







Division - Soil Processes and Properties | Commission - Soil Chemistry

How sulfate content and soil depth affect the adsorption/desorption of selenate and selenite in tropical soils?

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ABSTRACT: Sorption of selenate (SeO_4^{2-}) and selenite (SeO_3^{2-}) is poorly understood in Brazilian agroecosystems, especially in soils from agricultural areas containing different contents of competing anions, such as sulfate (SO_4^{2-}). This study aimed to assess the sorption behavior of selenate and selenite at different soil layers of a tropical soil treated with different rates of agricultural gypsum (thus, containing different contents of sulfate), collected under a coffee plantation. Soil samples from an experimental area where phosphogypsum has been previously applied at different rates (0, 7, 14, and 56 t ha⁻¹) were taken at the following soil layers: 0.15-0.25, 0.35-0.45, and 1.25-1.35 m. Adsorption experiments were carried out adding 20 mL of solutions containing 100 and 500 µg L⁻¹ of selenate and 10 and 15 mg L⁻¹ of selenite to 2 grams of soil. Desorption experiments were also performed using a soil:solution ratio of 1:10. Adsorption of selenate increased with soil depth and decreased upon increasing sulfate contents in the soil, by contrast, selenite was consistently adsorbed at higher contents - when compared with selenate - at any soil depth and its sorptive behavior was not affected by the presence of sulfate. Furthermore, selenite was less desorbed than selenate under all conditions. In conclusion, selenite is much more retained in tropical soils and less available to plants than selenate. Also, although sulfate has shown to be able to hinder selenate retention, it has no substantial effect on the sorption behavior of selenite in tropical agroecosystems.

Keywords: selenium, adsorption/desorption, phosphogypsum, competitive anions, retention/availability.

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INTRODUCTION

Selenium (Se) availability in soils depends on the content and the chemical form of Se (i.e., selenate - SeO_4^{2-} - or selenite - SeO_3^{2-}) in the soil, as well as on soil properties (e.g., texture, mineralogy, pH, Eh) and the presence of competing anions (e.g., S-sulfate and P-phosphate) (Huang et al., 2015; Yasin et al., 2015). Under natural conditions, selenate and selenite are the predominant inorganic forms of Se in soils. Selenate occurs mainly in soils with high pH and Eh, and it is more mobile than selenite, while this last Se species occurs in soils with low pH and it is strongly adsorbed on oxides (Duc et al., 2003; Kabata-Pendias, 2015).

Selenium is an essential element for humans and a component of amino acids with important biological functions, being particularly important in the antioxidant system (Rayman, 2012; Oliver and Gregory, 2015). Both deficiency and toxicity of Se are of concern worldwide, and the limit between essentiality and toxicity for Se is very narrow (Natasha et al., 2018; Ramalho et al., 2020). However, in tropical countries with low Se contents in soils, such as in Brazil (Gabos et al., 2014a; Matos et al., 2017; Carvalho et al., 2019), problems related to Se deficiency are expected and the consumption of Se-rich staple foods is an important way to increase the intake of Se by population (Pietinen et al., 2010; Natasha et al., 2018).

Selenium-rich food might be produced via agronomic biofortification (Lopes et al., 2017; Ramalho et al., 2020), a strategy that provides Se to plants by means of soil or foliar fertilization. If soil application of Se is the choice for producing Se-rich crops, then Se availability in soils needs to be better understood, since this is the main factor affecting the content of this element in edible parts of food crops. This availability should be well evaluated for driving the production of food crops with adequate and safe levels of Se. Therefore, studies involving adsorption/desorption reactions of Se under different soil management systems are relevant for predicting Se availability in tropical soils.

Soil management practices that add oxyanions (e.g., phosphate and sulfate) in soils may interfere on the availability of selenate and selenite due to their competition for sorption sites (Nakamaru et al., 2006; Constantino et al., 2017). Similarly, increasing the organic matter content of tropical soils promotes an increase of net surface negative charges, hence decreasing anionic adsorption. Thus, the addition of agricultural gypsum (hereafter called phosphogypsum) and phosphate fertilizers, as well as the adoption of management practices that increase the soil organic matter content are relevant to increase Se availability in soils (Lessa et al., 2016).

Besides being a relevant source of calcium (Ca) and sulfur (S) for plants, phosphogypsum has been applied in many crops in Brazil to improve subsurface soil layers that are rich in Al^{3+} and/or poor in Ca^{2+} . Such management practice provides better conditions for root growth and plant development (Dias, 1992). Phosphogypsum is a by-product generated by phosphate fertilizer industries and its estimated average chemical composition includes 45 % of sulfur trioxide (SO_3), 33 % of calcium oxide (CaO), 0.9 % of P_2O_5 , H_2O (15-20 %), and other elements with lower percentages (1-5 %) (Dias, 1992; Alcorido and Rechcigl, 1993).

Selenium and sulfur belong to the same group of the periodic table (16), which gives them similarities in chemical and physical properties (Dauphas, 2013; Wang and Becker, 2013). Considering that both elements (Se and S) are anions, they may compete for positive charges in soil colloids. Selenate and sulfate exist in soil environments as deprotonated species, SeO_4^{2-} and SO_4^{2-} , having the same geometry (tetrahedral), which may explain their competition for adsorption sites (Chubar, 2018). Although selenite (SeO_3^{2-}) has a different geometry (i.e., trigonal pyramidal) and is more retained in soils than selenate, its adsorption capacity may be also affected by the presence of sulfate, mainly when this last element is added in high amounts, as when high rates of phosphogypsum are

applied in soils. In plants, selenate and sulfate follow the same uptake, translocation, and assimilation pathways (Balistrieri and Chao, 1990; Gupta and Gupta, 2017; Liu et al., 2017).

While some studies have shown a competition between selenate and sulfate (Constantino et al., 2017; Chubar, 2018), studies assessing the sorptive behavior of selenate and selenite in soils containing different concentrations of sulfate are still required, mainly for tropical soils. Moreover, the assessment of Se sorption at different soil layers is relevant for evaluating, among other factors, the influence of organic matter upon Se sorption capacity. Therefore, this study aimed to evaluate the sorptive behavior of selenate and selenite at different soil layers of a tropical soil treated with different rates of phosphogypsum (thus, containing different contents of SO_4^{2-}), collected under a coffee plantation.

MATERIALS AND METHODS

Soil description and sampling

Soil samples examined in this study were collected in an experimental area with coffee plantation, at São Roque de Minas, located in the state of Minas Gerais, Brazil ($20^\circ 14' 42''$ S and $46^\circ 21' 57''$ W), where different rates of phosphogypsum were applied. The soil was classified as *Latosolo Vermelho distrófico típico* (Santos et al., 2013), which corresponds to an Oxisol (Soil Survey Staff, 2014), and details regarding this experimental area can be found in other studies (Ramos et al., 2013; Silva et al., 2013; Carducci et al., 2015). In this experimental area, seven months after establishing the coffee crop, different rates of phosphogypsum were applied at the plant rows, as follows: 0, 7, 14, and 56 t ha^{-1} . For assessing the influence of sulfate - added through the application of phosphogypsum - on the sorption behavior of Se, soil samples were collected 76 months following its application in the coffee rows at the following soil layers: 0.15-0.25, 0.35-0.45, and 1.25-1.35 m.

Soil characterization

Soil samples were air-dried, passed through a 2-mm sieve, and characterized by analyses of soil fertility and texture (Teixeira et al., 2017) before being submitted to selenate and selenite adsorption/desorption tests (at room temperature). Total SiO_2 , Al_2O_3 , Fe_2O_3 , and P_2O_5 contents were measured after sulfuric acid digestion, following the methodology proposed by Vettori (1969), with modifications (Teixeira et al., 2017), while the point of zero salt effect (PZSE) was measured following the procedure recommended by Keng and Uehara (1974). The physical and chemical properties of the assessed soils are presented in tables 1 and 2.

Adsorption and desorption procedures

Adsorption/desorption experiments with selenate (SeO_4^{2-}) and selenite (SeO_3^{2-}) were performed in soil samples previously described to assess the effect of sulfate on the sorption behavior of Se in the evaluated tropical soil. Selenium adsorption was evaluated reacting 2.0 g of soil (in triplicates) with 20 mL of solutions containing Se into centrifuge tubes having NaCl 15 mmol L^{-1} as the background electrolyte solution. Sodium selenate (Na_2SeO_4) was added at the initial Se concentrations (C_i) of 100 and $500 \mu\text{g L}^{-1}$, whereas sodium selenite (Na_2SeO_3) was added at C_i of 10 and 15 mg L^{-1} . With the soil:solution ratio of 1:10 used (i.e., 2 g of soil and 20 mL of a solution containing Se), these added concentrations correspond to 1 and 5 mg kg^{-1} for Se-selenate, and 100 and 150 mg kg^{-1} for Se-selenite.

No further corrections in the ionic strength (IS) of the adsorption solutions ($\text{NaCl } 15 \text{ mmol L}^{-1}$) were performed during the sorption process since these possible variations that may occur after the beginning of the adsorption reaction are inherent to the treatment characteristics

Table 1. Chemical properties of the studied soil samples

Phosphogypsum rate	Soil layer	pH	PZSE	SOM	Ca ²⁺	Mg ²⁺	K ⁺	P	S-SO ₄ ²⁻	Al
t ha ⁻¹	m			%	— cmol _c dm ⁻³ —		— mg dm ⁻³ —		cmol _c dm ⁻³	
0	0.15-0.25	4.6	4.1	2.4	2.3	0.8	181	1.1	8.7	0.10
0	0.35-0.45	4.8	4.9	2.3	2.9	0.9	114	0.5	14.9	0.05
0	1.25-1.35	5.0	5.5	0.9	0.9	0.5	13	1.6	6.5	0.10
7	0.15-0.25	4.8	5.6	2.5	3.1	0.5	174	1.9	44.5	0.15
7	0.35-0.45	5.1	5.8	2.3	3.0	0.5	158	0.9	46.3	0.15
7	1.25-1.35	4.8	6.0	1.1	2.1	0.1	12	0.8	38.3	0.11
14	0.15-0.25	5.1	5.8	2.5	2.8	0.3	119	2.1	63.5	0.25
14	0.35-0.45	5.3	5.3	2.3	2.5	0.4	92	0.9	82.6	0.15
14	1.25-1.35	5.5	5.9	0.9	1.0	0.3	11	0.3	30.9	0.10
56	0.15-0.25	6.4	5.8	2.3	8.5	0.4	146	1.1	135.8	0.10
56	0.35-0.45	5.6	5.7	2.3	7.8	0.2	167	0.7	148.6	0.10
56	1.25-1.35	5.5	6.8	1.0	3.9	0.4	13	0.3	174.0	0.10

PZSE: point of zero salt effect. Exchangeable sulfate extracted with monocalcium phosphate in acetic acid and analyzed by colorimetric spectrophotometry (Ferraz, 2017); SOM: soil organic matter; pH: determined in water using a soil:water ratio of 1:2.5; Ca²⁺, Mg²⁺, and K⁺: exchangeable (Ca and Mg) and available (K) contents; P: available phosphorus; S-SO₄²⁻: available sulfur; Al: exchangeable Al. All soil properties were measured according to Teixeira et al. (2017), except the PZSE, which was determined according to Keng and Uehara (1974).

Table 2. Texture and contents of different oxides for the studied soil layers

Soil layer	Clay	Silt	Sand	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	P ₂ O ₅
m	— g kg ⁻¹ —			— g kg ⁻¹ —			
0.15-0.25	630	250	120	102	355	157	1.32
0.35-0.45	690	220	90	102	371	163	1.22
1.25-1.35	820	110	70	105	392	169	0.98

Clay, silt, and sand contents were determined according to Teixeira et al. (2017); "Total" oxides (SiO₂, Al₂O₃, Fe₂O₃, and P₂O₅) were determined by sulfuric acid digestion, being part of these results adapted from Ramos et al. (2013).

(phosphogypsum doses). The pH values of solutions added for the adsorption study were adjusted to 5.5 using HCl or NaOH, both at 0.1 mol L⁻¹. This is the pH value considered suitable for adequate growth of several crops in Brazil. The Se doses were chosen based on previous studies where selenite has shown to be much more adsorbed than selenate, which thus require greater concentrations of selenite to be added (Gabos et al., 2014b; Jang et al., 2015; Araujo et al., 2018, 2020).

Centrifuge tubes were shaken for the adsorption process for 24 h. Next, they were centrifuged at 2300 rpm (approximately 530 g) for 20 min, and the supernatants were used for selenium analysis using Graphite Furnace Atomic Absorption Spectrophotometry (GFAAS). The limits of detection (LOD) and quantification (LOQ) of the used technique (GFAAS) for measuring Se contents were 0.82 and 2.73 µg L⁻¹, respectively.

After the Se analysis, the amounts of Se (selenate or selenite) adsorbed (µg kg⁻¹) by each studied soil sample was calculated as follows:

$$Se_{ads} = [(C_i - C_e) \times V] / Ms \quad \text{Eq. 1}$$

in which: Se_{ads} is the Se adsorbed by the soil (µg kg⁻¹); C_i is the initial Se concentration added (µg L⁻¹); C_e is the equilibrium Se concentration (µg L⁻¹); V is the final volume used in the adsorption procedure (mL); and Ms is the soil mass used for performing the adsorption test (g).

Desorption was performed immediately after adsorption. For that, 20 mL of the electrolyte solution (15 mmol L⁻¹ NaCl) were added in the previously mentioned centrifuge tubes for evaluating Se desorption. The weight of the tubes was measured before and after the addition of the desorption electrolyte solution to consider the volume and concentration of the remaining adsorption solution in the tubes (i.e., entrained solution) for an accurate calculation of desorbed Se.

To obtain the desorbed amount (mg kg⁻¹) in the soil, the initial desorption concentration was calculated, considering the remaining adsorption volume, according to the following equation:

$$C_{iDes} = \frac{C_{eAds} \times V_{RemAds}}{V_{Total}} \quad \text{Eq. 2}$$

Then, the desorbed amount was calculated based on the equation below:

$$Se_{Des} = \frac{(C_{eDes} - C_{iDes})}{Ms} \times V_{Total} \quad \text{Eq. 3}$$

in which: C_{iDes} is the initial desorption concentration ($\mu\text{g L}^{-1}$); C_{eAds} is the equilibrium concentration of the adsorption solution ($\mu\text{g L}^{-1}$); V_{RemAds} is the remaining volume of the adsorption solution (mL); V_{Total} is the volume of solution added for desorption test, including the remaining volume of the adsorption solution (mL); Se_{des} is the selenium desorbed amount in soil (mg kg⁻¹); C_{eDes} is the equilibrium concentration of the desorption solution ($\mu\text{g L}^{-1}$); and Ms is the soil mass (g).

Adsorption and desorption results of Se (selenate or selenite) were statistically analyzed for variance using the Sisvar software (Ferreira, 2000). The mean values found were compared among treatments by the Scott-Knott test at 5 % significance ($p < 0.05$) (Scott and Knott, 1974).

RESULTS

Selenium adsorption

Table 1 shows that the contents of Ca²⁺ and SO₄²⁻ were higher in treatments where phosphogypsum was applied, mainly at the highest rate, as expected. Sulfate contents were greater at the soil layer of 0.35-0.45 m for all treatments, except when the highest phosphogypsum dose was applied, where the sulfate content was higher at the deepest soil layer evaluated. As expected, the contents of organic matter did not change with the application of phosphogypsum and were higher at the superficial soil layers compared with the deeper soil depths. The point of zero salt effect (PZSE) increased with increasing soil depths (Table 1). It should be stated that differences between PZSE and point of zero charges (PZC) values in soils are inherent to the charges that are generated by isomorphic substitution (permanent charges). Thus, PZSE and PZC are similar in tropical soils, since these are variable charge soils due to their high degree of weathering (van Raij and Peech, 1973; Gallezet al., 1976).

Results of adsorption and desorption as a function of sulfate contents (i.e., phosphogypsum doses) and soil layers are found in figures 1, 2, 3, and 4. Considering the treatment where phosphogypsum was not applied (Figure 1a), the adsorption of selenate increased upon increasing soil depth. When phosphogypsum application occurred at rates of 7, 14, and 56 t ha⁻¹, the percentages of selenate adsorbed were higher at the deepest soil layer (1.25-1.35 m), and no statistical differences in the adsorption values were found comparing the soil layer of 0.15-0.25 m with the soil layer at 0.35-0.45 m (Figures 1b, 1c, and 1d).

Figure 1 also shows that the adsorbed selenate amounts decreased (considering the same soil depth), with increasing gypsum rates applied. The exception for this trend was for the deepest soil layer (1.25-1.35 m), where reduction in the selenate adsorbed contents was verified only when 56 t ha⁻¹ of phosphogypsum were applied.

The adsorption of selenite was less influenced by soil depth and sulfate content than selenate. Selenite adsorption percentages were statistically different comparing the evaluated soil layers only when the highest phosphogypsum dose was used. In this case, the adsorption percentage was higher at the deepest soil layer (1.25-1.35 m) (Figure 2). The adsorbed percentages of selenite were much higher than those of selenate. These percentages for selenite reached values higher than 80 % for all treatments, while the adsorbed percentages of selenate ranged from 20 to approximately 100 %, varying greatly as a function of the soil layer and sulfate content. Adsorption percentages did not vary between the two assessed Se doses for both Se chemical forms (i.e., 100 and 500 µg L⁻¹ for selenate, and 10 and 15 mg L⁻¹ for selenite) (Figures 1 and 2).

Selenium desorption

Although selenate was adsorbed in lower amounts, its desorbed percentages were greater when compared with selenite. The desorbed percentages of selenite were close to 5 % in all treatments, while it ranged from approximately 15 to 30 % in the case of selenate.

In terms of the evaluated soil layer, selenate desorbed amounts were much higher at the deepest soil layer (1.25-1.35 m). This soil layer also showed higher adsorbed amounts of selenate (Figure 1). Thus, the amount of selenate desorbed is related to the quantity previously adsorbed (Figure 3). In contrast to what was observed for selenate, desorbed amounts of selenite were low and revealed no variation with changes in sulfate contents and soil layers, which may indicate that selenite is strongly adsorbed by ligand exchange and/or inner-sphere complexes.

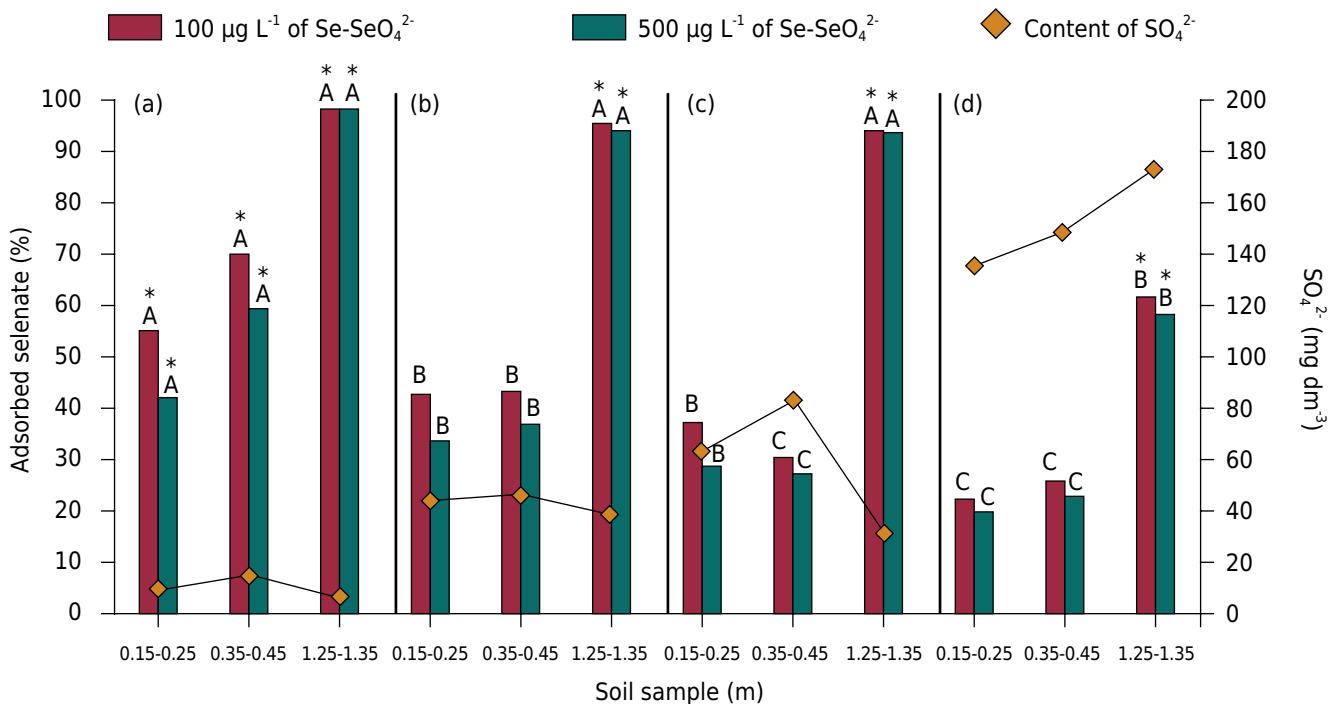


Figure 1. Selenate (SeO_4^{2-}) adsorption (%) at three soil layers of a *Latossolo Vermelho distrófico* (Oxisol). The letters (a), (b), (c), and (d) correspond respectively to the rates of phosphogypsum applied to the soil, as follows: 0, 7, 14, and 56 t ha⁻¹. The letters and the (*) above the bars compare the means by the Scott-Knott test at 95 % probability. The letters compare the adsorption of SeO_4^{2-} under the influence of different sulfate (SO_4^{2-}) contents for the same soil layers. Bars with (*) indicate statistical differences in SeO_4^{2-} adsorption rates among soil layers within the same applied phosphogypsum doses.

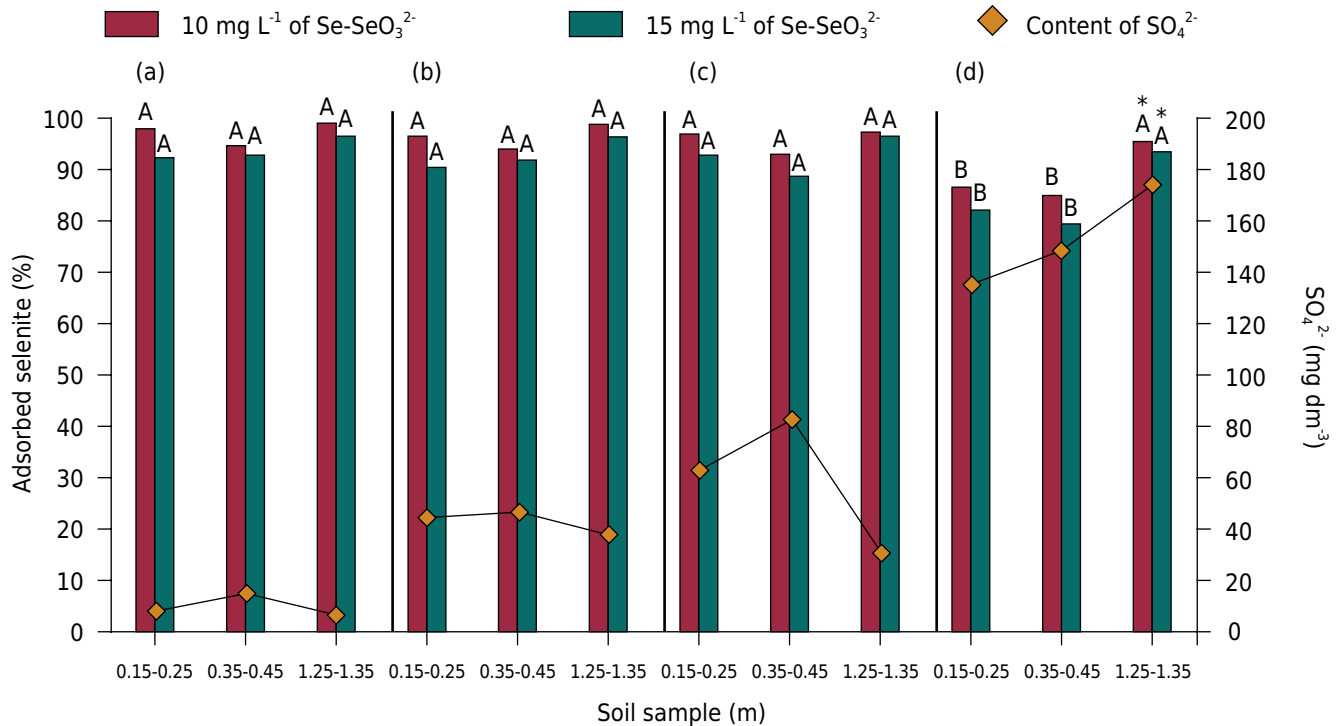


Figure 2. Selenite (SeO_3^{2-}) adsorption (%) at three soil layers of a *Latosolo Vermelho distrófico* (Oxisol). The letters (a), (b), (c), and (d) correspond respectively to the rates of phosphogypsum applied to the soil, as follows: 0, 7, 14, and 56 t ha⁻¹. The letters and the (*) above the bars compare the means by the Scott-Knott test at 95 % probability. The letters compare the adsorption of SeO_3^{2-} under the influence of different sulfate (SO_4^{2-}) contents for the same soil layer. Bars with (*) indicate statistical differences in SeO_3^{2-} adsorption rates among soil depths within the same applied phosphogypsum doses.

DISCUSSION

Selenium adsorption

In general, selenate (SeO_4^{2-}) adsorption capacity was influenced by both, the sulfate content and soil layer. On the other hand, selenite (SeO_3^{2-}) adsorption was affected only when the highest phosphogypsum dose was applied (i.e., with the highest sulfate contents) and for the most superficial soil layer. This indicates that SeO_3^{2-} retention in tropical soil is little influenced by the anionic competition of SO_4^{2-} .

The increase in the adsorption of selenate upon increasing soil layers can be explained due to the greater availability of adsorption sites (i.e., net positive charges) at deeper soil layers. Moreover, the contents of organic matter and of competing anions, such as S-sulfate and P-phosphate, were lower at these deeper soil layers (Table 1). With lower contents of competing anions, much more positive charges were available for adsorbing selenate, thus increasing its adsorbed amounts. Also, the reduction in organic matter contents with soil layer decreases negative charges, allowing for positive charges to prevail at these deeper soil layers. These positive charges found in tropical soils, mainly at deeper soil layers, are commonly generated by Fe and Al oxides, which are solid phases relevant to retain anions, such as selenate (van Raij, 1973; Fernandes et al., 2008). As tropical soils are variable charge soils, the increase in the generation of positive charges as soil depth increases can be confirmed since the values of the point of zero salt effect (PZSE) of the soil increased at deeper soil layers (Table 1).

The higher selenate adsorbed amounts by the deepest soil layer when 56 t ha⁻¹ of phosphogypsum were applied were verified even with the greatest sulfate contents in the soil (Figure 1). This can be linked to the fact that this soil layer presents the higher clay contents (Table 2) as well as due to the predominance of positive surface charges as discussed earlier.

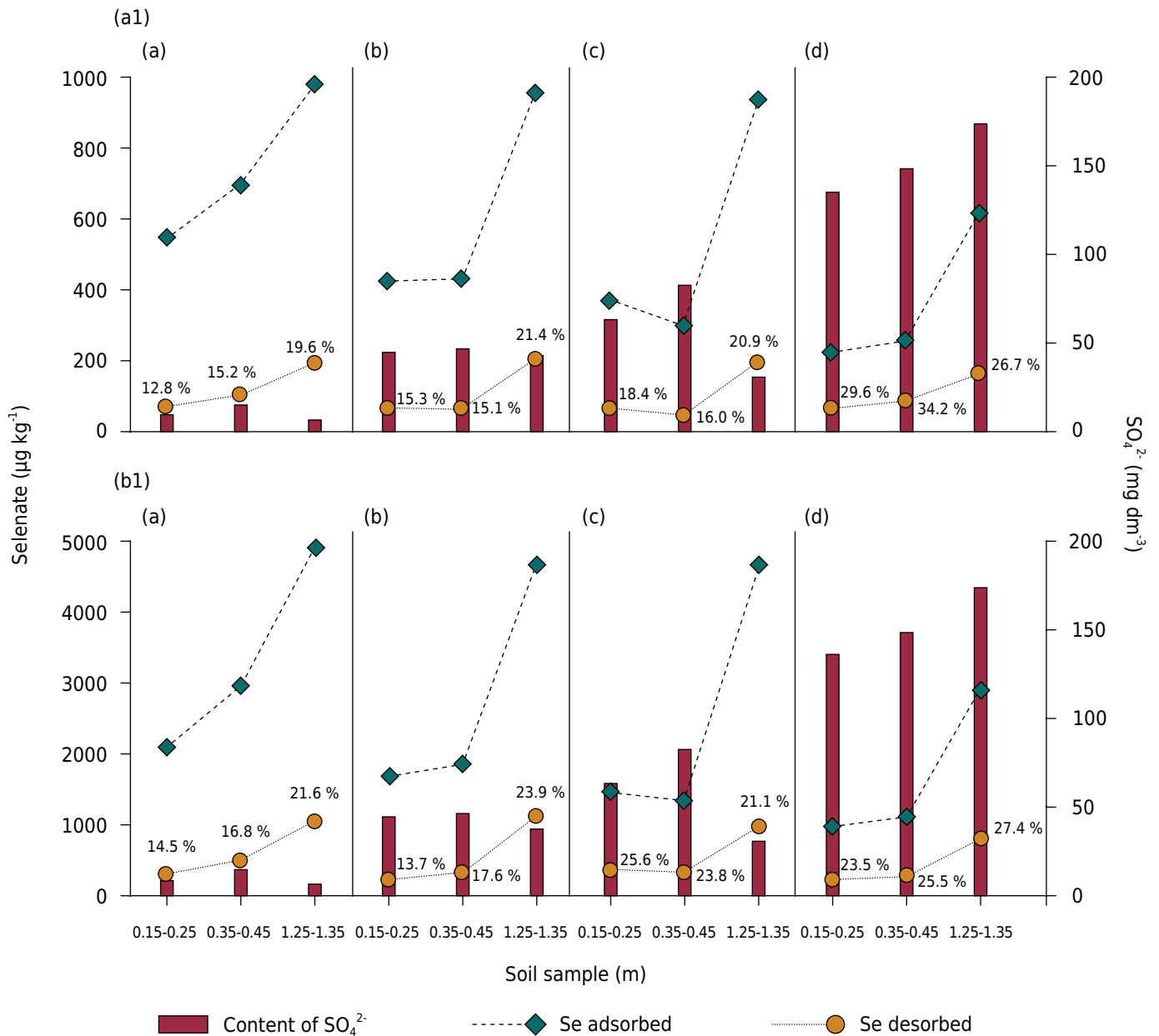


Figure 3. Adsorbed and desorbed amounts of selenate (SeO_4^{2-}) at different soil layers of a *Latossolo Vermelho distrófico* (Oxisol). The percentages shown above the desorption points refer to the desorbed percentages as a function of the adsorbed amount. The letters (a), (b), (c), and (d) correspond respectively to the rates of phosphogypsum applied to the soil, as follows: 0, 7, 14, and 56 t ha^{-1} . (a1) and (b1) refer to SeO_4^{2-} doses of 100 and 500 $\mu\text{g L}^{-1}$, respectively.

The direct and positive relationship of clay content with selenate adsorption has been reported in other studies in Brazilian soils (Mouta et al., 2008; Abreu et al., 2011; Lessa et al., 2016; Araujo et al., 2018). In this context, Wang and Chen (2003) stated that soils with a clay fraction rich in Fe and Al oxides are of great importance for the adsorption of anions, such as selenate, since they have high values of point of zero charge, and, therefore, have positive charges at the pH values normally found in tropical soils. Selenium adsorption by Fe and Al oxides is an important control factor in Se availability in soils with low organic matter contents (Xu, 2013). Similar results were observed by Jia et al. (2019), who reported that Fe and Al oxide contents were the major factors controlling/reducing Se bioavailability in soils.

The present study clearly shows that the different concentrations of sulfate directly influenced selenate adsorption values. In this context, Constantino et al. (2017), evaluating the effect of the anions nitrate, sulfate, and phosphate on Se adsorption and desorption

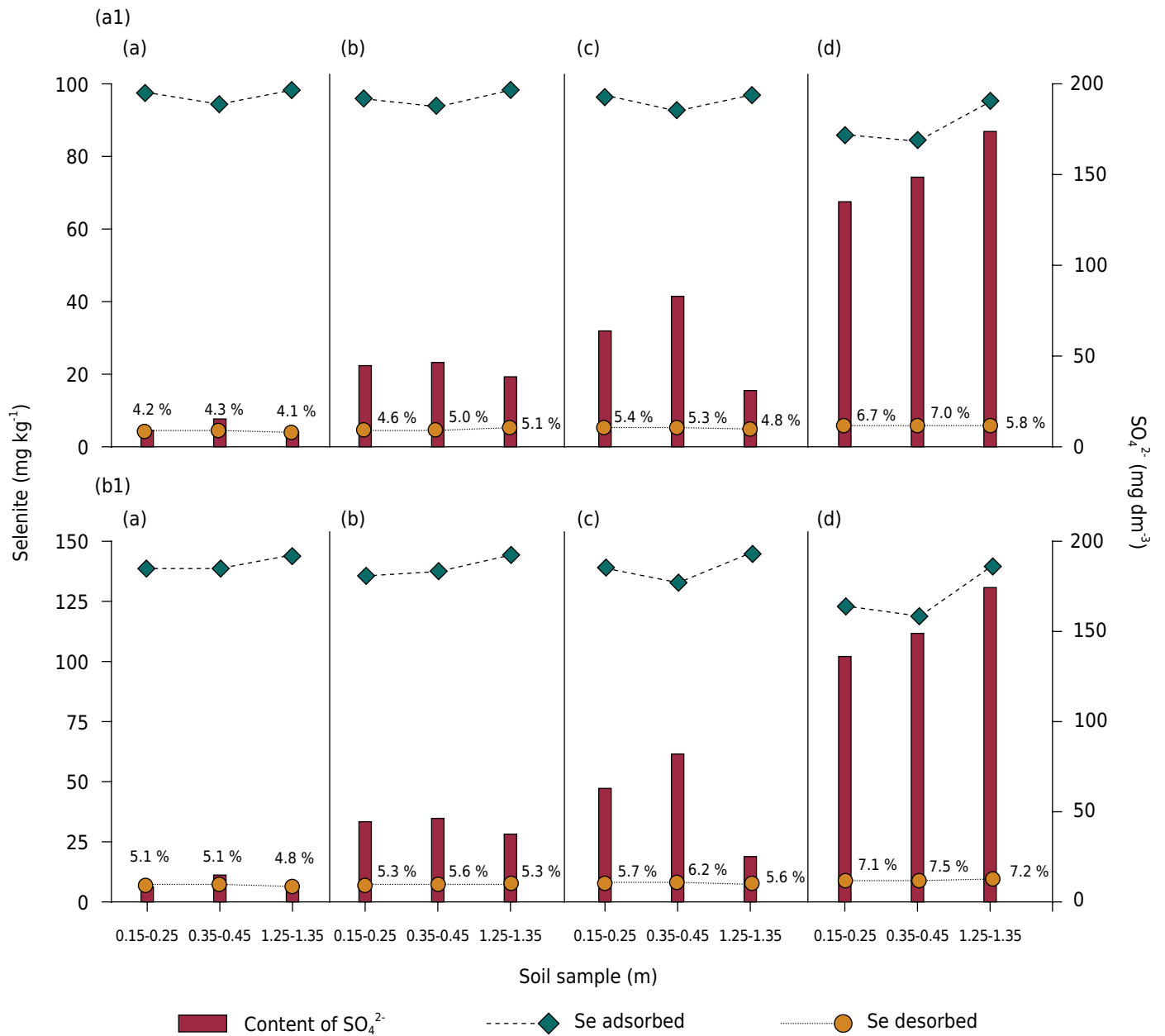


Figure 4. Adsorbed and desorbed amounts of selenite (SeO_3^{2-}) at different soil layers of a *Latossolo Vermelho distrófico* (Oxisol). The percentages shown above the desorption points refer to the desorbed percentages as a function of the adsorbed amount. The letters (a), (b), (c), and (d) correspond respectively to the rates of phosphogypsum applied to the soil, as follows: 0, 7, 14, and 56 t ha⁻¹. (a1) and (b1) refer to SeO_3^{2-} doses of 10 and 15 mg L⁻¹, respectively.

found that sulfate was the anion with the greatest influence on selenate adsorption. The authors mentioned that SO_4^{2-} and SeO_4^{2-} have the same tetrahedral symmetry and behavior in soils, and they may compete for the same adsorption sites. Chubar (2018), assessing the effect of sulfate on selenate adsorption in synthetic material (Mg-Al-CO_3), used as an ion exchanger in aqueous treatment and removal technologies, found that the presence of sulfate reduced selenate adsorption, demonstrating a competitive relationship between these ions, which, according to the authors, is governed by their anionic charge and the availability of adsorption sites.

Differently from what was reported for SeO_4^{2-} , sulfate contents and soil depth had little impacts on the adsorption of selenite (Figure 2). This fact indicates that the SO_4^{2-} presents low capacity to modify the adsorption of selenite, which is an opposite behavior compared with selenate. Other studies evaluating the adsorption of Se and arsenic

(As) in tropical soils found that arsenate (AsO_4^{3-}) and SeO_3^{2-} had higher adsorption capacities and were less affected by SO_4^{2-} competition than arsenite (AsO_3^{3-}) and SeO_4^{2-} (Goh and Lim, 2004).

Similar results were also reported by Nakamaru and Sekine (2008), who assessed the influence of H_2PO_4^- and SO_4^{2-} on SeO_3^{2-} adsorption in Japanese soils. These authors found that SeO_3^{2-} sorption did not alter with increasing SO_4^{2-} concentration, but decreased with increasing H_2PO_4^- . Soil samples assessed in the present study are very different from the soils studied by Nakamaru and Sekine (2008), however this study is relevant for showing the effect of H_2PO_4^- and SO_4^{2-} on selenite retention in soils that present high anions adsorption capacity. In this context, Gonzalez et al. (2010), evaluating an iron/manganese oxide-based nanomaterial for selenite and selenate treatment and removal technology, found that the sorption of both Se chemical forms was affected by the presence of phosphate with a greater decrease in selenate sorption than in selenite. Instead, sulfate only affected selenate sorption, as it was verified in the present study. The presence of nitrate and chloride had no influence on the adsorption of Se for both species, selenite or selenate.

The high adsorption of selenite by the studied soil samples, even at higher sulfate concentration, suggests a greater affinity between this ion and the solid components of tropical soils. This trend has been reported in other studies. Mouta et al. (2008), evaluating Se adsorption in Brazilian soils, verified, through the quantitative adsorption parameters (Langmuir Ads_{max} and Freundlich K_f), a great selenite immobilization potential mainly in *Latassolos* (Oxisols). Gabos et al. (2014b), also evaluating selenite adsorption in Brazilian soils, observed that selenite adsorption reached high values for all 15 evaluated soils and was highly linked to the presence of Fe and Al oxides.

The fact that selenate is less adsorbed, with its sorption capacity being more influenced by competitive anions, compared with selenite, can also be related to the adsorption mechanisms by which these Se forms are bound to soil particles. Studies have shown that selenate is adsorbed predominantly by outer-sphere complexes, whereas selenite is retained by inner-sphere complexes, which are considered much strong adsorption mechanisms that are less affected by competing anions (Snyder and Um, 2014; Dinh et al., 2019). Researches assessing the mechanisms of selenate and selenite retention in soils were also performed in tropical soils in recent studies conducted by our research group (Araujo et al., 2018, 2020).

Selenium desorption

The amount of selenate (SeO_4^{2-}) desorbed was associated to the quantity previously adsorbed by the soil. Araujo et al. (2018) and Lessa et al. (2016), assessing the adsorption and desorption of selenate in tropical soils, found that selenate desorption changed depending on the amount of Se previously adsorbed in the soil, being higher in soils with higher adsorption capacities. These authors reported that these high adsorption values for selenate were verified in soils with greater clay contents and with lower contents of competing anions, such as sulfate and phosphate.

In contrast to what occurred with selenate, the desorbed amounts of selenite (SeO_3^{2-}) were very low (close to 5 % in all treatments) and have no significant variations as a function of sulfate content and soil depth. These results indicate that sulfate presents low or no capacity to interfere on the desorption of selenite. Moreover, the fact that selenite had a lower desorption rate and is adsorbed in greater amounts than selenate suggests that the main mechanism involving its retention is the formation of inner-sphere complexes, being, therefore, little affected by the presence of sulfate in the adsorption media. Similar results were reported by Lee et al. (2011) in a study evaluating selenite adsorption/desorption in South Dakota soils. The authors found that the selenite desorption tends to be little

influenced by sulfate, suggesting the formation of inner-sphere complexes as the major mechanism involved in the adsorption process.

Li et al. (2015), evaluating selenite adsorption and desorption in 18 Chinese agricultural soils, found that soils with high adsorption capacity showed low desorption rates, which significantly reduced selenite bioavailability in these soils. Agreeing with that, Gabos et al. (2014b), in a study aiming to model selenite and selenate sorption in soils using capacitance model, reported that selenite was strongly sorbed on soil particles and, as a result, less available to plants when compared with selenate. Therefore, selenite is strongly bound to tropical soils, being not influenced by sulfate contents and much less available to plants than selenate. Then, if one is aiming to apply selenium in tropical soils in order to biofortify agricultural crops with Se, selenate is the target species to be used, since more Se is expected to be absorbed by plant roots. However, as pointed out in this study, the retention of selenate is affected by soil properties, such as soil organic matter and sulfate contents. Therefore, further studies involving the effects of these properties in the selenate sorption process in soils are stimulated and still relevant to assist in the definition of the best Se addition rates for agronomic biofortification studies.

CONCLUSIONS



Selenate (SeO_4^{2-}) adsorption and desorption in tropical soils are affected by the sulfate status in the soil, with selenate adsorbed amounts decreasing under higher sulfate contents provided by high rates of phosphogypsum addition in agricultural soils. In terms of desorption, selenate desorbed amounts increased when the highest content of sulfate was present (higher phosphogypsum rate was applied), thus, suggesting a competition involving sulfate and selenate for adsorption sites. Conversely, selenite (SeO_3^{2-}) is strongly retained in tropical soils, presenting high adsorption and low desorption values, and being little affected by the presence of sulfate in the sorption media. Selenium adsorption was also influenced by soil depth, mainly for selenate, with the adsorbed amounts increasing with soil depth.



The high adsorption capacities of selenite, even in sulfate-rich soil samples, as well as the low desorbed percentages of this Se species, indicate that selenite is bound to soil particles of tropical soils by ligand exchange and/or via formation of inner-sphere complexes. Because of that, selenite is much strongly retained and less available to plants than selenate.




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