	0.39	0.76
-47.07, -22.87	Ultisol	Siltstone (Permian)	0.0-0.6	0.7-1.2	4.7	4.7	7.0	3.5	60	63	34.7	68.0	0.32	0.16
-47.41, -21.99	Ultisol	Siltstone (Permian)	0.0-0.2	0.5-0.8	5.2	5.4	7.0	4.1	22	59	9.0	36.2	0.09	0.19
-47.68, -22.92	Ultisol	Siltstone (Permian)	0.0-0.3	0.5-0.8	5.8	5	5.2	2.3	17	51	6.2	15.8	0.04	0.13
-47.72, -23.00	Ultisol	Claystone (Permian)	0.0-0.2	0.2-0.4	5.6	4.5	2.9	3.5	12	47	4.5	14.7	0.06	0.23
-47.70, -22.98	Ultisol	Claystone (Permian)	0.0-0.2	0.3-0.7	5.7	4.6	4.1	2.3	17	38	9.6	24.5	0.12	0.14
-46.88, -22.18	Ultisol	Sandstone	0.0-0.2	1.0-1.2	5.1	5.1	8.7	2.3	22	37	10.2	16.8	0.05	0.04
-46.79, -22.16	Ultisol	Granite	0.0-0.1	0.4-1.1	5	5.1	6.4	3.5	14	54	10.4	42.4	0.04	0.11
-46.78, -22.50	Ultisol	Amphibolite	0.0-0.2	0.4-0.9	5.5	5.4	13.4	4.1	35	62	52.1	77.3	0.22	0.31

Table 1 - Geographic coordinates, soil order, parent material and some chemical characteristics of each soil. Superficial and subsurface samples are denoted by A and B respectively.

(conclusion)

-49.83, -22.22	Ultisol	Sandstone (Cretaceous)	0.0-0.2	0.7-0.8	4.8	5	2.3	1.7	3	29	3.5	13.7	0.02	0.13
-49.54, -22.40	Ultisol	Sandstone (Cretaceous)	0.0-0.2	0.8-1.2	5.1	5	2.9	1.7	6	15	5.2	10.9	0.05	0.09
-47.85, -23.33	Ultisol	Claystone (Permian)	0.0-0.1	0.4-0.8	6.5	4.3	16.3	1.7	52	65	42.1	54.7	0.26	0.29
Average	-	-	-	-	5.3	5.2	10.3	3.8	28	41	27.1	33.9	0.18	0.20
Median	-	-	-	-	5.2	5.1	9.0	2.9	23	42	11.4	21.5	0.10	0.13
1st quartlile	-	-	-	-	4.9	4.8	4.2	1.7	14	26	6.7	11.4	0.05	0.07
3st quartlie	-	-	-	-	5.6	5.5	16.3	4.7	35	56	34.7	47.0	0.22	0.25

The soil samples from different depths were analyzed separately. Low correlation was observed between the contents of Se in superficial and subsurface samples. A scatterplot for the Se concentration in both layers is presented in Figure 1. The original data were log-transformed, and the correlation coefficient was 0.49. Zhang et al. (2008) made the same comparison and observed a correlation coefficient of 0.75 for samples of Chinese soils with low to medium Se concentrations. Samples from the superficial layer (0-0.2 m) are subject to higher influence of external factors, such as weathering and atmospheric deposition, than the subsurface ones. Additionally, the heterogeneous composition of carbon compounds results in different Se contents in different soil layers.

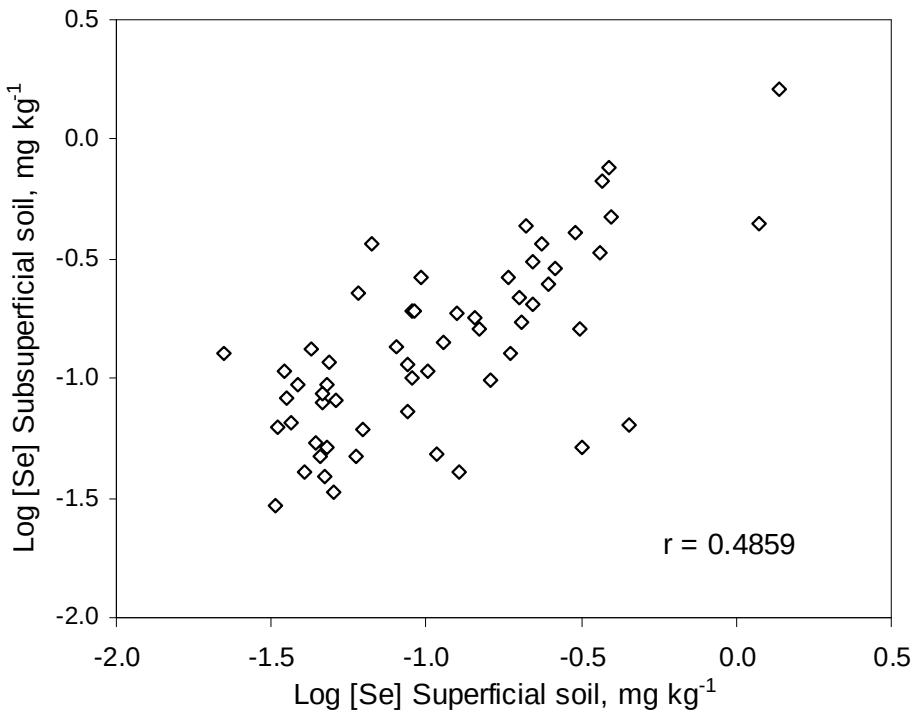

Figure 1- Scatterplot showing the correlation between log-transformed Se concentrations in superficial and subsurface soil layers.

The range of Se concentrations observed in the soils of São Paulo state was similar to those observed in other parts of the world where Se contents are classified from deficient to medium (KABATA-PENDIAS, 2010). The number of soils with very low Se concentrations, however, was much larger than in our study. The medians were 0.093 and 0.127 mg kg^{-1} Se for superficial and subsurface layers, respectively. This large number of samples with low Se contents represents a huge area of

agricultural soils across the state of São Paulo. While other researchers have described similar Se ranges and averages, their medians and quartiles were higher than those in soils from São Paulo. In Guangdong, China, median values were 0.24, 0.32, and 0.27 mg kg^{-1} (horizons A, B, and C, respectively), almost twice as high as the values detected in our study (ZHANG, et al., 2008). PEREZ-SIRVENT et al. (2010) analyzed 490 samples from Spain's Murcia region and observed that less than one quarter of soils had a Se concentration of <0.2 mg kg^{-1}.

The content of Se in foods is a consequence of the amount of Se available in soils for plants to absorb, and approximately 1% of total Se is soluble (KESKINEN et al., 2009). Total concentrations of Se in soils are commonly measured by researchers for two reasons: (i) the difficulty of determining very low concentrations of available Se in solution (SHAND et al., 2010); and (ii) the lack of a soluble Se extractor that is valid for all different soils (KESKINEN et al., 2009). In this way, Se contents extracted by aqua regia have been considered a good indicator of total Se in soil (SHAND et al., 2010).

2.3.2 Correlations among Se contents and soil attributes

Given that Se reaches food through soil, understanding the geochemical aspects correlated with Se concentrations in soil is essential. Soil is an oxidizing environment, and its relationship with Se is linked to soil attributes such as pH, OC content, and Al and Fe oxide contents that are associated with sites of positive charges in soil colloids (WINKEL et al., 2012). Correlations between Se and soil attributes were somewhat similar for superficial and subsurface soil samples (Table 2). Se concentration in the topsoil layer was strongly correlated with the charges of the soil. OC and clay contents were positively correlated with Se concentrations in soil. Both soil attributes are directly related to soil CEC, which had the most significant correlation with Se contents in the samples collected from the superficial layer. In addition, the OM may be a source of Se to the soil in its process of decomposition. Concentrations of Fe and Al oxides also showed positive correlations with Se contents in the samples from the superficial layer.

Table 2 - Correlation between Se concentration and soil attributes for superficial and subsurface samples of 58 soils of Sao Paulo state, Brazil

Superficial			Subsuperficial		
	r	*p* value		r	*p* value
CEC	0.428	**0.0008**	pH H_20	-0.319	**0.0148**
Al [d]	0.405	**0.0016**	CBD-Al	0.297	**0.0234**
Sand	-0.355	**0.0063**	pH $CaCl_2$	-0.264	**0.0450**
Clay	0.327	**0.0123**	C_{org}	0.230	0.0818
C_{org}	0.316	**0.0155**	Mn [a]	-0.206	0.1199
SiO_2 [c]	0.294	**0.0251**	Ca [b]	-0.202	0.1319
CBD-Al	0.290	**0.0275**	Clay	0.199	0.1330
CBD-Fe	0.262	**0.0471**	Al [d]	0.195	0.1417
pH H_20	-0.227	0.0861	Al_2O_3 [c]	0.170	0.2029
Silt	0.208	0.1168	Sand	-0.161	0.2273
Al_2O_3 [c]	0.201	0.1311	CBD-Fe	0.153	0.2525
pH $CaCl_2$	-0.165	0.2163	Cu [a]	-0.152	0.2537
Zn [a]	0.142	0.2884	SiO_2 [c]	0.151	0.2566
Ox-Fe	0.140	0.2935	CEC	0.111	0.4069
Ca [b]	0.070	0.5991	TiO_2 [c]	-0.091	0.4962
K [b]	0.049	0.7143	Ox-Al	-0.063	0.6406
Mn [a]	-0.028	0.8374	Fe_2O_3 [c]	-0.061	0.6486
Fe [a]	0.024	0.8603	Silt	-0.038	0.7752
Fe_2O_3 [c]	0.014	0.9172	Ox-Fe	-0.035	0.7966
Cu [a]	-0.008	0.9529	Zn [a]	-0.029	0.8269
Ox-Al	-0.007	0.9587	Fe [a]	0.023	0.8667
TiO_2 [c]	-0.005	0.9689	K [b]	-0.013	0.9254

Bold *p* value indicates a significant correlation ($p < 0.05$)
[a] Aqua regia extraction (ISO 11466:1995)
[b] Resin extraction
[c] Sulfuric acid extract
[d] KCl 1 mol L^{-1}

OC content is frequently described as the attribute most strongly correlated with Se levels in soils (YAMADA et al., 2009; PEZZAROSSA; PETRUZZELLI, 2001; ROCA-PEREZ et al. 2010). Shand et al. (2009) cited OC concentration as the only soil characteristic necessary to construct a crude map of Se distribution in topsoils from Scotland. The organic form of Se can represent more than a half of total Se in soil (YAMADA et al. 2009). In our study OC content was positively correlated with total Se in the superficial samples. The same was not observed for the subsurface samples. OC is the main provider of charges for soils in the wet tropics, and this may explain the high positive correlation between CEC and Se. The amount of OC decreased with depth, but Se concentration in the subsurface layer did not follow the same behavior. In these cases, other compounds such as Al and Fe oxides are especially important, mainly in highly weathered tropical soils.

Se levels in the samples from the subsurface layers showed high correlations with pH and the quantity of Al oxides (Table 2), and both attributes are strongly linked to the balance of charge in highly weathered soils. In the subsurface layers, where the effect of OC is less pronounced, the pH-dependent charges from oxides' surfaces are the most important source of charge. pH had a negative correlation with Se concentration: as pH increases, there is an increase in negative charge (FONTES; ALLEONI, 2006), thus repelling Se anionic species. In China, Zhang et al. (2008) evaluated a large number of samples from different depths and observed a high negative correlation between soil Se concentration and soil pH. The predominant species of Se in soil are SeO_3^{2-} and SeO_4^{2-}. As a consequence, Se adsorption is intensified as positive charges increases. In depth, OC levels were not sufficient to correlate with Se concentration in soils (Table 2).

In highly weathered soils, the surfaces of Al and Fe oxides, under acidic conditions (low pH) have an excess of positive charge that binds selenite and selenate (HAYES, et al. 1987; PEAK, 2006). In our study, Al and Fe oxide contents were positively correlated with Se contents irrespective of depth. Soils from temperate areas have not shown significant correlations between Se content and Fe oxide content (PÉREZ-SIRVENT et. al., 2010; SHAND et. al., 2010). As the charge on the surfaces of Al and Fe oxides is pH-dependent, the effect of such oxides on Se adsorption is accentuated in acidic tropical soils. Many studies regarding Se adsorption in soils have been carried out (PEAK; SPARKS, 2002; FOSTER; BROWN; PARKS, 2003; LOFFREDO et al., 2011) providing information about the high affinity of Se to oxides and its variation with pH. In most cases, Se is strongly adsorbed on Al and Fe oxides as inner-sphere surface complexes, and the affinity decreases with increasing pH (HAYES et al., 1987).

In natural areas without human interference, parent materials are the most important geochemical parameter related to Se content in soils. Although all kinds of parent rock may contain significant concentrations of Se, sedimentary rocks tend to contain higher Se levels (KABATA-PENDIAS, 2010). In our study, parent material was not correlated with total Se content in soils, not even between the different geologic periods of the sedimentary rocks. This fact may be a consequence of the very low Se concentrations in most samples. However, within the highest quartile (0.217 and 0.237 mg kg^{-1} for superficial and subsurface samples, respectively) there was a tendency for a positive correlation with sedimentary rock sources. Two of 14

soils were derived from non-sedimentary rocks, one was derived from organic matter deposition, and another from igneous rock. In Scotland, Fordyce et al. (2010) concluded that information on the geological parent material of soils can partly predict differences in Se concentration. In areas with seleniferous soils, correlations with soil proprieties were not observed. This may be a consequence of inappropriate soil management (ZHU et al., 2008) or Se-rich parent material, such as black slates in China (KUNLI et al., 2003).

Different soil types did not show consistently different Se concentrations. The two exceptions were the Histosol and the Inceptisols (average 0.28 and 0.44 mg kg^{-1} Se in superficial and subsurface layers, respectively). Because the Histosol contains a large amount of organic matter, it can adsorb or immobilize Se, which increases the total content of Se in the soil. The Inceptisols in our study were mostly derived from sedimentary rocks, which may have caused a higher mean Se level compared to the other soils. In addition, Inceptisols are more strongly influenced by parent material than the other soils, so the effects of weathering are less accentuated in this soil type. All other soil classes had lower mean Se concentrations, ranging from 0.13 to 0.2 mg kg^{-1}.

The Brazilian regulatory agency has defined the 75% percentile as the standard concentration for soil quality (CONAMA, 2009). In our experiment, the value representing the 75% percentile was 0.22 mg kg^{-1} Se. This result is very similar to the preliminary value established by the Environmental Agency of São Paulo State (CETESB, 2005), 0.25 mg kg^{-1}.

In conclusion, Se levels in soil were dependent on parent material supply. In tropical soils, the maintenance of Se in the soil phase is mainly determined by the contents of organic matter (mainly in topsoil) and oxides. In São Paulo state, the background levels of Se in soils are not sufficient to supply the requirements of plants and may produce food with low levels of Se.

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3 EFFECTS OF VARYING pH ON SELENITE AND SELENATE ADSORPTION IN SELECTED TROPICAL SOILS

Abstract

The adsorption of selenium (Se) on soil is important due to the relevance of Se to environmental and health issues. The adsorption of Se(IV) and Se(VI) was evaluated on soil samples from São Paulo state, Brazil, as a function of varying pH, and the experimental data were fitted to the constant capacitance model. Adsorption experiments were conducted for 15 soil samples, after the addition of 20 µmol L^{-1} of either Se(IV) or Se(VI), and the adjusted pH ranged between 2.5 and 10. Se(IV) adsorption was high for all soils, decreased with increasing pH, was strongly correlated to Fe and Al oxides contents. On the other hand, Se(VI) adsorption was very low at pH values commonly found in agricultural soils, except for the highly weathered Rhodic Acrudox. The constant capacitance model fit the Se(IV) and Se(VI) adsorption data well. Optimizations of mono and bidentate complexation and surface protonation constants were used for the Se(IV) adsorption data. For Se(VI), optimizations for the two monodentate species were employed.

Key words: Se(IV); Se(VI); surface complexation model; Brazilian soils; FITEQL

3.1 Introduction

Selenium (Se) is a metalloid present in trace amounts in all biogeochemical environments. Low quantities of Se are essential for animal and human nutrition. The recommended daily intake for an adult is 40 - 55 µg (KABATA-PENDIAS; MUKHERJEE, 2007), although Se can have deleterious effects on health in a narrow concentration range (40 to 400 µg per day). The presence of Se in food is strongly correlated to the concentration of Se in the soils where the food was grown (MINORSKY, 2003). Se has not been proven to be a required micronutrient for plants, but it can accumulate in plant tissues and can produce toxic symptoms in extreme cases (KABATA-PENDIAS, 2010). However, Se accumulation in plants is important because the ingestion of plants is the main pathway by which Se enters the food chain. Both Se toxicity and Se deficiency are the result of Se content in soils and Se behavior in different soil phases.

The amount of Se in soils depends on natural sources or human activities. Both Se-deficient and Se-contaminated areas have been reported (TAN et al., 2002). Deficient areas require strategies for crop and livestock amendment. Soil fertilization is an option that has been adopted in some areas, like Finland (KESKINEN et al. 2009). The behavior of Se in soils is mostly pH-dependent. So, the knowledge of the

effect of pH on Se adsorption is important mainly in highly weathered humid tropical soils, where studies are scarce.

The two forms of Se usually found under natural soil conditions are selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}), which behave differently in soils. Se(IV) forms strong bonds with soil surfaces as inner-sphere complexes (HAYES et al., 1987), and for this reason is considered the less available from an environmental perspective. Se(VI) is less adsorbed in soil and consequently more bioavailable (GOH; LIM, 2004) because it forms outer- and inner-sphere complexes, as several authors have reported for pure minerals (MANCEU; CHARLET, 1994; PEAK; SPARKS, 2002; FOSTER; BROWN; PARKS, 2003; ROVIRA et al., 2008).

Se adsorption occurs on soil sites with net positive balance of charges particularly present on the surface of sesquioxides. Se adsorption in pure minerals has been studied to better understand the relationship between Se(IV) and Se(VI) on the one hand and soil colloids (GOLDBERG et al., 2007), yielding some interesting results. For example, Se adsorption was positively correlated with free Fe oxide content (DHILLON; DHILLON, 1999; HYUN et al., 2006), and pH was negatively correlated with selenite and selenate adsorption (BARROW; WHELAN, 1989; GOH; LIM, 2004).

Surface complexation models based on a thermodynamic approach are able to describe surface species, mass balance, and chemical reactions (SPOSITO, 1983). Empirical models, such as Freundlich and Langmuir, are valid only for the conditions under which the experiment was conducted (GOLDEBERG; LESCH; SUAREZ; 2007). The constant capacitance model (CCM) has been used successfully to describe Se adsorption in soils (GOLDBERG; GLAUBIG, 1988; SU; SUAREZ, 2000; GOLDBERG; LESCH; SUAREZ; 2007; GOLDEBERG; HYUN; LEE, 2008). The assumptions of the CCM are: i) only inner-sphere complexes are formed; ii) anion adsorption occurs via a ligand exchange mechanism with reactive surface hydroxyl groups; iii) ions from the background electrolyte do not form surface complexes; and iv) the relationship between surface charge and surface potential is linear (SPOSITO, 1983).

The objectives of our study were to investigate the sorption of selenite and selenate on 15 tropical soils from São Paulo State in Brazil. The constant capacitance model was fit to the experimental data as a function of varying pH in the equilibrium solution.

3.2 Material and Methods

Fifteen soils with contrasting attributes (texture; Al and Fe oxides; and organic matter contents) was selected from soil orders representative of the Brazilian state of São Paulo (Table 1). All soil samples were collected from the upper layer (0.0-0.2 m) in areas with native vegetation. A subsurface sample (1.2-1.6 m) of the Rhodic Acrudox (LVwf-B) was also collected, because of its net positive balance of charge, thus representing conditions of extreme weathering due a low presence of OM. Samples were air dried, crushed, and passed through a 2-mm sieve.

Some soil chemical characteristics are given in Table 1. The pH was measured potentiometrically in a 1:2.5 soil/water solution. Carbon components were determined by carbon coulometer. Total carbon was determined by furnace combustion at 950°C; inorganic carbon was measured using the acidification module and heating; and organic carbon content was calculated as the difference between total and inorganic carbon. Specific surface area was determined by Cihacek and Bremner's (1979) method, using ethylene glycol monoethyl ether (EGME) adsorption. Free Fe and Al were extracted by dithionite-citrate-bicarbonate (DCB) (MAHRA; JACKSON, 1960), and the contents were determined via inductively coupled plasma (ICP) emission spectrometry. The cation exchange capacity (CEC) was determined by compulsive exchange proposed by Gillman (1979) for highly weathered soils. Data on mineralogy and additional information about our soil samples can be found in Soares (2004).

Table 1 - Classification and chemical characteristics of soils

Soil	pH_{water}	Clay	OC	IOC	SA	Fe	Al	CEC	SOH
		---- g kg^{-1}----		µg g^{-1}	m^2 g^{-1}	----- g kg^{-1}-----		$mmol_c$ kg^{-1}	µmol kg^{-1}
CX (sandy-clay-loam, Typic Haplustept)	4.3	243	14.4	*	38.9	19.3	2.3	22.7	149.1
GM (clay, Aquic Haplohumults)	4.9	476	22.9	*	105.3	4.9	4.8	50.4	404.0
LA-1 (sandy-clay-loam, Xanthic Hapludox)	4.8	222	51.1	*	25.9	19.7	2.2	23.4	99.2
LAwf (clay, Anionic Acrudox)	4.7	470	8.7	*	88.4	113.3	3.9	16.9	339.1
LV-2 (clay, Rhodic Eutrudox)	4.6	530	18.9	*	60.4	86.6	5.1	30.6	231.6
LVA-2 (sandy-clay-loam, Typic Hapludox)	4.2	221	14.3	*	6.2	13.6	1.2	15.5	23.6
LVef (clay, Rhodic Hapludox)	7.3	684	29.7	178.6	86.5	185.2	4.4	60.4	331.6
LVwf- A horiz. (clay, Rhodic Acrudox)	4.7	716	14.4	*	92.4	208.2	5.7	23.7	354.6
LVwf- B horiz. (clay, Rhodic Acrudox)	5.6	663	29.8	*	56.2	232.0	6.1	23.7	215.7
MT (clay, Mollic Hapludalfs)	5.8	543	18.7	*	165.6	113.3	4.7	105.5	635.1
NVef (clay, Rhodic Eutrudult)	5.5	658	4.3	*	90.3	192.2	4.8	61.1	346.6
PV-2 (sandy loam, Typic Rhodudalfs)	5.7	427	118.5	*	64.8	51.3	2.0	54.4	248.5
PVA-3 (loam, Typic Hapludults)	5.4	247	15.3	*	25.7	32.9	4.4	44.6	98.5
RL (loam, Lithic Dystrudepts)	5.9	142	26.1	*	34.3	7.5	0.3	33	131.7
RQ (loamy sand, Typic Quartzipsamment)	4.4	80	22.2	*	2.0	3.0	0.6	7.6	7.5

* Below detection limit (150 µg g^{-1})
pH: in water extract
SA: Specific surface area (CIHACEK; BREMNER, 1979)
Fe and Al: dithionite-citrate-bicarbonate (MAHRA; JACKSON, 1960)
*S*OH: Total number of reactive sites

The adsorption envelope experiment was carried out in a batch system. One gram of soil and 25 ml of solution were added to 50-ml polypropylene centrifuge tubes. For both Se(IV) and Se(VI), the concentration was 20 µmol L^{-1}, added as Na_2SeO_3 and Na_2SeO_4, respectively. The pH varied from 2.5 to 10 and was adjusted by adding either 1.0 mol L^{-1} HCl or 1.0 mol L^{-1} NaOH solutions. The supporting electrolyte was 0.1 mol L^{-1} NaCl, and the reaction time was 2 h on a reciprocating shaker at room temperature (24.5^{o}C ±0.2). Solutions were subsequently centrifuged for 20 min at 10,000 rpm, the pH of the supernatant solutions determined, and the solution passed through a 0.45-µm membrane filter. Se concentration was determined in all solutions using ICP emission spectrometry. The concentration of adsorbed Se was calculated as the difference between the amount added and the

amount remaining in solution after equilibrium. As observed by Goldberg; Lesch; Suarez (2007) and Hyun et al. (2006), the oxidation of Se(IV) to Se(VI) during the adsorption process was lower than 10%, even with shaking times longer than 2 h. For this reason, Se oxidation was not taken into account in this study.

The constant capacitance model (STUMM et al., 1980) was fit to the Se(IV) and Se (VI) adsorption data, as described in detail by Goldberg et al. (1992). FITEQL 4.0 computer software (HERBELIN; WESTALL, 1999) fit the surface capacitance constant to the sorption data using a non-linear least squares optimization routine (GOLDBERG; LESCH; SUAREZ, 2007). Considering *S*OH as a functional group of oxide minerals from the clay particle soil fraction, protonation and deprotonation are defined as

$$SOH_{(s)} + H^{+}_{(aq)} \leftrightarrow SOH^{+}_{2(s)} \tag{1}$$

$$SOH_{(s)} \leftrightarrow SO^{-}_{(s)} + H^{+}_{(aq)} \tag{2}$$

The surface complexation reactions with Se(IV) are presented in equations 3, 4 and 5, while the reactions with Se(VI) are described in equations 6, 7 and 8:

$$SOH_{(s)} + H_2SeO_{3(aq)} \leftrightarrow SHSeO_{3(s)} + H_2O \tag{3}$$

$$SOH_{(s)} + H_2SeO_{3(aq)} \leftrightarrow SSeO^{-}_{3(s)} + H^{+}_{(aq)} + H_2O \tag{4}$$

$$2SOH_{(s)} + H_2SeO_{3(aq)} \leftrightarrow S_2SeO_{3(s)} + 2H_2O \tag{5}$$

$$SOH_{(s)} + H_2SeO_{4(aq)} \leftrightarrow SHSeO_{4(s)} + H_2O \tag{6}$$

$$SOH_{(s)} + H_2SeO_{4(aq)} \leftrightarrow SSeO^{-}_{4(s)} + H^{+}_{(aq)} + H_2O \tag{7}$$

$$2SOH_{(s)} + H_2SeO_{4(aq)} \leftrightarrow S_2SeO_{4(s)} + 2H_2O \tag{8}$$

The intrinsic equilibrium constants considered for the previously described complexation reactions are

$$K_{+}(\text{int}) = \frac{[SOH_2^+]}{[SOH][H^+]}\exp(F\psi / RT) \tag{9}$$

$$K_{-}(\text{int}) = \frac{[SO^-][H^+]}{[SOH]}\exp(-F\psi / RT) \tag{10}$$

$$K^1_{\text{Se(IV)}}(\text{int}) = \frac{[SHSeO_3]}{[SOH][H_2SeO_3]} \tag{11}$$

$$K^2_{\text{Se(IV)}}(\text{int}) = \frac{[SSeO_3^-][H^+]}{[SOH][H_2SeO_3]}\exp(-F\psi / RT) \tag{12}$$

$$K^3_{\text{Se(IV)}}(\text{int}) = \frac{[S_2SeO_3]}{[SOH]^2[H_2SeO_3]} \tag{13}$$

$$K^1_{\text{Se(VI)}}(\text{int}) = \frac{[SHSeO_4]}{[SOH][H_2SeO_4]} \tag{14}$$

$$K^2_{\text{Se(VI)}}(\text{int}) = \frac{[SSeO_4^-][H^+]}{[SOH][H_2SeO_4]}\exp(-F\psi / RT) \tag{15}$$

$$K^3_{\text{Se(VI)}}(\text{int}) = \frac{[S_2SeO_4]}{[SOH]^2[H_2SeO_4]} \tag{16}$$

where F is the Faraday constant, C mol_c^{-1}; ψ is the surface potential in V; R is the universal gas constant in J mol^{-1} K^{-1}; T is absolute temperature in K; and species in brackets are their concentrations in mol L^{-1}. Bidentate bonds require at least twice the sites required in the monodentate surface complexes (GOLDBERG; LESCH; SUAREZ, 2007). For this reason, in the bidentate equations (eq.13 and 16), the surface complex charges were squared.

The mass balance of the surface functional groups for monodentate and bidentate, respectively, for Se(IV) are

$$[SOH]_T = [SOH] + [SOH_2^+] + [SO^-] + [SHSeO_3] + [SSeO_3^-] \tag{17}$$

$$[SOH]_T = [SOH] + [SOH_2^+] + [SO^-] + 2[S_2SeO_3] \quad (18)$$

and the mass balance for Se(VI) – monodentate and bidentate – are

$$[SOH]_T = [SOH] + [SOH_2^+] + [SO^-] + [SHSeO_4] + [SSeO_4^-] \quad (19)$$

$$[SOH]_T = [SOH] + [SOH_2^+] + [SO^-] + 2[S_2SeO_4] \quad (20)$$

The expressions of charge balance for monodentate are

Se(IV): $$\sigma = [SOH_2^+] - [SO^-] - [SSeO_3^-] \quad (21)$$

Se(VI): $$\sigma = [SOH_2^+] - [SO^-] - [SSeO_4^-] \quad (22)$$

and the charge balance expression for bidentate for both redox states is

$$\sigma = [SOH_2^+] - [SO^-] \quad (23)$$

where σ is the surface charge ($mol_c\ L^{-1}$). The surface potential is related to the surface charge according to equation 24, in which *C* is capacitance in F m^{-2}; S_a is surface area in $m^2\ g^{-1}$; and C_p is suspension density in g L^{-1}.

$$\sigma = \frac{CS_aC_p}{F}\psi \quad (24)$$

The FITEQL initial inputs were taken from previous studies. The capacitance value that we used (C=1.06 F m^{-2}) was considered optimum for Al oxide by Westall; Hohl (1980). The protonation and the deprotonation constants were $logK_-(int)$=-8.95 and $logK_+(int)$=7.35, following Goldberg; Sposito (1984). The number of the reactive site was recommended by Davis; Kent (1990) for natural materials as N_s=2.31 sites nm^{-2}; this information is necessary to calculate the total sites as shown by Karamalidis; Dzombak (2010). Variance or goodness-of-fit (V_y) was calculated by the software as

$$V_Y = \frac{SOS}{df} \quad (25)$$

where *SOS* is the weighted sum of squares of residuals and *df* is degrees of freedom (HERBELIN; WESTALL, 1996).

3.3 Results and Discussion

3.3.1 Effect of pH on Se(IV) adsorption

Selenite adsorption was high for the majority of the soils examined (Figures 1 to 3). The three exceptions (LVA-2, RL and RQ) were sandy-textured soils which have the lowest number of sites for adsorption. For all soils Se(IV) adsorption decreased with increasing pH of the solution. This behavior is a consequence of the decrease in the number of positive charges on the variable charge soil components. In humid tropical soils, positive charges are attributed to sesquioxides and organic matter (ALLEONI et al., 2009). Several researchers have reported decreasing Se(IV) adsorption as a function of increasing pH (BARROW; WHELAN, 1989; GOLDBERG; HYUN; LEE, 2008; LEE; DOOLITTLE; WOODARD, 2011). Soil acidity is commonly corrected with lime in Brazilian soils, and pH increased to approximately 6.0. At that level of pH, most of the soil samples in our study adsorbed between 70 and 100% of the total Se(IV) in solution in our experiments.

The Se(IV) adsorption data fell into two distinct groups of soils. The first comprises soils where a gradual decrease of Se(IV) adsorption was observed as pH increased (Figures 1 and 3). A different trend was observed in the second group (LAwf, LVef, LVwf-A, LVwf-B, MT, NVef). In these soils, a plateau was observed at low pH values. Decreases in Se(IV) adsorption were observed under more alkaline conditions, starting at pH values of approximately 7 (Figure 2).

The only soil with high OM content (GM) showed a special trend, because adsorption was less affected by pH increases than for the other soils across the entire pH range (Figure 1). In a laboratory study, Se(IV) was strongly adsorbed by pure humic acid in solution (KAMEI-ISHIKAWA et al., 2008). The sandy-textured soils (LVA-2, PVA-3, RL, RQ) had lower Se(IV) adsorption. The main soil compounds responsible for Se(IV) adsorption are present in the clay fraction (GOLDBERG, 2011). In Indian soils, a significant correlation was observed between Se(IV) adsorption and clay content (DHILLON; DHILLON, 1999). The soil samples CX, LA-1, LV-2, PV-2, had high clay content, although a constant decrease in Se(IV) adsorption with increasing pH was observed. This may reflect the fact that the mineralogy of these soils is primarily kaolinite, as described by Bar-Yosef; Meek (1987). LVA-2 and PVA-3 have similar textures, but show different Se(IV) adsorption trends because of the higher concentration of Fe oxides in PVA-3.

The highest levels of Se(IV) adsorption, even at high pH, occurred in soils with the highest degree of weathering: LAwf, LVef, LVwf-A, LVwf-B, MT, NVef (Figure 1 and 2). These soils had high amounts of oxides and showed maximum Se(IV) adsorption across a large range of pH, decreasing only at medium alkalinity. The high affinity of Se(IV) for these minerals is well known, as it is for hematite (DUC; LEFÈVRE; FÉDOROFF, 2006; ROVIRA et al., 2008), goethite (HIEMSTRA et al., 2007), aluminum oxide (PEAK, 2006), and magnetite (MARTÍNEZ et al., 2006). LVwf-A and LVwf-B are superficial and subsurface samples of the same soil profile horizons, respectively. In the B-horizon adsorption of Se(IV) was higher than in the superficial horizon at pH higher than 6.7, probably because of the lower amount of OM covering the surfaces of the oxide colloids.

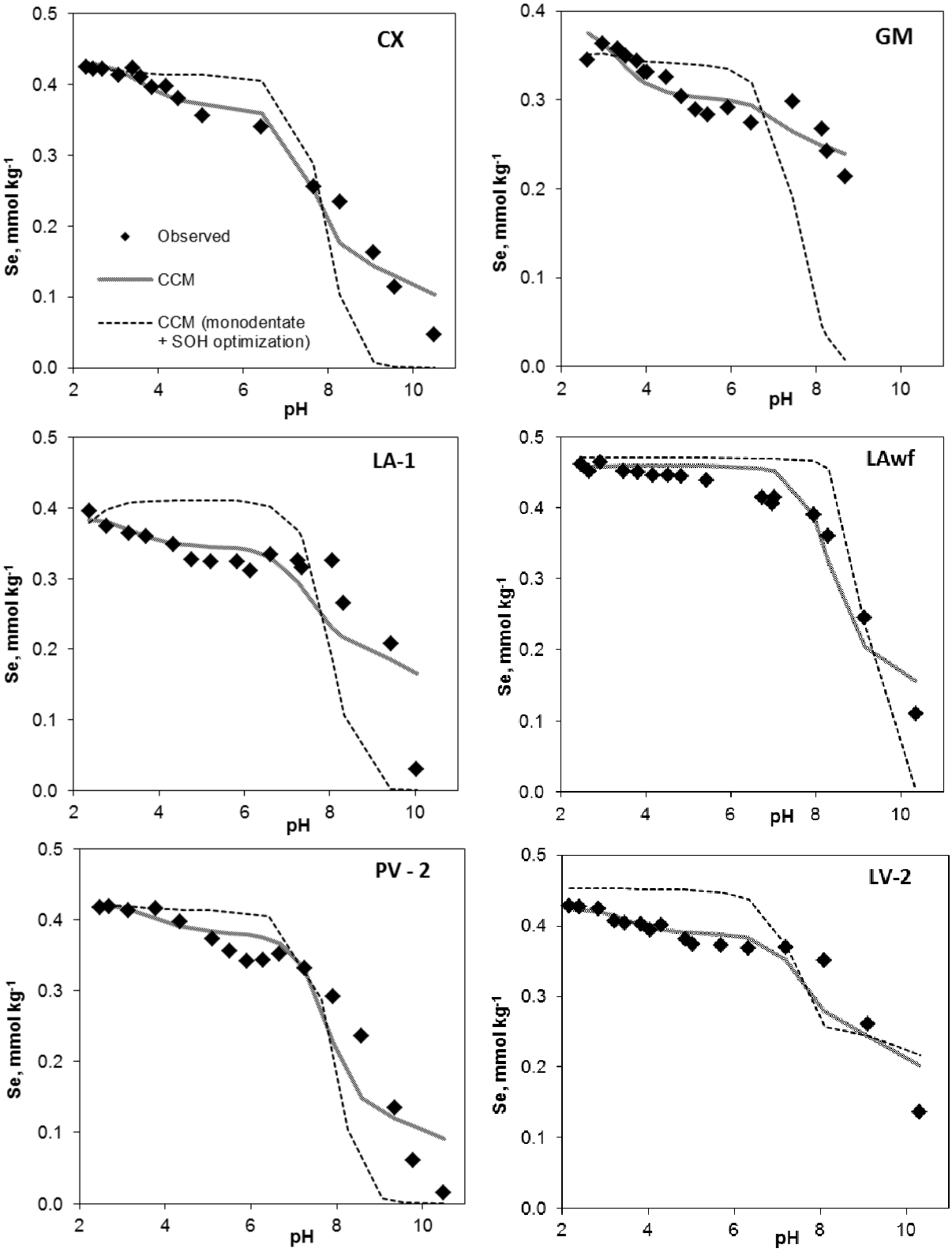

Figure 1- Se(IV) adsorption envelopes of the soils with the highest adsorption, and showing the fit of the constant capacitance model.

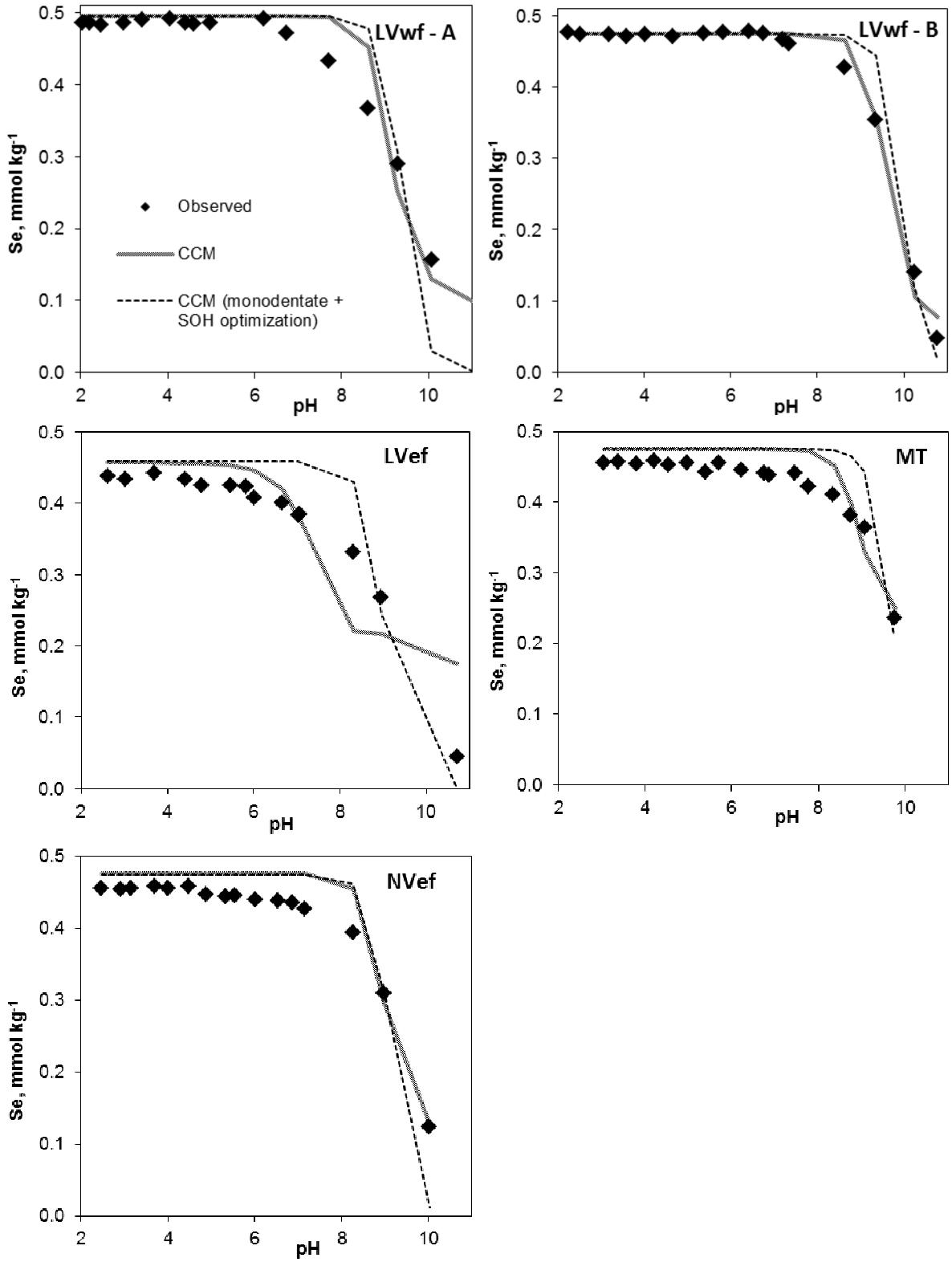

Figure 2 - Se(IV) adsorption envelopes of the soils with the highest adsorption, showing the fit of the constant capacitance model.

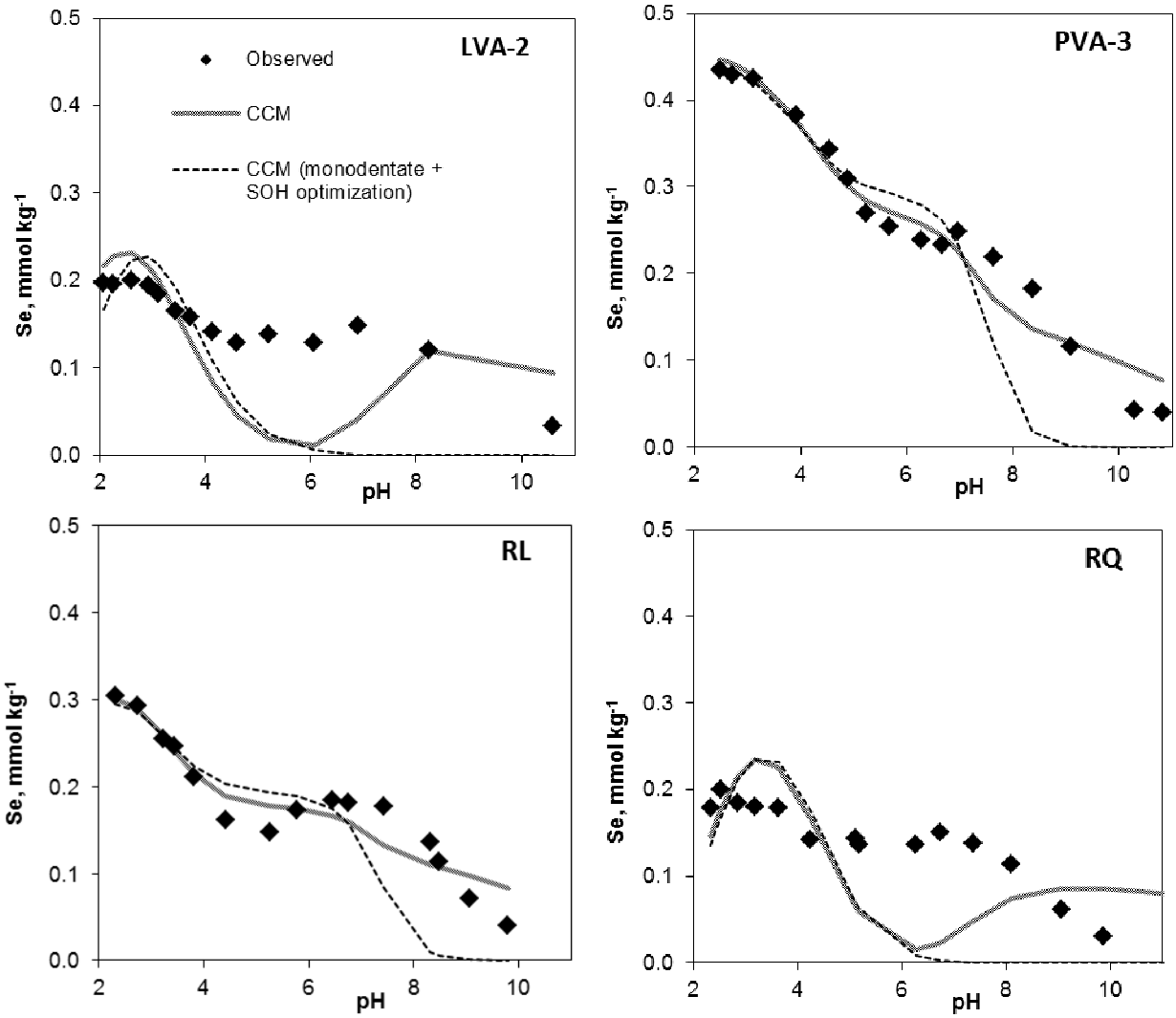

Figure 3 - Se(IV) adsorption envelopes of the soils with the lowest adsorption, showing the fit of the constant capacitance model.

3.3.2 Effect of pH on Se(VI) adsorption

Se(VI) adsorption was lower than Se(IV) adsorption on the soils, as has been reported previously by several authors (BARROW; WHELAN, 1989; GOH; LIM, 2004; HYUN et al., 2006). This is a consequence of the weak bonding of selenate with iron oxide (HAYES et al., 1987). Se(VI) adsorption behavior was similar for most soil samples, and maximum Se(VI) adsorption was observed at the lowest pH. Adsorption decreased sharply until around pH 4 and at higher pH values it was very low (Figures 4 to 6). In this case, Se(VI) adsorption is negligible for pH values between 5.5 and 6.5, commonly found in Brazilian agricultural soils. OM was not an important soil component for Se(VI), diverging from the observed for selenite adsorption as can be seen in soil GM (Figure 4). This behavior was explained by

Loffredo et al. (2011) as a consequence of the low zero point of charge of the humic substances.

As observed in the adsorption of Se(IV), selenate adsorption was very low in soils with high content of sand (LVA-2, PVA-3, RL and RQ in Figures 5 and 6). This negative correlation between Se(VI) adsorption in sandy to sandy-loamy textured-soils has been reported for tropical soils (ABREU et al., 2011). Low amounts of adsorbed Se(VI) were observed in 18 sandy-textured soils from the United States (clay contents between 10 and 29 g kg^{-1}), and decreased gradually as pH increased in soil containing of 5.22 µmol L^{-1} of Se (HYUN et al., 2006).

The only exception to this trend among the soils was the Rhodic Acrudox at both depths (LVwf-A and LVwf-B in Figure 5). LVwf showed a maximum Se(VI) adsorption higher than that of all other soils: 100% in LVwf compared to less than 70% in the others. The second difference observed in the LVwf was a plateau of maximum adsorption up to pH values of 3.5 and 4.5 (A and B horizons, respectively, of LVwf). At higher pH levels, Se(VI) adsorption decreased with increasing soil solution pH, and became insignificant at pH values higher than 6.5 and 7.5, for superficial and subsurface samples respectively. A possible cause of such behavior is the high amount of oxides present in the LVwf samples (208.2 and 232.0 g kg^{-1} of DCB-Fe for the A and B horizons, respectively).

Adsorption of Se(VI) on pure oxides has been studied in detail. Rovira et al. (2008) described Se(VI) adsorption on hematite and goethite, both of which adsorbed high amounts of Se(IV), but with different curve trend. Se(VI) adsorption on goethite decreased gradually with increasing pH. On the other hand, Se(VI) adsorption on hematite was similar to Se(VI) adsorption in LVwf, the maximum adsorption observed at pH 6. This different affinity was explained by PEAK; SPARKS (2002) as follows: Se(VI) only forms inner-sphere surface complexes on hematite, but it forms a mixture of outer- and inner-sphere surface complexes on goethite. Peak (2006) evaluated Se(VI) adsorption on a pure Al oxide and found a curve similar to that observed for the LVwf samples. These results reinforce the importance of hematite and aluminum oxide in Se(VI) adsorption on highly weathered tropical soils.

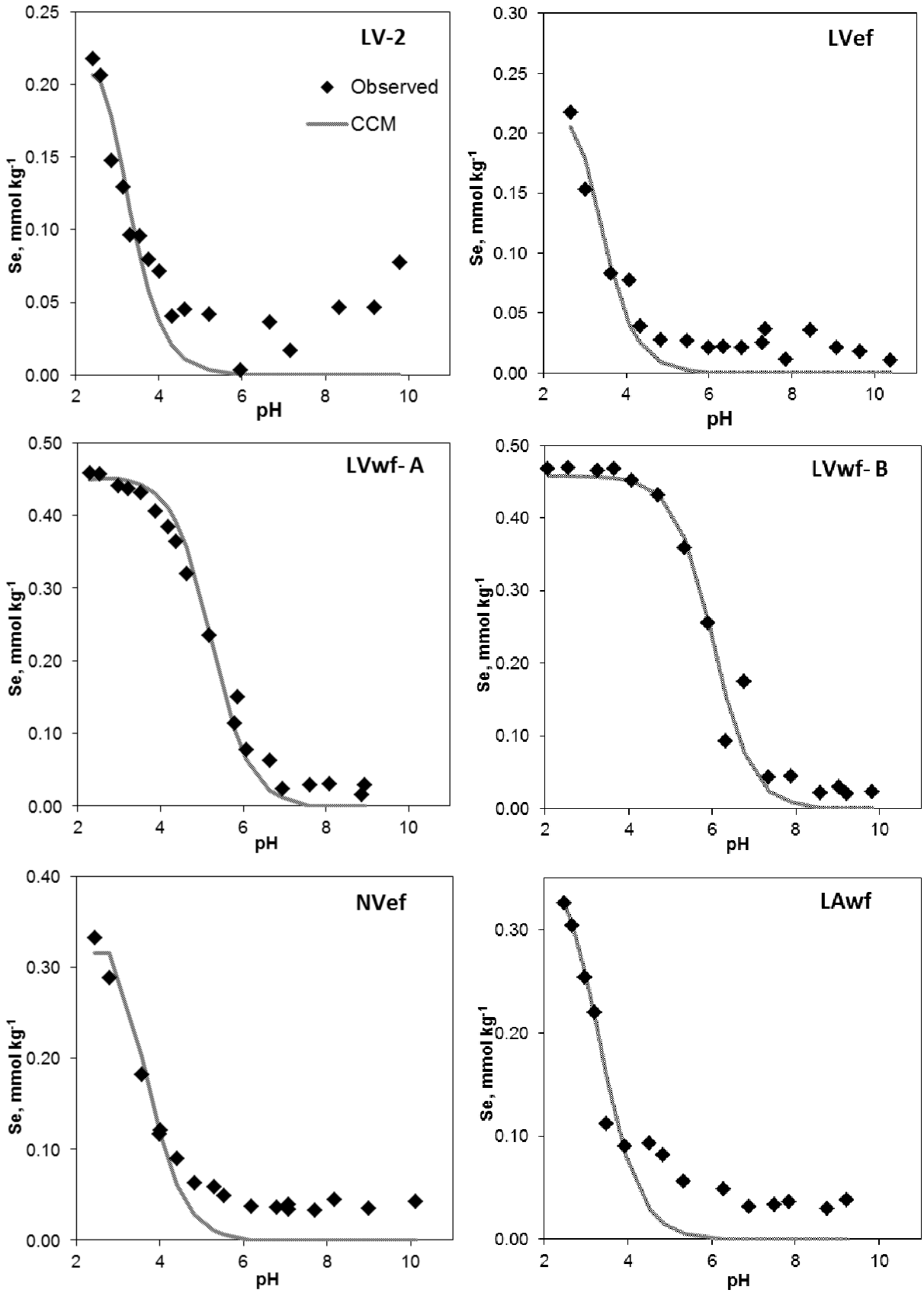

Figure 4 - Se(VI) adsorption envelopes of the soils with the highest adsorption, showing the fit of the constant capacitance model.

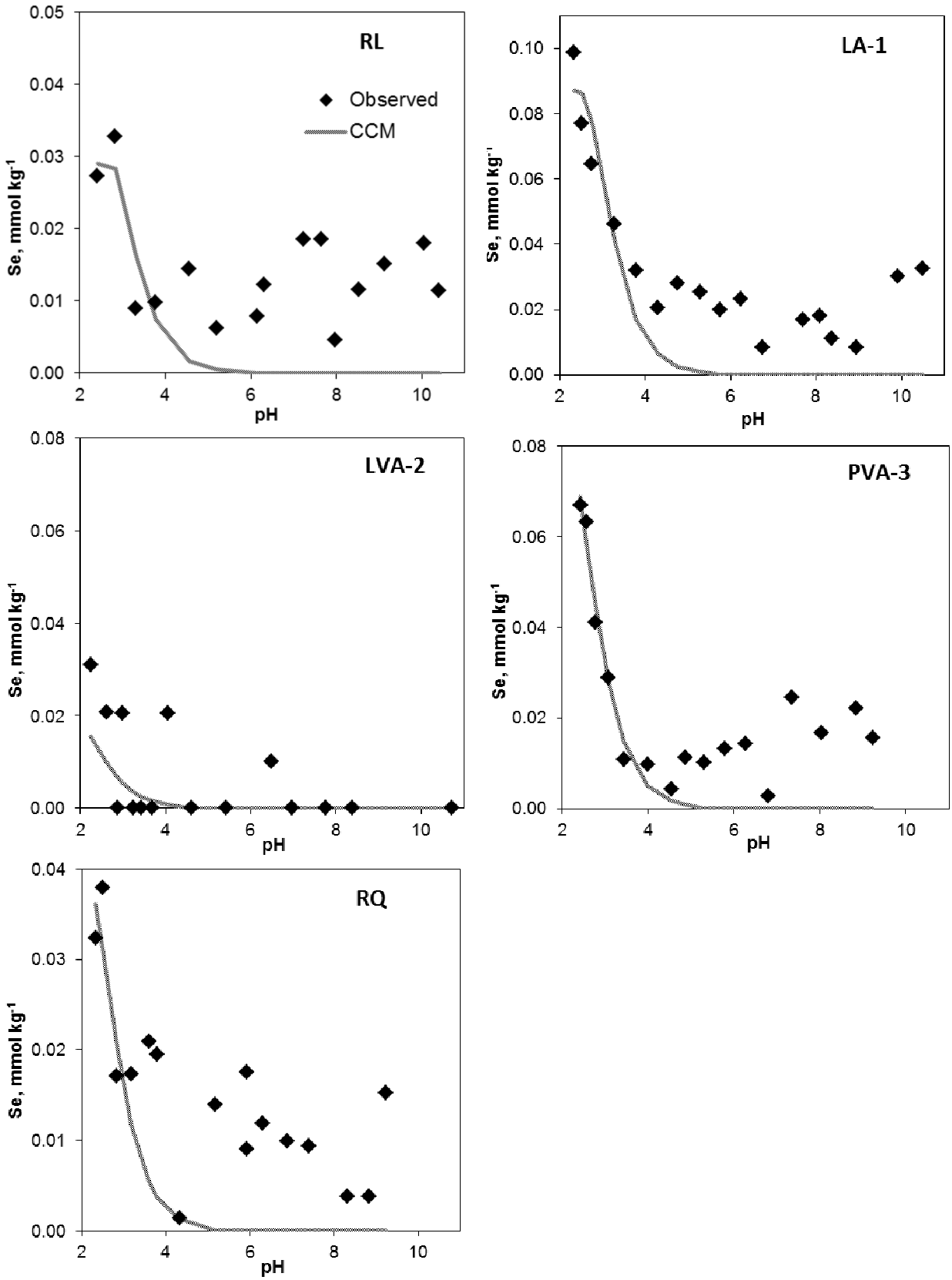

Figure 5 - Se(VI) adsorption envelopes of the soils with the lowest adsorption, showing the fit of the constant capacitance model.

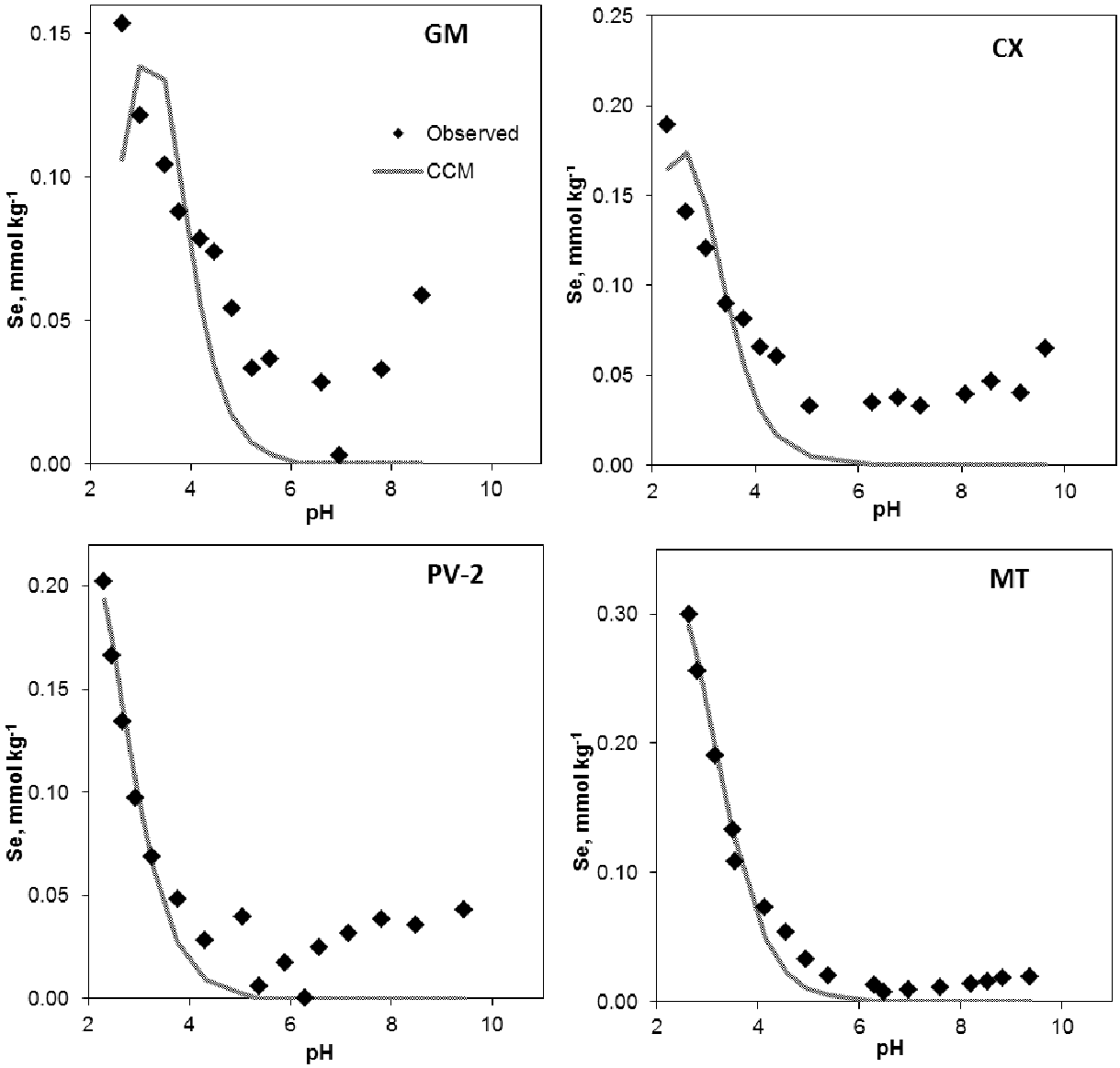

Figure 6 - Se(VI) adsorption envelopes of the soils with the median adsorption, showing the fit of the constant capacitance model.

3.3.3 Chemical modeling of Se adsorption on soil

For both Se(IV) and Se(VI), the surface complexation constants were optimized separately for monodentate and bidentate inner-sphere surface complexation constants. In selenite optimization, only the monodentate Se(IV) surface species *S*HSeO$_4$ (Log $K^1_{Se(IV)}$) did not converge. The simultaneous optimization of monodentate (*S*SeO$_3^-$) and bidentate improved the quality of fit, when evaluated by goodness-of-fit, an error parameter calculated by the FITEQL software. Additionally, protonation constant values were optimized simultaneously with the former optimization (Log $K^2_{Se(IV)}$ and Log $K^3_{Se(IV)}$) in order to improve model fit. These optimizations did not converge for five soil samples with higher oxide contents (LVef;

LVwf-A; LVwf-B; MT; NVef). The complexation constants were underpredicted for the two sandy-textured soils (LVA-2 and RQ) that adsorbed low amounts of Se(IV). All surface complexation constants from each soil sample and their respective errors are provided in Table 2. In a study of selenite adsorption envelopes carried out with 45 soil samples from the United States, Goldberg; Lesch; Suarez (2007) obtained optimization only for Log $K^2_{Se(IV)}$ and Log K_+ (int). On average the surface complexation constants for the United States soils were lower than the constants observed for tropical Brazilian soil samples.

Table 2 - Constant capacitance model surface complexation constants and goodness of fit (error) in the pH-dependent adsorption of Se IV

Soil	Log $K^2_{Se(IV)}$	Log $K^3_{Se(IV)}$	Log K_+ (int)	Variance *
CX	0.371	-5.532	2.542	0.882
GM	-0.518	-6.140	2.161	0.487
LA-1	0.473	-4.936	2.070	3.791
LAwf	1.054	-6.030	1.251	1.127
LV-2	0.369	-5.490	2.325	1.111
LVA-2	-3.295	-3.527	8.494	7.205
LVef	-0.440	-5.792	NC	4.349
LVwf-A	2.208	-6.207	NC	1.497
LVwf-B	3.169	-5.924	NC	0.371
MT	1.761	-6.239	NC	1.099
NVef	1.929	-6.165	NC	1.231
PV-2	0.373	-6.013	2.703	2.575
PVA-3	0.054	-5.288	3.448	1.123
RL	-0.409	-5.659	2.491	0.949
RQ	-2.606	-1.957	9.578	8.254

* Goodness-of-fit equals the sum of squares divided by the degrees of freedom
NC: No Convergence

Inner-sphere surface complexation is an assumption of the constant capacitance modeling. Se(VI) complexation on soil components is not totally understood, however. Some researchers have reported weak bonding of Se(VI) to soil surface complexes (HAYES et al. 1987; PEAK; SPARKS, 2002; ROVIRA et al., 2008). In our study, inner-sphere surface complexation was taken into account in the Se(VI) adsorption data, as it has been already described for clay minerals (MANCEU; CHARLET, 1994; SU; SUAREZ, 2000; PEAK, 2006).

The two monodentate surface complexation constants for species ($SHSeO_4$ and $SSeO_4^-$) were optimized simultaneously and produced a lower data fit error

(Table 3). The optimizations of Se(VI) bidentate complexation (Log $K^3_{se(VI)}$) and the protonation complex (Log K_+ (int)) did not converge for any of the Se(VI) adsorption data. Three soil samples (LVA-2; LVwf-B; PV-2) did not converge for Log $K^2_{se(VI)}$, as a consequence of the very low concentration of $SSeO_4^-$ ($<10^{-35}$) complexed in the soil surface. The distinctive Se(VI) adsorption on LVwf described previously is reflected by the higher Log $K^1_{se(VI)}$ constant compared with the other soil samples. Considering the lower average of the goodness of fit parameter, it is possible to suggest that inner-sphere surface complexation is predominant in highly weathered Brazilian tropical soils. As a consequence, Se(VI) is strongly adsorbed, which may influence the rate of fertilizer applied to highly weathered soils, since Brazilian tropical soils have low amounts of Se (Chapter 2).

Table 3 - Constant capacitance model surface complexation constants and goodness of fit (error) values in the pH-dependent adsorption of Se VI

Soil	Log $K^1_{se(VI)}$	Log $K^2_{se(VI)}$	Variance *
CX	3.605	-0.853	2.355
GM	3.552	-0.265	1.441
LA-1	3.247	-0.939	0.609
LAwf	3.587	-2.044	2.487
LV-2	3.435	-1.273	1.847
LVA-2	2.723	NC**	1.293
LVef	3.396	-1.167	0.888
LVwf-A	5.407	-1.023	0.992
LVwf-B	6.347	NC**	1.778
MT	3.226	-2.509	0.466
NVef	3.856	-1.129	1.906
PV-2	3.043	NC**	0.925
PVA-3	2.895	-2.463	0.255
RL	2.738	-0.755	0.228
RQ	3.715	-0.739	0.185

* Goodness-of-fit equals the sum of squares divided by the degrees of freedom
** Low concentration of $SSeO^{4-}$ ($<10^{-35}$)

One of the advantages of using the constant capacitance model is the ability to calculate the distribution of Se surface species on soils as a function of varying pH (GOLDBERG et al., 2007). The effect of variation in pH on the distributions of the Se(IV) and Se(VI) species adsorbed to each soil surface is shown by Figures 7 and

8. The selenite species adsorbed in tropical soils were $S\mathrm{SeO_3^-}$ and $S_2\mathrm{SeO_3}$, with predominance of the monodentate complex. The proportion of $S_2\mathrm{SeO_3}$ was greater than that of $S\mathrm{SeO_3^-}$ only under alkaline conditions (high pH values), varying between 6 and 10.The pH value at which the conversion from one species to another occurred increased with increasing oxide content.

The two species of Se(VI) were the monodentate complexes, $S\mathrm{HSeO_4}$ and $S\mathrm{SeO_4^-}$. The predominant species was $S\mathrm{HSeO_4}$ for all of the soil samples. It was the only species for the soil samples in which Se(VI) adsorption was high. The $S\mathrm{SeO_4}$ species was predominant at low pH values (< 4) in some soil samples (CX, GM, LA-1 and RL). The probable species under natural pH values found in soils would be $S\mathrm{HSeO_4}$.

In conclusion, Se(VI) is more indicated in case of necessity of Se fertilization in Brazilian agricultural soils. At the pH range commonly found in the majority of the soils (4.5 to 7.0), Se(IV) is strongly adsorbed on the surface of soil colloids, what makes difficult the plants intake. On the other hand, Se(VI) is low adsorbed on soils at the same pH range. However, Se adsorption is high even for the Se(VI) species in highly weathered soils with positive balance of charge.

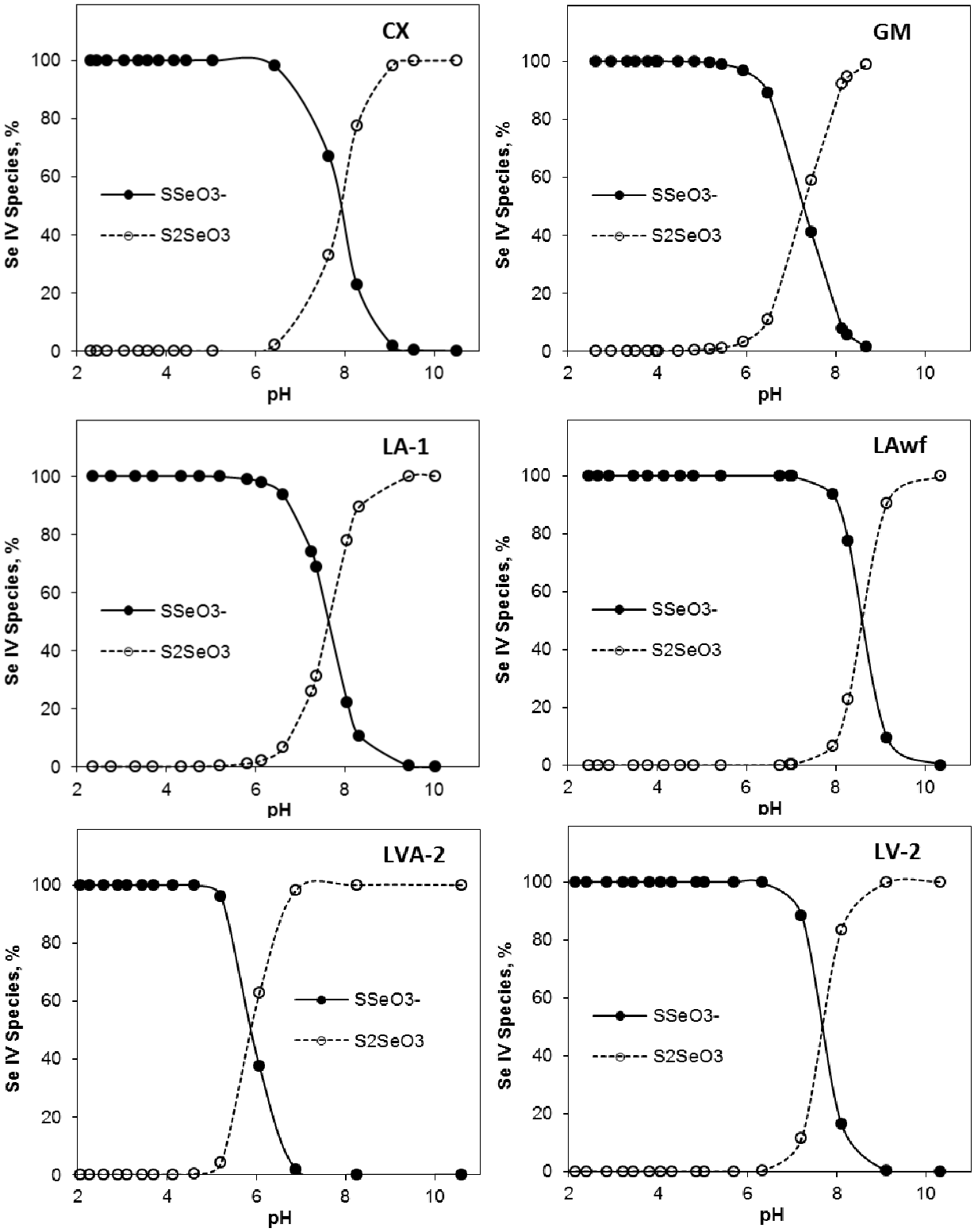

Figure 7 – Calculated Se(IV) surface species on soils with varying pH. Filled circles are $SSeO_3^-$ and hollow circles are S_2SeO_3 species

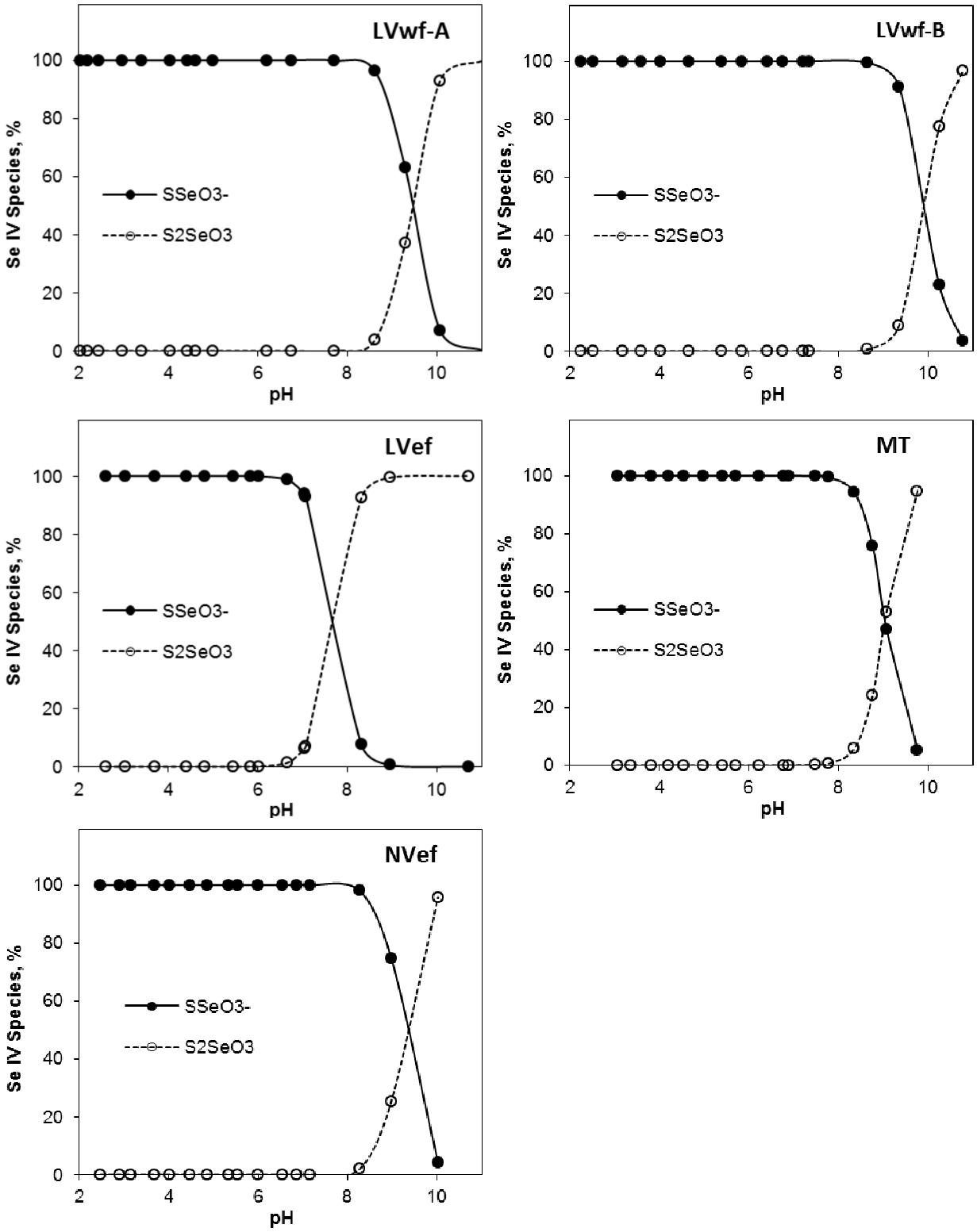

Figure 8- Calculated Se(IV) surface species on soils with varying pH. Filled circles are $SSeO_3^-$ and hollow circles are S_2SeO_3 species

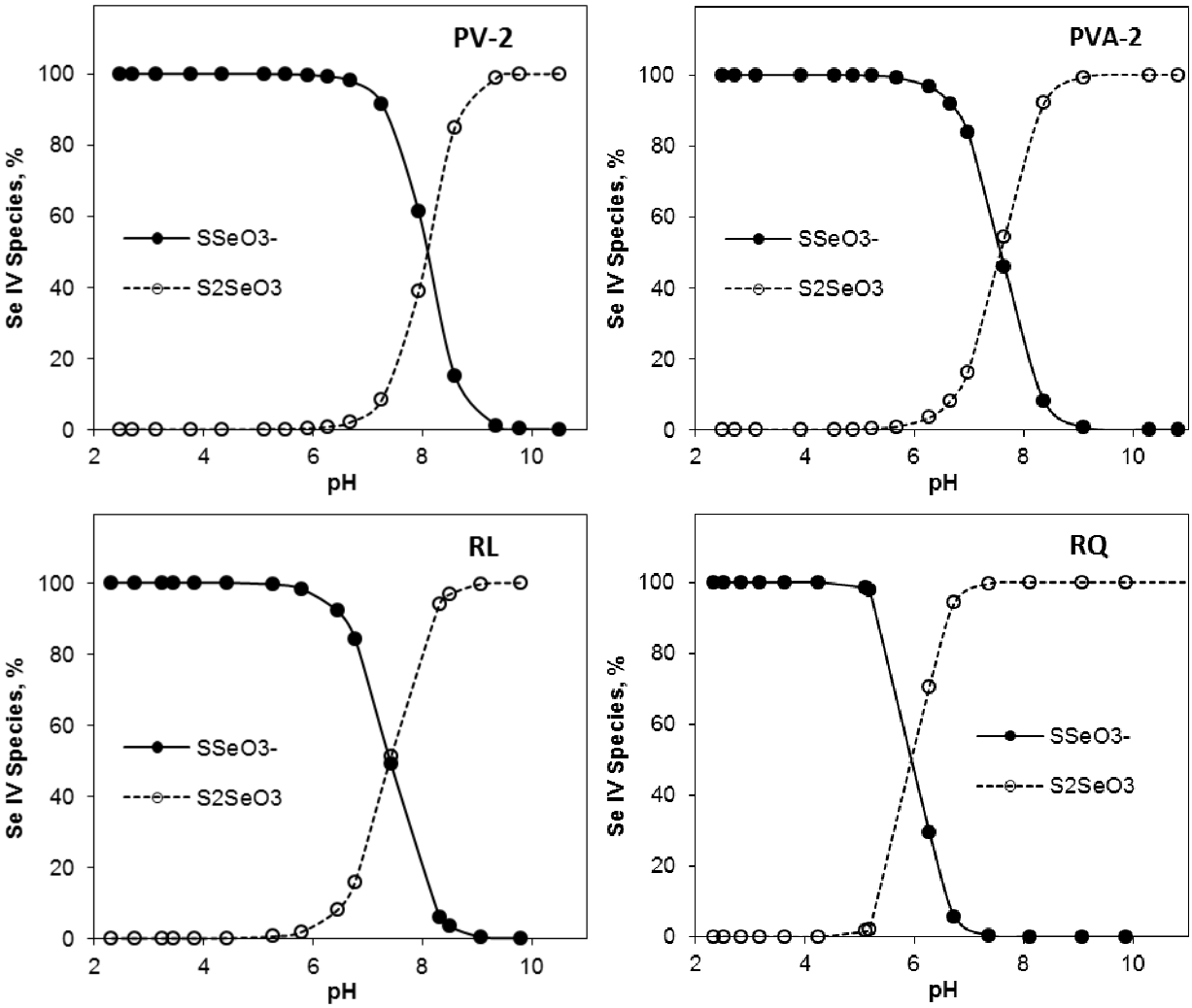

Figure 9 - Calculated Se(IV) surface species on soils with varying pH. Filled circles are $SSeO_3^-$ and hollow circles are S_2SeO_3 species

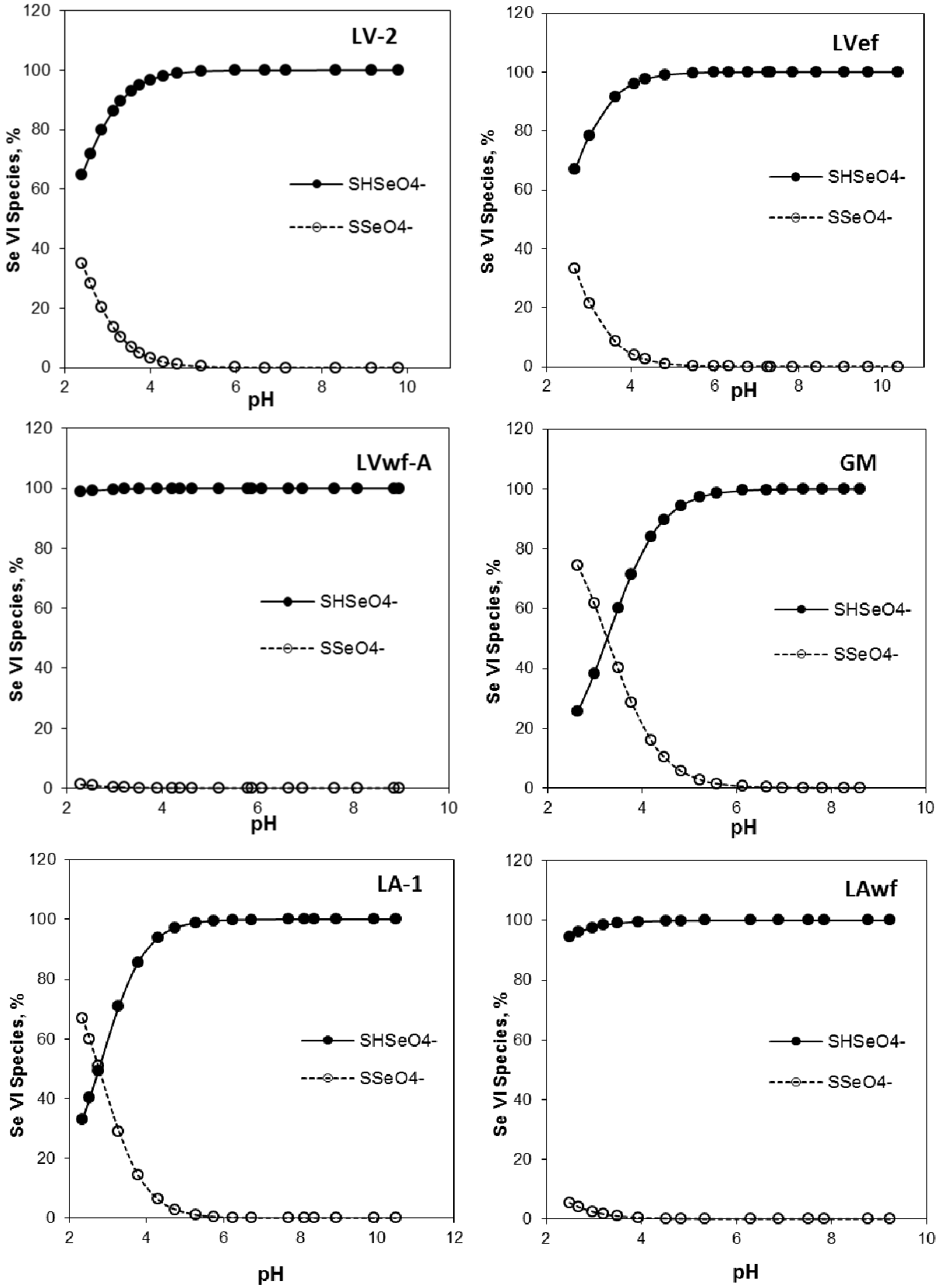

Figure 10 - Calculated Se(VI) surface species on soils with varying pH. Filled circles are $SHSeO_4^-$ and hollow circles are $SSeO_4^-$ species

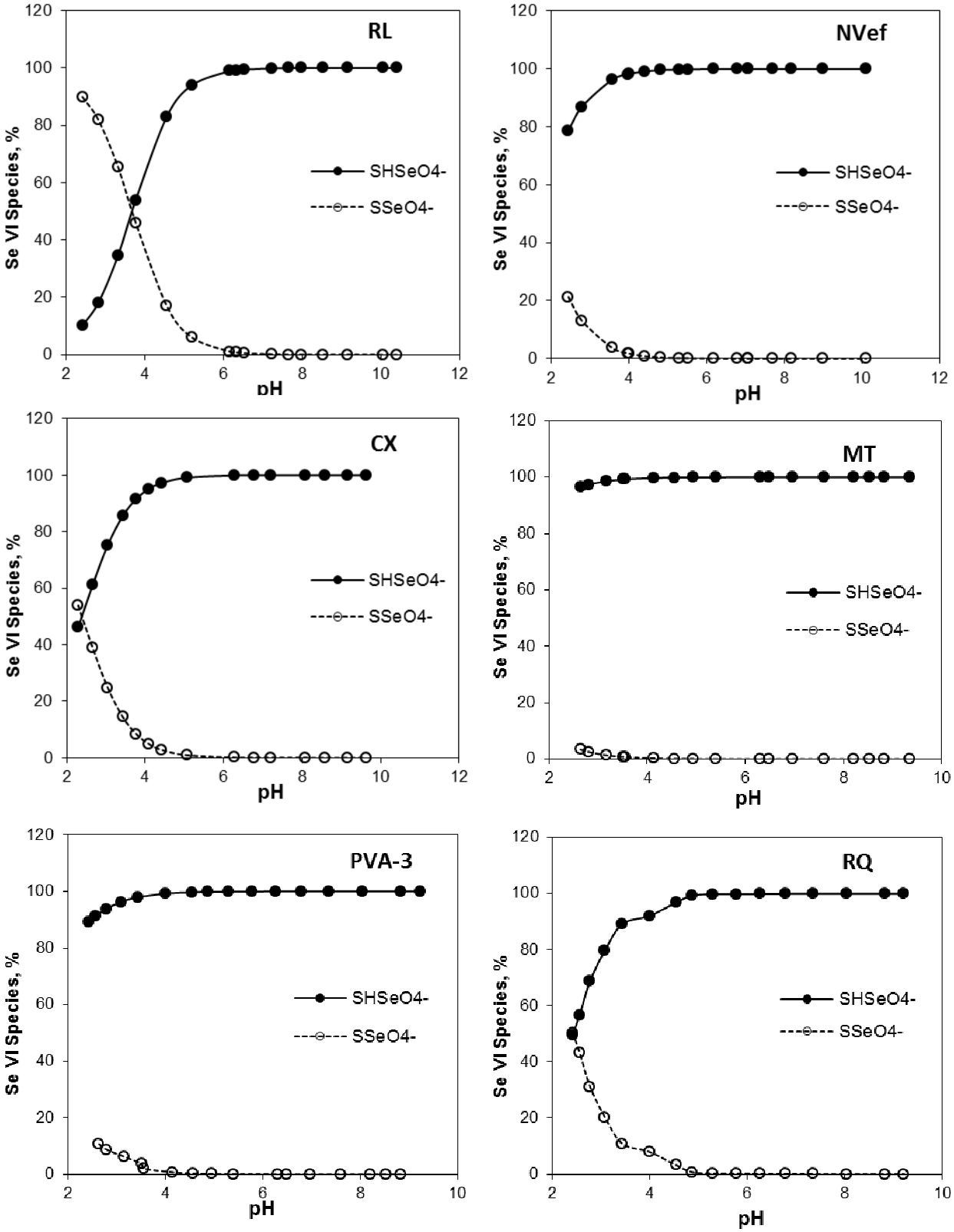

Figure 11 - Calculated Se(VI) surface species on soils with varying pH. Filled circles are $SHSeO_4^-$ and hollow circles are $SSeO_4^-$ species (conclusion)

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4 CHEMICAL MODELING OF SELENATE AND SELENITE ADSORPTION IN SELECTED TROPICAL SOILS

Abstract

Understanding selenium (Se) adsorption in soils is important because of the element's relevance to human health and environmental safety. In this study adsorption of selenite and selenate was evaluated in samples from eleven Brazilian soils with varying chemical, physical, and mineralogical attributes. The Langmuir and Freundlich empirical models and the Constant Capacitance Model (CCM) were fit to the experimental data. Se(IV) adsorption was higher in soils with more organic matter and higher Al and Fe oxide contents, while Se(VI) adsorption was positively correlated with the gibbsite content of soils. Rhodic Acrudox, the most weathered soil, adsorbed the highest amounts of Se(VI) and Se(VI). The CCM fit the experimental data well for both Se(IV) and Se(VI), as did the Langmuir and Freundlich empirical models.

Key words: Se(IV), Se(VI), Constant Capacitance Model, Brazilian soils

4.1 Introduction

Selenium is a trace element essential to animal health, but it can cause symptoms of toxicity when ingested above a narrow concentration range (consumption from 40 to 400 µg per day). Areas with seleniferous soils and Se deficient areas have been reported all over the world, and these are sometimes associated with endemic diseases (TAN et al., 2002). High levels of Se in soils are caused by natural sources or human activities, such as irrigation with Se-rich water or irregular placement. An understanding of Se behavior in soils is essential, even in soils with low Se concentration, where Se fertilization may become a common practice. Adsorption studies provide a better understanding of the distribution of the chemical species among the soil compartments, and the regulation of the ion concentration in the soil solution.

Se adsorption in soils is mainly regulated by the soil colloids whose surfaces exhibit positive balance of charge. Iron (Fe) and aluminum (Al) oxides present in weathered soils are important sources of positive sites (ALLEONI et al. 2009). For this reason, the presence of oxides is strongly correlated to Se adsorption. Selenite forms strong inner-sphere surface complexes with oxides (HAYES et al., 1987; DUC; LEFEVRE; FEDOROFF, 2006). By contrast, Se (VI) is adsorbed more weakly because it forms a mixture of inner- and outer-sphere surface bonds. The relative proportions of the two kinds of bonds depend on soil pH and on the contents and the

types of oxide minerals (PEAK; SPARKS, 2002). Both Al and Fe oxides adsorb Se(VI), but the adsorption is more extensive on the surfaces of Al oxides (CHAN et al., 2009). Organic matter (OM) can also provide positive charges to soils but only in a highly acidic medium. Organic matter content can play an important role in Se(IV) adsorption, but the same has not been reported for Se(VI) adsorption (LOFFREDO et al., 2011).

Adsorption models can be fit to experimental data obtained in adsorption studies to better understand the results. Empirical and chemical or surface complexation models are commonly used to interpret the results of adsorption experiments. Empirical models, such as Langmuir, Freundlich and the distribution Coefficient (Kd), describe adsorption phenomena without a theoretical basis, and are valid only under the specific experimental conditions. For this reason, they are not capable of accounting for the effects of variable chemical conditions, such as pH, on adsorption reactions (GOLDBERG et al., 2007).

Surface complexation models describe chemical reactions, surface species, equilibrium constant expressions, and electrostatic potential effects (GOLDBERG; SUAREZ, 2006). They provide a molecular description of the adsorption process using an equilibrium approach (GOLDBERG, 1995). An advantage of using surface complexation modeling is the possibility of predicting ion adsorption based on certain soil attributes (KARAMALIDIS; DZOMBAK, 2010). The constant capacitance model (CCM) has been used to successfully describe Se adsorption in soils and is more easily compared to other chemical models (GOLDBERG; LESCH; SUAREZ 2007; GOLDBERG; HYUN; LEE, 2008).

The objectives of this study were (i) to evaluate the adsorption of selenite and selenate in soils from the Brazilian state of São Paulo, as a function of Se concentration in equilibrium solution, and (ii) to compare fits the CCM model and to the Langmuir and Freundlich empirical models to the experimental data.

4.2 Material and Methods

Soils were selected from soil orders that are representative of São Paulo state, Brazil, and had varying attributes such as texture, OM content, and Al and Fe oxide contents. In this experiment, 11 soils from the previous chapter were evaluated. Soil samples were collected from the upper layer (0.0-0.2 m) under native vegetation. An additional sample of the Rhodic Acrudox (LVwf-B) was collected from a

subsurface layer (Bw-horizon located at 1.2-1.6 m), because of its positive balance of charge, thus representing conditions of extreme weathering. The samples were air dried, crushed, passed through a 2 mm sieve, and stored for subsequent analyses (Table 1).

A soil/water ratio of 1:2.5 was used to potentiometrically measure the pH of the soil solution. Cation exchange capacity (CEC) was determined by the compulsive exchange method proposed by Gillman (1979) for highly weathered soils. The carbon coulometer was used to quantify carbon components: total carbon was determined by furnace combustion at 950°C; inorganic carbon was measured using the acidification module and heating; and organic carbon was calculated as the difference between total and inorganic carbon. Free Fe and Al oxide contents were extracted by Na dithionite-citrate-bicarbonate (DCB) (MAHRA; JACKSON, 1960), and determined by inductively coupled plasma (ICP) emission spectrometry. Specific surface areas of the samples were estimated by using ethylene glycol monoethyl ether (EGME) adsorption (CIHACEK; BREMNER, 1979). Complementary information about the soil samples has been provided by Soares (2004).

Table 1- Some attributes of the soils

Soil	pH	ΔpH	Clay	OC	IOC	SA	Fe	Al	CEC	SOH
			g kg^{-1}	g kg^{-1}	µg g^{-1}	m^2 g^{-1}	g kg^{-1}		$mmol_c$ kg^{-1}	µmol kg^{-1}
CX (sandy-clay-loam, Typic Haplustept)	4.3	-0.7	243	14.4	*	38.9	19.3	2.3	22.7	149.1
GM (clay, Aquic Haplohumults)	4.9	-1.1	476	22.9	*	105.3	4.9	4.8	50.4	404.0
LAwf (clay, Anionic Acrudox)	4.7	-1.0	470	8.7	*	88.4	113.3	3.9	16.9	339.1
LVef (clay, Rhodic Hapludox)	7.3	-0.6	684	29.7	178.6	86.5	185.2	4.4	60.4	331.6
LVwf- A horiz. (clay, Rhodic Acrudox)	4.7	-0.9	716	14.4	*	92.4	208.2	5.7	23.7	354.6
LVwf- B horiz. (clay, Rhodic Acrudox)	5.6	0.2	663	29.8	*	56.2	232.0	6.1	23.7	215.7
MT (clay, Mollic Hapludalfs)	5.8	-1.7	543	18.7	*	165.6	113.3	4.7	105.5	635.1
NVef (clay, Rhodic Eutrudult)	5.5	-0.8	658	4.3	*	90.3	192.2	4.8	61.1	346.6
PV-2 (sandy loam, Typic Rhodudalfs)	5.7	-0.9	427	118.5	*	64.8	51.3	2.0	54.4	248.5
PVA-3 (loam, Typic Hapludults)	5.4	-0.8	247	15.3	*	25.7	32.9	4.4	44.6	98.5
RL (loam, Lithic Dystrudepts)	5.9	-1.0	142	26.1	*	34.3	7.5	0.3	33	131.7

* Below detection limit (150 µg g^{-1})
pH: in water extract
SA: Specific surface area (CIHACEK; BREMNER, 1979)
OC: Organic Carbon (carbon coulometer)
IOC: Inorganic Carbon (carbon coulometer)
“Free” Fe and Al oxide contents: extracted by Na dithionite-citrate-bicarbonate (MAHRA; JACKSON, 1960)
*S*OH: Total number of reactive sites

Adsorption experiments were carried out via a batch system at 24.5 ± 0.3 ^{o}C. Two grams of soil and 20 ml of a solution containing either Se(IV) or Se(VI) (0.01M $NaNO_3$ as background electrolyte) were added to 50-mL polypropylene centrifuge tubes. The Se doses were 0.00; 0.06; 0.13; 0.32; 0.63; 1.27; 2.15; 3.17 mmol L^{-1} of Se(IV) and 0.00; 0.01; 0.03; 0.06; 0.13; 0.19; 0.25; 0.32 mmol L^{-1} of Se(VI), added from stock solutions of Na_2SeO_3 and Na_2SeO_4, respectively. A difference of 10 times between the doses of the two Se forms was employed because of the lower adsorption of Se(VI), even in highly weathered tropical soils. Reaction time was 24 h on a reciprocating shaker. In sequence, the solutions were centrifuged for 20 min at 10,000 rpm, and then immediately passed through a 0.45-µm membrane filter. pH was measured in the remaining solution, and Se concentration determined by ICP emission spectrometry. The amount of adsorbed Se was calculated as the difference between the amount added and the amount remaining in solution after equilibrium was reached. The experiment was conducted in triplicate for each soil and Se concentration in solution. As observed by Goldberg; Lesch; Suarez (2007) and Hyun et al. (2006), oxidation of Se(IV) to Se(VI) during the adsorption process was lower than 10%, even with shaking times exceeding 2 h. For this reason, Se oxidation was not taken into account in this study.

The Langmuir, Freundlich, and CCM models were fit to the experimental data for Se(IV) and Se(VI). Nonlinear regression was used to fit the Langmuir and Freundlich models to the data because linearizations can change the original error distribution (KINNIBURGH, 1986). The ISOTHERM software program developed by Kinniburgh (1985) was used for the optimization procedure. The Langmuir equation (eq.1) and the Freundlich equation (eq. 2) are:

$$x = \frac{bKc}{1 + Kc} \tag{1}$$

$$x = Kc^{\beta} \tag{2}$$

where *x* is the amount adsorbed; *c* is the equilibrium solution concentration; *b* is the estimated maximum adsorption, *K* is the affinity constant, and *β* is an empirical parameter (KINNIBURGH, 1986).

The constant capacitance model (STUMM et al., 1980) was chosen because of the good results obtained for Se adsorption in soils and because of its simplicity

when compared to other surface complexation models (GOLDBERG, 2011). The FITEQL 4.0 software program (HERBELIN; WESTALL, 1999) was used to fit the surface complexation constants to the sorption data, via a non-linear least squares optimization routine (GOLDBERG; LESCH; SUAREZ, 2007). Details regarding this model are presented by Goldberg (1992).

Considering *S*OH as the functional group of oxide minerals and from the clay particle soil fraction, protonation and deprotonation are defined as

$$SOH_{(s)} + H^{+}_{(aq)} \leftrightarrow SOH^{+}_{2(s)} \tag{3}$$

$$SOH_{(s)} \leftrightarrow SO^{-}_{(s)} + H^{+}_{(aq)} \tag{4}$$

The surface complexation reactions with Se(IV) and Se(VI) were considered to be the same as in Chapter 3. The intrinsic equilibrium constants considered for the complexation reactions were thus

$$K_{+}(\text{int}) = \frac{[SOH_2^{+}]}{[SOH][H^{+}]}\exp(F\psi / RT) \tag{5}$$

$$K_{-}(\text{int}) = \frac{[SO^{-}][H^{+}]}{[SOH]}\exp(-F\psi / RT) \tag{6}$$

$$K^{1}_{\text{Se(IV)}}(\text{int}) = \frac{[SHSeO_3]}{[SOH][H_2SeO_3]} \tag{7}$$

$$K^{2}_{\text{Se(IV)}}(\text{int}) = \frac{[SSeO_3^{-}][H^{+}]}{[SOH][H_2SeO_3]}\exp(-F\psi / RT) \tag{8}$$

$$K^{3}_{\text{Se(IV)}}(\text{int}) = \frac{[S_2SeO_3]}{[SOH]^2[H_2SeO_3]} \tag{9}$$

$$K^{1}_{\text{Se(VI)}}(\text{int}) = \frac{[SHSeO_4]}{[SOH][H_2SeO_4]} \tag{10}$$

where *F* is the Faraday constant, C mol_c^{-1}; ψ is the surface potential in V; *R* is the universal gas constant in J mol^{-1} K^{-1}; *T* is absolute temperature in K; and species between brackets are their concentrations in mol L^{-1}. Bidentate bonds require at least twice as many sites as monodentate bonds (GOLDBERG; LESCH; SUAREZ, 2007).

The mass balances of the surface functional groups for monodentate and bidentate, for Se(IV) are, respectively:

$$[SOH]_T = [SOH] + [SOH_2^+] + [SO^-] + [SHSeO_3] + [SSeO_3^-] \quad (11)$$

$$[SOH]_T = [SOH] + [SOH_2^+] + [SO^-] + 2[S_2SeO_3] \quad (12)$$

and the mass balances for Se(VI) are:

$$[SOH]_T = [SOH] + [SOH_2^+] + [SO^-] + [SHSeO_4] \quad (13)$$

$$[SOH]_T = [SOH] + [SOH_2^+] + [SO^-] \quad (14)$$

The expressions of charge balance for monodentate are:

Se(IV): $$\sigma = [SOH_2^+] - [SO^-] - [SSeO_3^-] \quad (15)$$

Se(VI): $$\sigma = [SOH_2^+] - [SO^-] \quad (16)$$

and for Se(IV) bidentate the charge balance equation is:

$$\sigma = [SOH_2^+] - [SO^-] \quad (17)$$

where surface charge is σ ($mol_c\ L^{-1}$). Surface potential is related to the surface charge to according equation 18, in which *C* is capacitance in F m^{-2}; S_a is surface area in $m^2\ g^{-1}$; and C_p is suspension density in g L^{-1}.

$$\sigma = \frac{CS_aC_p}{F}\psi \quad (18)$$

The FITEQL initial inputs were taken from previous studies. The capacitance value (C = 1.06 F m^{-2}) used is considered the optimum for Al oxide by Westall; Hohl (1980). The protonation and the deprotonation constants were $logK_-$(int) = -8.95 and $logK_+$(int) = 7.35, following Goldberg; Sposito (1984). The number of reactive sites was recommended by Davis; Kent (1990) for natural materials as N_s=2.31 sites nm^{-2}; this information is necessary to calculate the total sites, as shown by Karamalidis; Dzombak (2010). Variance or goodness-of-fit (V_y) was also provided by the software, as presented in equation 19:

$$V_Y = \frac{SOS}{df} \tag{19}$$

where *SOS* is the weighted sum of squares of residuals, and *df* is degrees of freedom (HERBELIN; WESTALL, 1996).

4.3 Results and Discussion

4.3.1 Selenite adsorption

Adsorption of Se(IV) as a function of Se(IV) concentrations in solution varied for the 11 soil samples. Six samples (GM, LAwf, LVef, LVwf, MT and NVef) had high Se(IV) adsorption (Figures 1 and 2) even at high doses of added Se, such as 2.15 and 3.17 mmol L^{-1}. In the GM soil sample, high Se(IV) adsorption was directly correlated to high levels of OM. This positive influence of OM content on Se adsorption was also observed by Kamei-Ishikawa et al. (2008) in humic acid, where a linear increase of Se adsorption with OM content was found. All other soils with high Se adsorption (LAwf, LVef, LVwf, MT and NVef) had high soil surface area and high oxide contents. Several researchers have described the high affinity of Se(IV) to pure oxides, such as hematite (DUC; LEFEVRE; FEDOROFF, 2006), goethite, as inner-sphere complexes (HAYES et al., 1987), and Al oxides, as inner-sphere monodentate surface complexes (PEAK, 2006).

The Rhodic Acrudox (LVwf) adsorbed large amounts of Se in both soil layers when compared to the other soils (Figure 1). The subsurface Bw sample of the LVwf is the soil sample with the highest degree of weathering, with low CEC, high concentrations of Fe and Al oxides, and positive balance of charge. Maximum Se(IV) adsorption was 20 mmol kg^{-1} for the LVwf-B soil sample. By comparison, Se(IV) adsorption was more than 100 times lower in soils from South Dakota, USA, with surface areas approximately 50 times higher but having very low amounts of Fe and Al oxides (LEE; DOOLITTLE; WOODARD, 2011). Dhillon; Dhillon (1999) observed a maximum Se(IV) adsorption between 1.3 and 5.8 mmol kg^{-1} in Indian soils, correlated with pH, OM, and clay and $CaCO_3$ content. In our study, a relationship between Se(IV) adsorption and pH was not observed, probably because of the narrow range of soil pH investigated.

A second group of soil samples (PV-2, PVA-3, RL and CX) showed low Se (IV) adsorption. Maximum Se (IV) adsorption in these soils was observed at

concentrations lower than 5 mmol kg^{-1} (Figure 1). These soils had low clay and OM contents, and therefore also a low SA. Mouta et al. (2008) also reported low Se (IV) adsorption on samples of Oxisols with low clay contents.

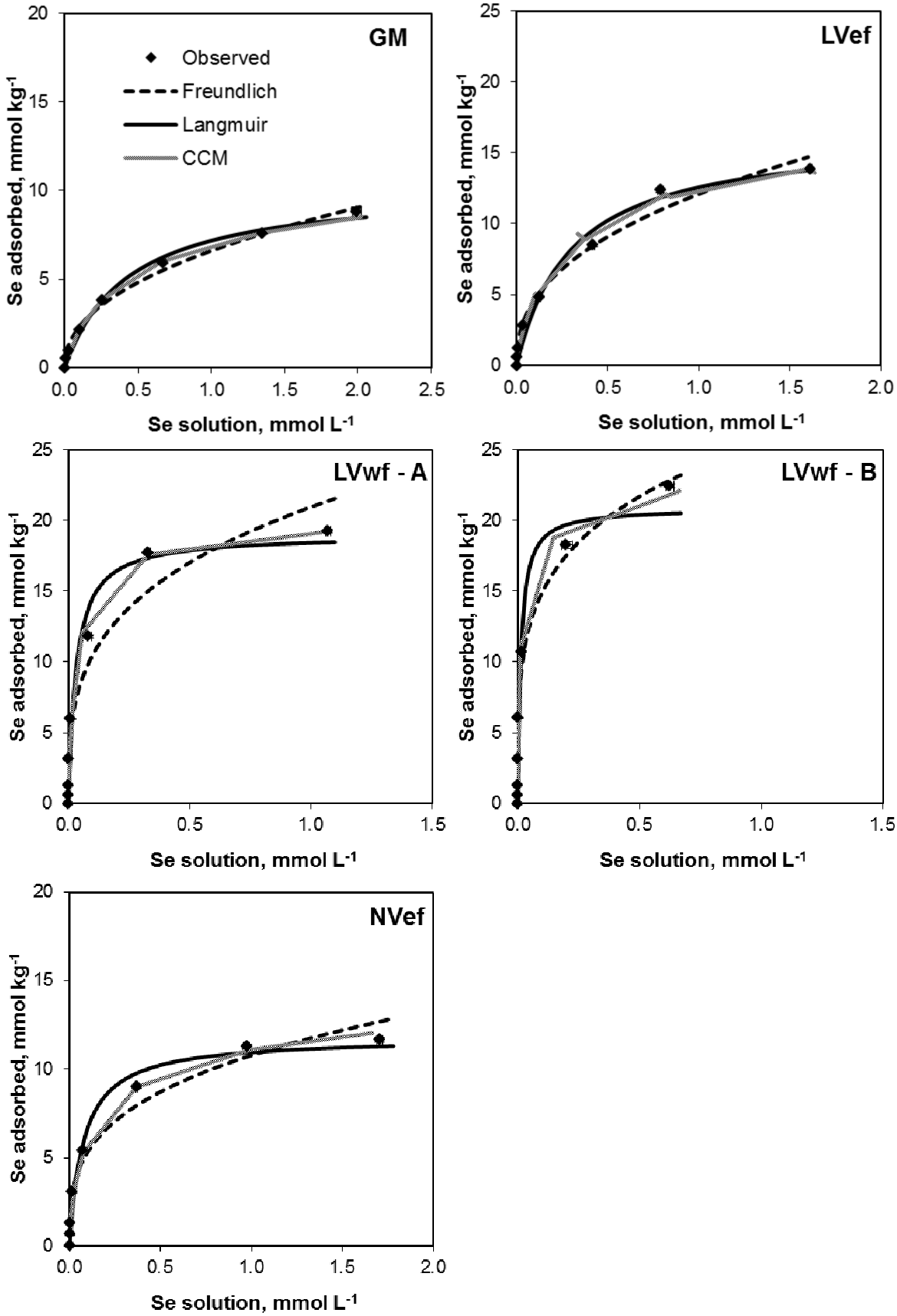

Figure 1 - Se(IV) adsorption on the soils with the highest adsorption, showing fits of the constant capacitance, Langmuir, and Freundlich models

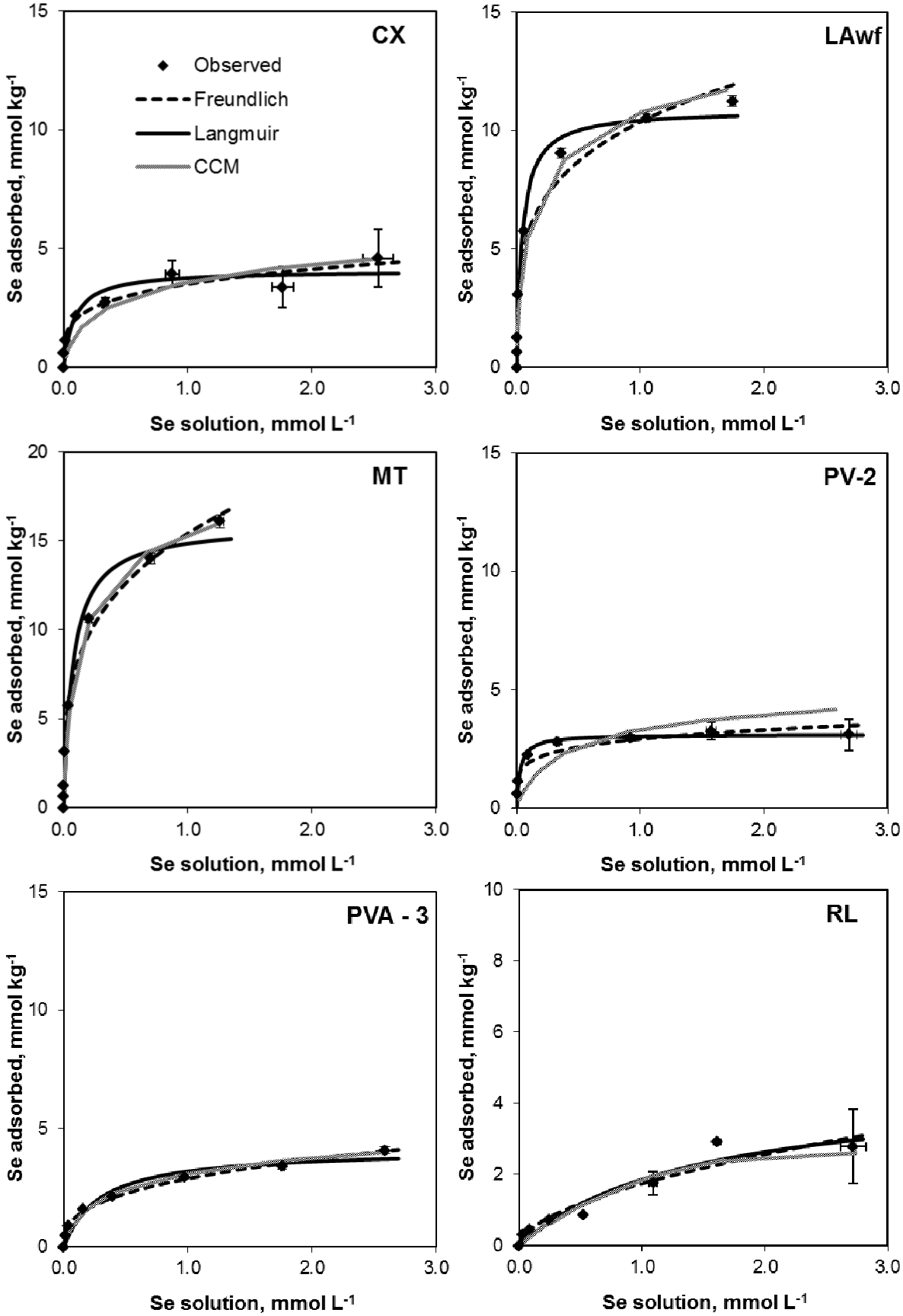

Figure 2 - Se(IV) adsorption on the soils with the lowest adsorption, showing fits of the constant capacitance, Langmuir, and Freundlich models

4.3.2 Selenate adsorption

As had already been observed for Se adsorption as a function of solution pH (Chapter 3), as expected, Se(VI) adsorption on the soils was lower than Se(IV) adsorption. However, as with the Se(IV) adsorption isotherms, the samples with the highest Se(VI) adsorption were LVwf A and B (Figure 3). The soil with the second highest Se(VI) adsorption was LAwf (Figure 3). This similarity between LVwf and LAwf can be attributed to their higher amounts of gibbsite than the other soils. Chan et al. (2009) reported that Se(VI) adsorption on Al oxides was five times higher than on Fe oxides. Se(VI) forms inner-sphere monodentate surface complexes on Al oxide surfaces at pH 4.5 and above (PEAK, 2006). In another study involving pure phases, Loffredo et al. (2011) observed that only Al hydroxide adsorbed Se(VI) throughout the pH range (5.4 to 8.0).

Moreover, Fe oxides are important surfaces for Se(VI) adsorption: Se(IV) forms inner-sphere surface complexes on hematite and a mixture of inner- and outer-sphere surface complexes on goethite (PEAK; SPARKS, 2002). The maximum adsorption levels of Se(VI) on goethite and hematite at pH 4 were 2.2 and 3.1 mmol kg^{-1}, respectively (ROVIRA et al. 2002). In our experiment, LVef, MT, and NVef had high Fe oxide contents, but Se(VI) adsorption was low (Figure 4). This fact may be due to the pH of the equilibrium solution, since the charge on the surface of Fe oxides is pH-dependent. Charges are negative at high pH levels and adsorption of Se(VI) decreases dramatically under such circumstances, as observed in Chapter 3.

Other soil samples – LVef, MT, NVef, PV-2, PVA-3, and RL – showed low Se(VI) adsorption, where the maximum equilibrium concentrations were lower than 0.2 mmol kg^{-1} of Se(VI) (Figure 4). Abreu et al. (2011) evaluated Se(VI) adsorption in four soils from Central Brazil and observed low adsorption in soils with low oxide contents. Organic matter content did not influence Se(VI) adsorption, as shown by the graph in Figure 3 of the GM sample, which had the highest OM content (Figure 3). Loffredo et al. (2011) observed that Se(VI) was not adsorbed on the surface of humic acid.

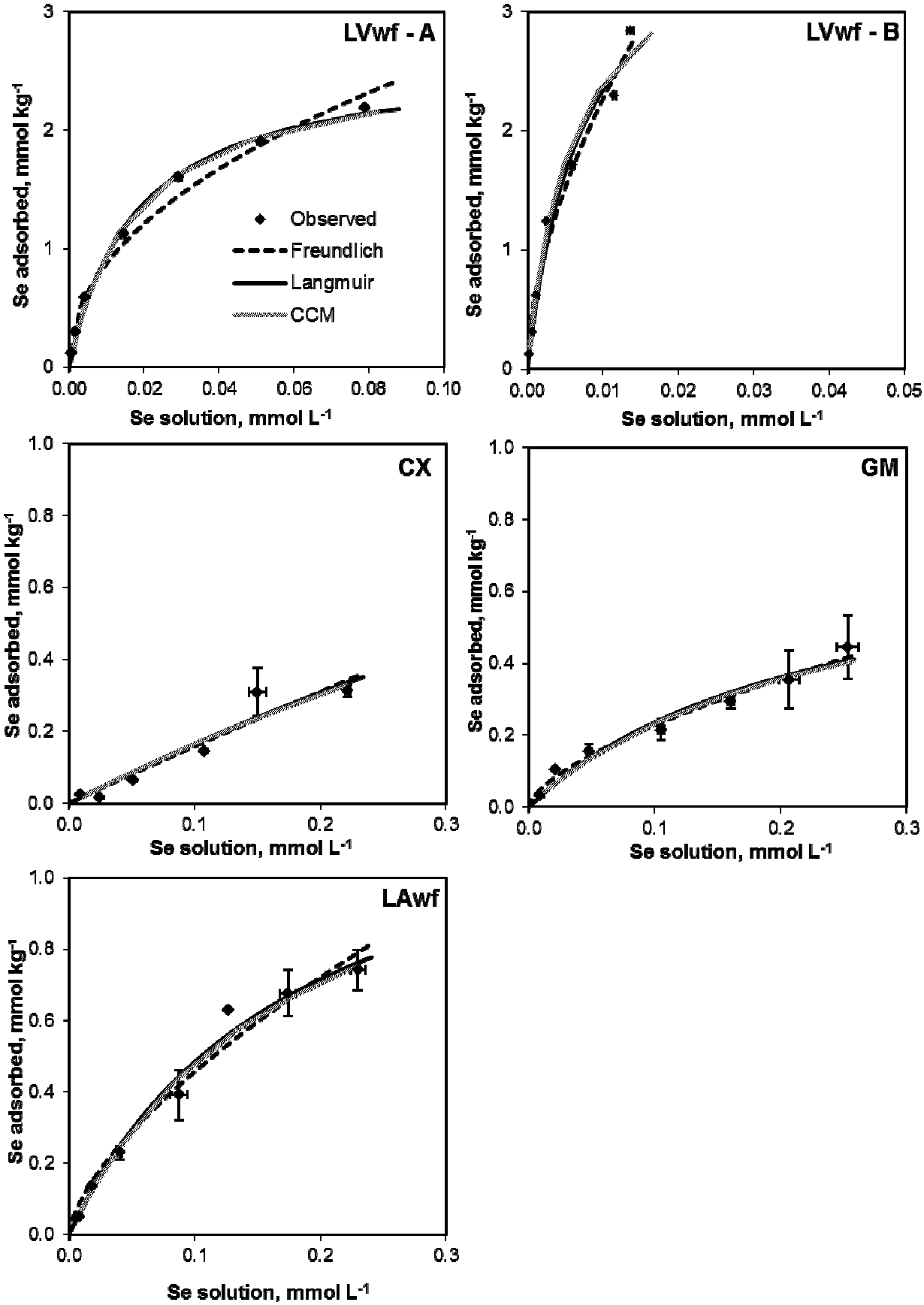

Figure 3 – Se(VI) adsorption on the soils with the highest adsorption, showing fits of the constant capacitance, Langmuir, and Freundlich models

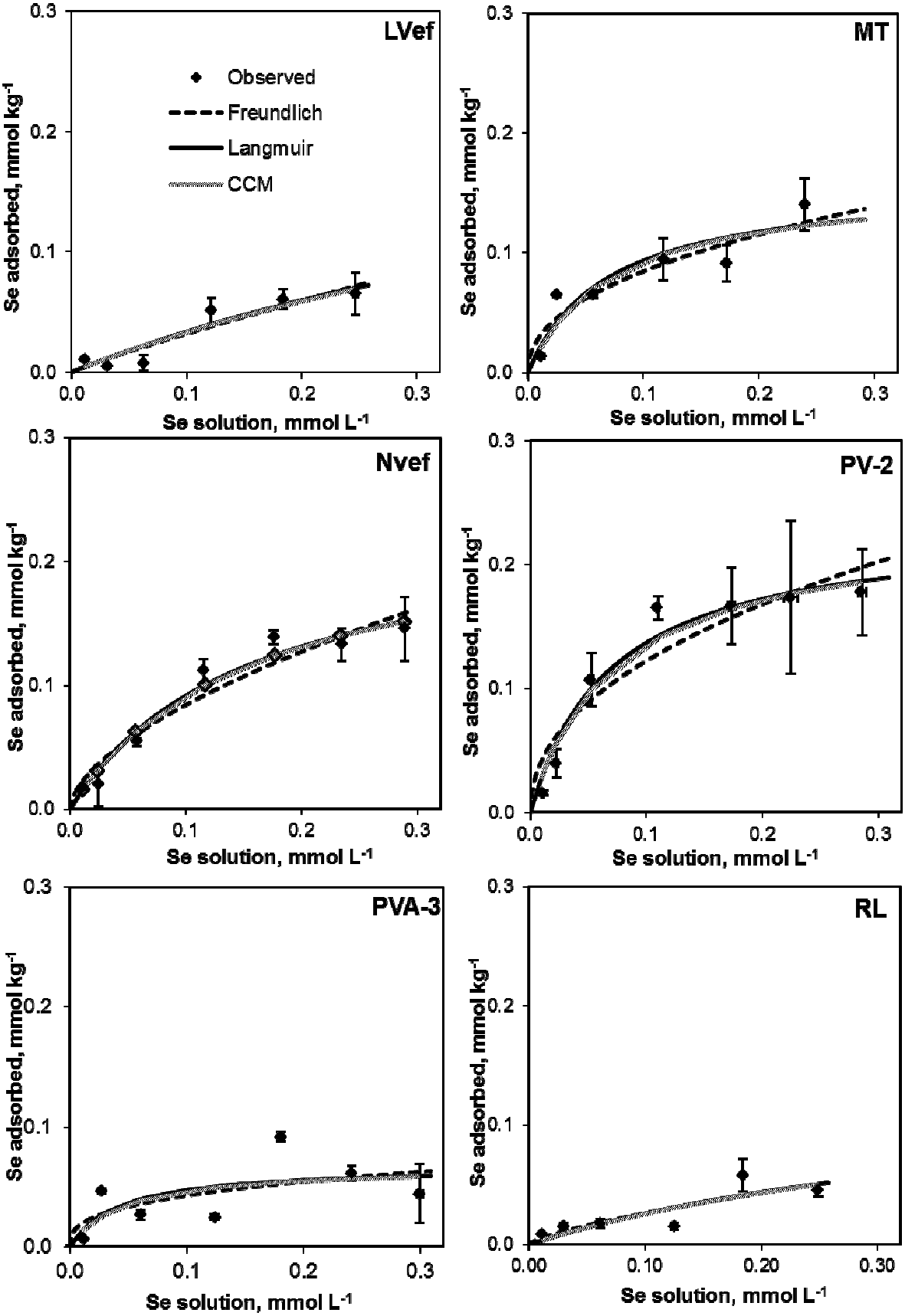

Figure 4 - Se(VI) adsorption on the soils with the lowest adsorption, showing fits of the constant capacitance, Langmuir, and Freundlich models

4.3.1 Chemical modeling

The three types of adsorption models represented the experimental data satisfactorily (Figures 1 and 2 for Se(IV) adsorption; Figures 3 and 4 for Se(VI) adsorption). Langmuir and Freundlich parameters are shown in Table 2. Correlation coefficients (R^2) were similar for both models, but Langmuir had a better fit, especially for Se(IV) adsorption. Mouta et al. (2008) recommended the Langmuir equation for fitting Se(IV) adsorption data on Oxisols. Abreu et al. (2011) also suggested the Langmuir equation for fitting Se(VI) adsorption data. By contrast, Go; Lim (2004) reported good fits of the Freundlich equation to experimental Se(IV) adsorption data on different classes of soils, and good fits of the Langmuir equation to Se(VI) adsorption data.

Table 2 – Parameters derived from the fitting of Langmuir and Freundlich isotherms to Se(IV) and Se(VI) adsorption data in tropical soils.

Se	Soil	Langmuir			Freundlich		
		K	b	R^2	log K	β	R^2
		L mmol^{-1}	mmol kg^{-1}		L mmol^{-1}		
	CX	11.87	4.08	0.84	2.33	0.23	0.87
	GM	2.30	10.30	0.99	1.81	0.45	0.99
	LAwf	23.37	10.87	0.98	4.04	0.25	0.98
	Lvef	3.35	16.33	0.98	2.62	0.41	0.98
	LVwf-A	32.75	18.99	0.98	4.42	0.30	0.94
Se(IV)	LVwf-B	84.68	20.88	0.94	6.09	0.23	0.96
	MT	13.83	15.92	0.96	4.13	0.29	0.99
	Nvef	13.10	11.80	0.98	3.38	0.31	0.97
	PV-2	37.02	3.11	0.95	2.61	0.18	0.91
	PVA-3	3.43	4.13	0.96	1.31	0.35	0.99
	RL	0.70	4.51	0.85	0.44	0.55	0.84
	CX	0.81	2.20	0.90	0.17	0.97	0.89
	GM	4.35	0.78	0.90	0.01	0.65	0.91
	LAwf	5.46	1.37	0.97	0.48	0.66	0.96
	Lvef	1.46	0.26	0.84	-0.68	0.89	0.84
	LVwf-A	55.67	2.62	1.00	1.88	0.47	0.98
Se(VI)	LVwf-B	142.42	3.98	0.97	2.62	0.57	0.97
	MT	14.39	0.16	0.88	-1.39	0.45	0.89
	Nvef	6.50	0.23	0.94	-0.81	0.60	0.92
	PV-2	14.35	0.23	0.87	-0.99	0.46	0.82
	PVA-3	23.83	0.07	0.50	-2.97	0.35	0.48
	RL	2.33	0.14	0.73	-1.20	0.72	0.73

Although they may show good fits, empirical models provide descriptions of adsorption data without a theoretical basis. Chemical models provide more information about ion behavior from the adsorption solution (GOLDBERG, 1995). In our experiment, the CCM fits for Se(IV) and Se(VI) adsorption was similar to the empirical models (Figures 1 to 4).

In the Se(IV) adsorption experiment, the pH of the solution varied in response to the addition of Na_2SeO_3 solution. The highest variation was observed for the LVwf-B sample, with pH ranging from 5.7 to 7.9. For this reason, the CCM was fit in two parts, one considering the actual of pH value of each datum point and another taking the average of the solution pH into account (Table 3). The CCM isotherms with the best fit are presented in Figures 1, 2, 3 and 4. The CX, GM, LAwf, MT, Nvef, PV-2, and PVA-3 samples were modeled using the average pH. Conversely, datum point specific pH values were used for the Lvef, LVwf-A, LVwf-B and RL samples.

In the fit with fixed pH, the monodentate surface complexation constants (Log $K^1_{Se(IV)}$ and Log $K^2_{Se(IV)}$) were optimized separately. These constants were then used to optimize the bidentate surface constants (Log $K^3_{Se(IV)}$), thus providing an improved goodness-of-fit (Table 3). The same procedure was employed when considering datum point specific pHs, but the bidentate surface complexation constants did not converge because their concentrations were lower than 10^{-32}. The CCM fits with varying pH were better for the soils in which the pH range was large and the highest pH was 7 or greater. The high error in some soil samples was a consequence of high variation between replicates for the same Se dose. GOLDBERG; LESCH; SUAREZ (2008) used monodentate Se(IV) surface species to model Se(IV) adsorption on soils from the United States. On the other hand, DUC; LEFEVRE; FÉDOROFF (2006) observed for Se(IV) adsorption on hematite that while surface complexation modeling assuming a bidentate complex ($>FeO_2SeO_3$) allowed a fit to the experimental data, other possibilities (monodentate complexes) could not be ruled out.

Table 3 – Constant capacitance model surface complexation constants and goodness-of-fit (error) of the adsorption isotherm of Se(IV)

Soil	Average pH	Fixed pH				pH-dependent		
		log $K^1_{Se(IV)}$	log $K^2_{Se(IV)}$	log $K^3_{Se(IV)}$	Error	log $K^1_{Se(IV)}$	log $K^2_{Se(IV)}$	Error
CX	4.79	NC	3.010	4.955	158.4	7.844	NC	431.8
GM	4.66	7.507	3.237	NC	4.2	7.651	2.908	54.3
LAwf	5.41	NC	3.381	3.080	1.2	8.410	NC	31.7
LVef	7.53	8.466	2.161	NC	33.9	8.733	1.492	6.9
LVwf-A	6.06	8.854	2.885	NC	0.8	9.201	2.150	0.5
LVwf-B	6.64	8.743	3.721	NC	3.4	NC	3.116	1.2
MT	6.56	7.998	2.275	-0.719	2.4	8.733	NC	8.3
NVef	6.27	NC	2.439	NC	3.4	NC	2.317	14.4
PV-2	6.55	NC	1.954	1.227	54.0	8.316	1.756	260.2
PVA-3	6.53	NC	1.361	-1.212	13.6	5.511	1.404	67.0
RL	6.43	1.079	7.138	NC	219.4	6.794	0.120	188.5

* Goodness-of-fit equals the sum of squares divided by the degrees of freedom
NC: No Convergence

The CCM was fit to the Se(VI) adsorption data using monodentate surface complexation constants. Since the monodentate species $SSeO_4^-$ did not converge because its concentration in solution was lower than 10^{-32}, only log $K^1_{Se(VI)}$ was optimized for the CCM (Table 4). Variation in pH was very low in the Se(VI) solutions, so average pH was used for all the soil samples. Goldberg; Hyun; Lee (2008) used only $SSeO_4^-$ in the optimization of Se(VI) adsorption data and had satisfactory goodness of fit.

Based in our results, it was possible to conclude that (i) the high capability of Se(IV) adsorption in highly weathered Brazilian soils is related to the oxides´ concentration; (ii) the constant capacitance model was similar to the empirical models to fit the adsorption data for both Se(IV) and Se(VI).

Table 4 – Constant capacitance model surface complexation constants and goodness of fit of the adsorption isotherm of Se(VI)

Soil	pH	log $K^{1}_{Se(IV)}$	Error*
CX	4.39	8.258	9.217
GM	4.45	9.054	11.484
LAwf	4.87	9.150	7.957
LVef	7.34	8.890	1.291
LVwf-A	5.14	10.172	0.271
LVwf-B	5.69	10.575	0.117
MT	6.21	9.609	2.583
NVef	6.03	9.258	1.781
PV-2	6.21	9.607	6.285
PVA-3	6.44	9.822	4.419
RL	5.73	8.796	1.243

* Goodness-of-fit equals the sum of squares divided by the degrees of freedom

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