

## Adsorption and desorption of arsenic and its immobilization in soils

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**ABSTRACT:** Arsenic (As) is a naturally occurring chemical element considered toxic and carcinogenic by health and environmental protection agencies. Studies of As adsorption/desorption behavior in soils are important to predictions of As' potential mobility in natural systems. The aim of this study was to assess the adsorption of As(V) in soils from Minas Gerais, Brazil, and determine its immobilization rate in order to identify soils with characteristics more favorable to its deployment as an As geochemical barrier. The adsorption experiment was performed using different As concentrations and the data pertaining to the maximum adsorption capacity of As(V) (MACAs) were determined by Langmuir and Freundlich isotherms. The Oxisols, due to their more oxidic mineralogy, especially more gibbsitic, and clayey texture, showed the highest MACAs, followed by Ultisols, Inceptisols, and Entisols. In terms of the desorption of As the Inceptisols were the soils that showed the most As desorption. Both As desorption and mobility was lower in the more oxidic and clayey soils. In all soils, the total amount of As was desorbed in due course, but the As release ratio tended to decrease with the passage of time. In general, soils with higher MACAs did not necessarily show less As desorption. For use as a geochemical barrier, as important as a high adsorption capacity of As by the soil is a low As desorption rate. The increase in As mobility may increase the risks of contaminating the supplies of water. To be a good As geochemical barrier the soil has to be a clayey Oxisol, with relatively high amounts of Fe and Al oxides, especially gibbsite.

**Keywords:** toxic contaminant, maximum adsorption capacity, mineralogy of soils, texture, geochemical barrier

## Introduction

Arsenic (As) is a toxic and carcinogenic element according to senior health and protection and health agencies (WHO, 2001; USEPA, 2007). In order to minimize the harmful effects of this chemical element on health, the value of 0.01 mg L<sup>-1</sup> of As was selected as the standard of the maximum permissible level by the World Health Organization (WHO, 1993) for drinking water quality.

Adsorption/desorption of As is the main factor that impacts As mobility in soils (Zhang and Selim, 2005). These adsorption and desorption balances are controlled by the mineral and organic matrices of soils (Dias et al., 2019). Many studies have sought to clarify the role of minerals, soils, and sediments in the retention and release of As into the environment (Ladeira and Ciminelli, 2004; Zhang and Selim, 2005; Mello et al., 2006; Borba et al., 2017; Dias et al., 2019; Fontes et al., 2019). Knowing the types of interaction involved makes it possible to predict the destination of As in relation to potential environmental changes (Zhang and Selim, 2005).

Oxidic surfaces, especially Fe and Al oxyhydroxides, have a high affinity for As (Cui and Weng, 2013), and they are important components of the clay fraction of soils in Minas Gerais (Fontes and Weed, 1991) where the mining process has caused problems with As contamination, e. g. in the municipalities of Ouro Preto, Mariana and Paracatu. In these counties As contents in the sediments and water are very high, and can reach as much as 4500 mg kg<sup>-1</sup> in sediments and 350 µg L<sup>-1</sup> in

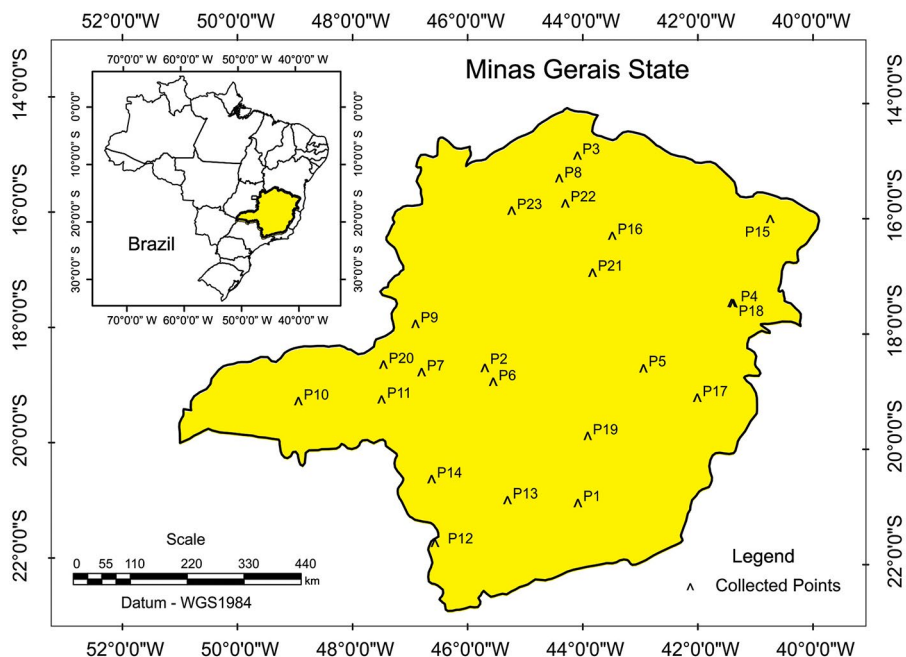
water (Pimentel et al., 2003; Mello et al., 2006; Varejão et al., 2011; Borba et al., 2017; Fontes et al., 2019).

For the geochemical purpose of immobilizing As, soils with high adsorption capacity and low desorption capacity of As are excellent for remediation procedures since they are able to form a natural seepage barrier to surrounding soils, groundwater and the environment (Ladeira and Ciminelli, 2004). Soils with predominantly oxidic mineralogy and clayey texture, such as Oxisols and certain Ultisols, are more favorable to retaining As in their application as a geochemical barrier to immobilize this element. Thus, the aim of this study was to determine the adsorption of As(V) in the A and B horizons of representative soils from Minas Gerais, and determine its mobilization rate by means of the desorption of As(V), in order to identify the most suitable soil class and attributes to be used as a geochemical barrier for As.

## Materials and Methods

### Soil sampling

Twenty-three representative profiles of the main soil classes of the state of Minas Gerais, Brazil (Figure 1), were collected at depths of 0 to 20 cm (A horizon) and 50 to 70 cm (B horizon) (Table 1). The soil samples were dried and sieved in order to obtain the air-dried fine earth (ADFE). The taxonomic classification of soils was based on the U. S. Soil Taxonomy (Soil Survey Staff, 2014) according to categorization system of the Brazilian System of Soil Classification (EMBRAPA, 2013).



**Figure 1** – Location of the collected soils in the state of Minas Gerais, Brazil.

### Physical, chemical and electrochemical analysis of soils

The clay content was determined by the pipette method after removal of organic matter and iron oxides (EMBRAPA, 2011). For separate particle size fractions, ADFE samples were subjected to slow shaking (16 h) in a vertical shaker with NaOH 0.1 mol L<sup>-1</sup>. The sand fraction was retained on a 53 μm sieve and then the clay and silt fractions were separated by sedimentation (Jackson, 1979).

The pH was potentiometrically measured using a combination glass electrode, calibrated with a buffer solution in pH 7.01 and 4.00 at room temperature, immersed in soil:liquid suspension in a ratio of 1:2.5 (EMBRAPA, 2011). Exchangeable Al was determined by titration, after extraction with KCl 1 mol L<sup>-1</sup> in a ratio of 1:10 (EMBRAPA, 2011). Total organic carbon was determined by titration of the remaining potassium dichromate with ammoniacal ferrous sulfate after the wet oxidation process (Yeomans and Bremner, 1988).

Iron and Aluminum forms were determined by the dithionite-citrate methods (Coffin, 1963) and 0.2 mol L<sup>-1</sup> ammonium acid oxalate at pH 3.0 (McKeague and Day, 1966). Quantification of the elements was carried out using an atomic absorption spectrophotometer (Varian SpectraAA 220A).

The point of zero salt effect (PZSE) was determined for all soil samples through potentiometric titration (Fontes et al., 2001), using modified traditional methods (Parks and Bruyn, 1962; Van Raij and Peech, 1972). A mass of 2 g of each sample was added to 12.5 mL of

NaCl solution (0.001, 0.01, and 0.1 mol L<sup>-1</sup>), in 50 mL polypropylene tubes for a period of 24 h. After the contact time the samples were acidified with HCl to a pH of ~3.0, and titrated with NaOH. The titration curves were derived by a graphic program where the equivalence point was determined with HCl. The overlap of the four curves permitted the obtaining of a crossing point where pH = PZSE.

### Mineralogical soils analysis

Minerals from sand, silt and clay fractions were identified by X-ray diffraction (XRD) analyses using an X'PERT PRO PANALYTICAL diffractometer (CoK $\alpha$  radiation) in the range of 4 to 45 °2 $\theta$  with intervals of 0.02 °2 $\theta$  to 1 step s<sup>-1</sup>, voltage of 40 kV, and current of 30 mA.

Thermogravimetric analyses were performed on Shimadzu TGA 50 equipment. The samples were packed in alumina cell. The thermobalance worked with constant flux of nitrogen atmosphere and the temperature range of the analysis was between ambient temperature and 800 °C, at a heating rate of 10 °C per min.

### Arsenic (V) adsorption

The experiment of As (V) adsorption was conducted in triplicate on the surface and subsurface horizons in twenty-three representative profiles of the main soil classes of the state of Minas Gerais (Table 1). Solutions of 0.001 mol L<sup>-1</sup> NaNO<sub>3</sub> containing Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O were used at doses of 0.0, 6.0, 12.0, 18.0, 30.0, 42.0, 54.0, 66.0, 84.0, 102.0, and 120.0 mg L<sup>-1</sup> of As(V) with a

**Table 1** – Soil classification and location of the studied soils, in the state of Minas Gerais.

Soil Identification	USDA Soil Taxonomy	Geographic coordinates		
		Elevation (m)	Latitude	Longitude
Oxisol				
P1	Acrudox	979	-44°05'06.79"	-21°06'31.32"
P2	Acrudox	1032	-45°42'01.39"	-18°46'05.26"
P3	Eustrtox	445	-44°05'47.95"	-15°05'09.75"
P4	Hapludox	306	-41°24'53.64"	-17°38'25.04"
P5	Hapludox	778	-42°56'48.60"	-18°46'22.19"
P6	Acrudox	886	-45°33'14.00"	-19°00'25.70"
P7	Hapludox	915	-46°47'56.67"	-18°50'21.82"
P8	Eustrtox	434	-44°24'37.12"	-15°28'35.71"
P9	Hapludox	654	-46°54'26.77"	-18°00'02.09"
P10	Hapludox	631	-48°56'21.79"	-19°20'35.69"
P11	Hapludox	910	-47°29'50.89"	-19°18'59.71"
P12	Hapludox	1530	-46°34'04.46"	-21°48'21.87"
Ultisol				
P13	Paleudults	864	-45°18'26.32"	-21°03'57.78"
P14	Paleudults	745	-46°37'44.03"	-20°41'43.90"
P15	Paleustults	205	-40°44'35.59"	-16°11'07.84"
P16	Paleustults	650	-43°29'27.97"	-16°28'43.32"
P17	Hapludults	318	-42°00'38.96"	-19°17'06.47"
P18	Paleustults	347	-41°23'01.28"	-17°38'37.14"
Inceptisol				
P19	Dystrudepts	751	-43°54'56.72"	-19°56'48.98"
P20	Dystrudepts	890	-47°27'55.86"	-18°42'30.34"
P21	Dystrudepts	676	-43°49'54.86"	-17°06'40.38"
P22	Haplustepts	602	-44°18'16.08"	-15°54'33.43"
Entisol				
P23	Quartzipsamments	499	-45°14'07.14"	-16°02'15.98"

USDA = Soil Classification based on the U.S. Soil Taxonomy (Soil Survey Staff, 2014).

pH adjusted to 5.5. This pH value was chosen because it was close to the average pH values recorded in previous studies on the soils in Minas Gerais (Skorupa et al., 2012).

We placed 50 mL of each solution and 0.5 g of soil in polypropylene tubes with a capacity of 50 mL. The soils were placed under suspension by vertical stirring at 45 rpm for 24 h. These suspensions were centrifuged and the supernatant filtered for dosing the As using a Perkin Elmer Optima 8300DV Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES), with a detection limit of 60 µg L<sup>-1</sup> for As.

#### Maximum adsorption capacity of As(V)

The maximum adsorption capacity of As(V) (MACAs) was modeled using the Langmuir isotherm equation  $x/m = abC/(1+aC)$ . In the equation,  $x/m$  is the amount of the adsorbed element (mg g<sup>-1</sup>),  $b$  the maximum adsorption capacity (MAC) of the element by the soil (mg g<sup>-1</sup>),  $C$  the concentration of the element in the equilibrium solution (mg L<sup>-1</sup>), and  $a$  a constant related to the binding energy of the element to the soil (L mg<sup>-1</sup>).

The model proposed by Freundlich ( $x/m = kC^{1/n}$ ) was used for purposes of comparison with the model previously described. In the equation,  $x/m$  is the concentration of the element adsorbed on the solid (mg g<sup>-1</sup>),  $C$  the concentration in the equilibrium solution (mg L<sup>-1</sup>), and  $k$  and  $n$  are the Freundlich parameters that characterize the adsorption isotherm. The parameter  $1/n$  is dimensionless, and was linearized with  $\log x/m$  as a function of  $\log C$ , building a line with slope  $1/n$  and intercept  $\log k$ , which were used to calculate the  $n$  and  $k$  values. This type of isotherm describes the adsorption of ions in a similar way to that of the Langmuir isotherm, but predicts that the adsorption continues to occur after the complete coverage of the adsorbent surface by a layer of ions, with the adsorption energy decreasing in a logarithmic function as the surface area increases.

#### Arsenic (V) desorption

The experiment of As desorption was performed in the subsurface horizons of the collected samples. Doses corresponding to the average of the MACAs were added to 250 g of each sample and packed in 500 mL capacity plastic containers. Solutions in a volume corresponding to 60 % of the soil field capacity, previously calculated according to EMBRAPA (2011), were added to the containers. The material was carefully homogenized.

After the contact periods (1, 30, and 60 days) had elapsed, the soils were oven dried at 40 °C and slightly ground in a mortar. Subsequently, 0.5 g of these soils were weighed in polypropylene tubes to which the extractive solutions (Na<sub>2</sub>HPO<sub>4</sub>H<sub>2</sub>O, Na<sub>2</sub>SO<sub>4</sub>, and NaNO<sub>3</sub>) were added, in accordance with a two-fold molar ratio between the added anions and As(V) in order to facilitate the desorption. Solutions with a pH value adjusted to 5.5 were used from the addition of 1 or 2 mol L<sup>-1</sup> HCl or NaOH according to the buffering power of the solution in order to minimize the change in solution volume. The solution was stirred vertically for 24 h and the supernatant filtered for dosing the As by inductively coupled plasma-optical emission spectrometry (ICP-OES). The fraction of As desorbed from the soils was calculated on the bases of the change in concentration in solution (before and after desorption).

## Results and Discussion

#### Arsenic (V) adsorption

The data of As(V) adsorption, adjusted according to the Langmuir and Freundlich equations, are shown in Tables 4 and 5, respectively. The values of the regression coefficient (R<sup>2</sup>) ranged from 0.96 to 0.99 (Equation Langmuir) and from 0.95 to 0.97 (Freundlich equation), indicating that both models efficiently describe the adsorption of As.

The studied soil profiles showed differences in the maximum adsorption capacity of arsenic (MACAs), which is due to the set of chemical, physical, and mineralogical characteristics of the soils (Tables 2 and

**Table 2** – Physical, chemical, electrochemical, and mineralogical characterization of the soils.

Soil Id.	Hor.	Clay (%)	Textural class	Al <sup>3+</sup>	TOC	Fe <sub>D</sub>	Fe <sub>ox</sub>	Fe <sub>ox</sub> Fe <sub>D</sub>	pH	PZSE	Gb	Kt
P1	A	64	Very clayey	0.51	2.73	7.43	0.10	0.01	4.94	3.64	24.4	38.6
P1	Bw	68	Very clayey	0.11	0.91	4.16	0.59	0.14	4.98	4.89	22.6	48.9
P2	A	80	Very clayey	0.51	2.99	6.34	0.13	0.02	4.94	3.85	41.9	24.0
P2	Bw	83	Very clayey	0.04	1.66	5.41	0.73	0.13	5.07	4.99	40.3	26.0
P3	A	11	Sandy loam	0.01	1.05	3.46	0.29	0.08	6.71	4.91	5.7	62.4
P3	Bw	27	Sandy clay loam	0.04	0.55	2.95	1.45	0.49	5.85	3.42	2.9	62.6
P4	A	48	Clay	0.75	1.55	1.74	0.11	0.06	5.06	3.25	2.2	85.3
P4	Bw	62	Very clayey	1.20	0.73	1.61	1.20	0.74	5.07	4.96	1.4	78.5
P5	A	56	Clay	0.14	2.20	5.55	1.31	0.23	5.70	4.55	6.5	70.4
P5	Bw	68	Very clayey	0.14	0.79	5.70	1.14	0.20	4.87	4.60	6.0	68.4
P6	A	65	Very clayey	2.23	8.22	2.47	0.18	0.07	4.50	3.99	15.2	40.9
P6	Bw	83	Very clayey	0.84	3.29	1.74	0.98	0.56	4.81	3.73	12.2	46.4
P7	A	29	Clay loam	1.17	1.55	4.09	2.02	0.49	4.87	3.52	nd	nd
P7	Bw	40	Clay	0.45	0.95	5.42	3.22	0.59	5.32	3.76	25.0	49.3
P8	A	30	Sandy clay loam	0.04	2.20	5.03	0.17	0.03	6.17	4.25	26.0	35.1
P8	Bw	42	Sandy clay	0.02	0.94	4.27	0.99	0.23	6.19	4.42	23.8	31.2
P9	A	42	Clay	0.04	2.87	7.37	0.19	0.02	6.27	5.13	6.0	70.1
P9	Bw	52	Clay	0.14	0.69	6.31	1.25	0.19	5.26	4.56	nd	66.7
P10	A	14	Sandy loam	0.23	1.15	5.61	1.99	0.35	5.97	3.57	11.1	32.4
P10	Bw	17	Sandy loam	1.54	0.43	10.38	2.03	0.19	4.84	5.37	15.2	26.4
P11	A	30	Sandy clay loam	1.42	4.04	9.69	0.56	0.05	4.89	3.50	10.1	39.8
P11	Bw	42	Sandy clay	0.05	0.77	10.47	0.44	0.04	5.28	3.54	9.4	36.8
P12	A	64	Very clayey	2.32	1.87	6.37	1.96	0.30	4.83	4.03	32.7	29.3
P12	Bi	69	Very clayey	2.29	0.77	8.48	1.12	0.13	5.13	4.94	32.9	24.1
P13	A	37	Clay loam	0.17	3.25	4.57	0.25	0.05	5.33	3.22	6.9	62.3
P13	Bt	56	Clay	0.35	0.80	4.22	0.95	0.22	5.15	4.43	nd	nd
P14	A	22	Sandy clay loam	0.05	6.4	4.83	0.47	0.09	7.19	5.98	15.6	40.8
P14	Bt	40	Sandy clay	0.11	1.2	5.41	2.34	0.43	5.66	3.37	7.9	33.8
P15	A	23	Sandy clay loam	0.04	1.2	1.86	0.14	0.07	6.56	4.66	0.7	67.7
P15	Bt	33	Sandy clay loam	0.03	0.7	0.75	0.19	0.25	5.96	3.34	2.1	66.0
P16	A	34	Silty clay loam	0.08	2.60	4.08	0.31	0.07	6.05	3.64	6.7	44.2
P16	Bt	50	Silty clay	1.54	0.90	3.38	2.12	0.05	4.26	5.32	3.0	32.2
P17	A	43	Clay	0.05	1.50	6.05	0.26	0.04	5.61	4.34	4.2	67.7
P17	Bt	66	Very clayey	0.05	0.50	6.01	0.85	0.14	5.47	2.86	2.0	70.4
P18	A	25	Sandy clay loam	0.51	2.90	1.52	0.21	0.13	5.19	3.16	3.0	80.8
P18	Bt	44	Sandy clay	1.05	0.80	1.34	1.00	0.74	4.60	2.98	1.3	79.3
P19	A	22	Silt loam	0.35	1.75	6.37	0.28	0.04	5.36	3.48	19.9	68.6
P19	Bi	37	Silty clay loam	2.57	0.91	4.66	4.95	1.06	4.95	2.98	7.0	34.6
P20	A	17	Sandy loam	1.57	1.05	1.07	0.23	0.21	5.19	3.08	5.7	56.5
P20	Bi	19	Loam	4.93	0.49	0.86	1.29	1.50	5.22	2.92	4.0	59.7
P21	A	33	Silty clay loam	1.84	1.80	6.39	0.22	0.03	5.46	2.72	nd	nd
P21	Bi	42	Silty clay	3.75	1.14	3.97	1.57	0.39	4.71	3.44	0.9	34.3
P22	A	35	Silty clay loam	0.08	1.83	3.38	0.23	0.06	5.73	4.58	0.7	18.3
P22	Bi	39	Silty clay loam	0.02	2.25	3.20	1.70	0.53	6.12	4.44	2.0	17.4
P23	A	07	Loamy sand	0.75	0.71	0.36	0.16	0.44	4.96	nd	1.6	80.6

Soil Id. = Soil Identification; Al<sup>3+</sup> (cmol<sub>c</sub> dm<sup>-3</sup>); TOC = total organic carbon (dag kg<sup>-1</sup>); Fe<sub>D</sub> = Fe extracted by dithionite-citrate; Fe<sub>ox</sub> = Fe extracted by ammonium oxalate; PZSE = Point Zero Saline Effect; nd = not determined; Gb = gibbsite; Kt = kaolinite.

3). The values of MACAs between the different soil classes presented the following order: Oxisols (P1 to P12) > Ultisols (P13 to P18) > Inceptisols (P19 to P22) > Entisol (P23). The Oxisols, Ultisols, and Inceptisols presented higher MACAs averages in the B horizon when compared to the A horizon. For the same soil

class, these differences may be attributed mainly to the texture and oxide content, which are the main factors that determined the variation in the capacity of the soil to act as an adsorbent surface of As. Oxidic soils have predominantly dependent charge surfaces that can attract ionic species such as As (Zhang et al., 2011).

**Table 3** – Mineralogical characterization of the soils.

Soil Identification	Sand	Silt	Clay
P1	Kt, Gb, Qz, Mt/Mh, Hm	Kt, Qz, Mi	Kt, Gb, Gt, Il, Hm
P2	Qz, Pg	Kt, Gb, Qz, Gt, Mi	Il, Kt, Gb, Hm, Gt
P3	Qz, Pg, Hm	Kt, Gb, Qz, Gt, Mi	Il, Kt, Gt, Qz, Hm
P4	Qz, Pg	Kt, Gb, Qz	Kt, Gb, Gt
P5	Kt, Gb, Qz, Pg, Hm	Kt, Gb, Gt, Qz	Kt, Gb, Gt, Hm
P6	Kt, Pg, Gb, Mi, Felds-K, Qz	Mi, Kt, Gb, Qz, Felds-K, Pg	Il, Kt, Gb, Gt
P7	Kt, Gb, Qz, Mt/Mh, Hm	Kt, Gb, Gt, An, Qz, Mh, Hm	Kt, Gb, Gt, Hm, Il
P8	Qz, Pg	Mi, Kt, Gb, Qz, Felds-K	HIV, Il, Kt, Gb, Gt, Mh, Hm,
P9	Qz, Pg	Kt, Qz, Pg, Hm	Il, Kt, Gt, Hm
P10	Qz, Pg, Hm	Qz	HIV, Il, Kt, Gb, Gt, Hm
P11	Qz, Pg	Qz, Hm	Il, Kt, Gb, Gt, Hm
P12	Kt, Gb, Qz, Pg, Hm	Mh, Kt, Gb, Qz, An, Hm	Kt, Gb, Gt, Il, Mh, Hm
P13	Qz, Pg, Felds-K	Mi, Kt, Qz, Pg, Felds-K	Il, Kt, Gb, Gt, Hm
P14	Mi, Qz, Pg	Kt, Mi, Qz, Pg	Il, Kt, Gb, Gt, Hm
P15	Qz, Pg	Kt, Qz	Il, Kt, Gt, Hm
P16	Qz, Pg	Mi, Kt, Qz, Pg, Felds-K	Il, Kt, Gt, Hm
P17	Qz, Pg	Kt, Mi, Qz, Pg	Kt, Gt, Il
P18	Qz, Pg	Kt, Qz	Il, Kt, Gt, Hm
P19	Mi, Qz, Gt, Pg	Mi, Kt, Qz, Pg, Felds-K	Il, Kt, Gt, Felds-K, Hm
P20	Mi, Qz, Pg, Felds-K	Mi, Kt, Qz, Pg, Felds-K	Vm/HIV, Il, Kt
P21	Qz, Pg, Felds-K, Mi	Mi, Kt, Qz	Il, Kt, Gt, Felds-K, Hm
P22	Mi, Qz, Felds-K, Pg	Mi, Qz, Kt	Il, Kt, Qz
P23	Qz, pg	Kt, Qz	Kt, Qz

Soil Id. = Soil Identification; Clay = Natural clay; An = anatase; Kt = kaolinite; Felds-K = potassium feldspar; Gb = gibbsite; Gt = Goethite; Hm = Hematite; Il = illite; Mi = mica; Mt/Mg = magnetite/maghemite; Mh = magheteite; Qz = quartz; Pg = plagioclase; HIV = hydroxy-interlayered vermiculite.

**Table 4** – Parameters related to the Langmuir equation for arsenic (V) adsorption in the soils.

Soil Identification (A horizon)	b	a	R <sup>2</sup>	Soil Identification (B horizon)	b	a	R <sup>2</sup>
P1	2.49	1.40	0.99	P1	2.55	1.53	0.99
P2	2.45	1.04	0.99	P2	2.67	1.12	0.99
P3	1.49	1.36	0.99	P3	1.56	1.33	0.99
P4	2.24	1.38	0.98	P4	2.85	1.16	0.99
P5	2.64	1.18	0.99	P5	2.91	1.21	0.99
P6	3.56	1.32	0.99	P6	3.58	1.37	0.98
P7	2.19	1.18	0.99	P7	2.46	1.26	0.97
P8	2.35	1.14	0.99	P8	2.34	1.12	0.99
P9	2.13	1.02	0.99	P9	2.22	1.05	0.97
P10	1.81	0.73	0.99	P10	1.78	1.33	0.99
P11	2.20	1.20	0.99	P11	2.77	1.34	0.99
P12	3.03	1.17	0.98	P12	3.08	1.51	0.98
P13	1.98	1.40	0.98	P13	1.93	1.34	0.99
P14	1.46	0.91	0.99	P14	1.98	0.82	0.97
P15	1.52	0.85	0.99	P15	1.63	0.98	0.99
P16	1.84	1.16	0.99	P16	1.88	1.12	0.98
P17	2.62	0.91	0.99	P17	3.25	0.94	0.96
P18	2.44	1.07	0.99	P18	2.33	1.34	0.97
P19	1.65	1.11	0.98	P19	1.81	0.73	0.98
P20	1.51	1.09	0.99	P20	1.55	1.16	0.96
P21	1.82	0.86	0.98	P21	1.71	0.75	0.98
P22	1.54	0.69	0.99	P22	1.67	0.85	0.99
P23	0.99	1.01	0.96				

**Table 5** – Parameters related to the Freundlich equation for arsenic (V) adsorption in the soils.

Soil Identification (A horizon)	K	n	R <sup>2</sup>	Soil Identification (B horizon)	K	n	R <sup>2</sup>
P2	1.19	0.35	0.97	P2	1.34	0.34	0.97
P3	0.84	0.28	0.98	P3	0.83	0.31	0.96
P4	1.31	0.27	0.98	P4	1.50	0.26	0.96
P5	1.19	0.31	0.97	P5	1.46	0.28	0.95
P6	1.30	0.37	0.97	P6	1.70	0.28	0.97
P7	1.66	0.36	0.97	P7	1.88	0.32	0.96
P8	1.07	0.35	0.97	P8	1.25	0.30	0.96
P9	1.17	0.32	0.97	P9	1.20	0.32	0.97
P10	1.03	0.35	0.97	P10	1.04	0.34	0.97
P11	0.78	0.39	0.98	P11	0.97	0.30	0.96
P12	1.10	0.34	0.97	P12	1.44	0.29	0.97
P13	0.99	0.34	0.98	P13	0.96	0.36	0.94
P14	0.68	0.33	0.97	P14	0.88	0.33	0.97
P15	0.65	0.38	0.97	P15	0.74	0.38	0.97
P16	0.93	0.33	0.98	P16	0.99	0.30	0.97
P17	1.24	0.34	0.97	P17	1.53	0.34	0.96
P18	1.23	0.33	0.98	P18	1.33	0.26	0.97
P19	0.87	0.26	0.95	P19	0.73	0.41	0.96
P20	0.80	0.33	0.96	P20	0.83	0.30	0.97
P21	0.85	0.33	0.98	P21	0.76	0.40	0.96
P22	0.65	0.41	0.98	P22	0.74	0.38	0.95
P23	0.27	0.52	0.95				

The highest As adsorption was correlated in studies conducted by Ladeira and Ciminelli (2004), with the highest Al and Fe oxy-hydroxide content. Oxides and their precursors have been extensively studied, either singly or in combination with other amendments promoting sorption, due to the fact that it provides greater As immobilization in contaminated soils (Komárek et al., 2013).

High As adsorption capacity in mine Fe-rich soils, showed that the mineralogical soil composition (especially Fe and Al oxy-hydroxide content) can be crucial to favoring As immobilization in soils (Arco-Lázaro et al., 2016). A similar conclusion was observed in studies conducted on laterite soils (soils with high Fe and Al oxides-hydroxides) (Maji et al., 2008).

Oxides of Fe may be used for the attenuation of arsenic in contaminated soils (Hartley and Lepp, 2008). The adsorption behavior of As is dependent on the concentrations of oxides in the soils (Khaska et al., 2018). Studies on sorption of As(V), using hematite and goethite, evaluated as a function of different physico-chemical parameters such as pH and ionic strength, evidenced the importance of Fe oxides in As immobilization in soils (Mamindy-Pajany et al., 2009).

Clay content showed a significant positive correlation with the adsorption capacity of As(V) at a probability of 99% in both the A and B horizons of the studied soils (Table 6). In addition to the textural class, gibbsite content in the soils was significant at 10 % in both horizons, showing the role of mineralogy in soil adsorption of As. Soils with clay texture and predominantly oxidic mineralogy, such as Oxisols and a number of Ultisols located in the state of Minas Gerais, favor the retention of As and these soil attributes are the

factors which determine a geochemical barrier for As (Almeida et al., not published data).

The As(V) adsorption in the Al and Fe surface is a product of inner-sphere complexation, preferably via bidentate complexes and a few monodentate complexes (Harrison and Berkheiser, 1982), a fact that portrays the role of Fe and Al oxides in the immobilization of arsenic in soils. The authors concluded that As is strongly attracted to sorption sites on solid surfaces, being effectively immobilized by the oxidic minerals present in the soils.

The results showed that the highest values for MACAs (3.56 and 3.58 mg g<sup>-1</sup> respectively in the A and B horizons) were determined in P6. This profile, in addition to being classified as a very clayey textured soil, showed a high content of gibbsite, hematite, and goethite (Table 3), with amounts of 25 % of the first mineral (Table 2). Another aspect to be emphasized is the relatively high values of Fe poorly crystallized in these soils, according to the Fe<sub>ox</sub>/Fe<sub>D</sub> ratio (Table 2).

The Oxisol P3 presented the opposite behavior to that observed in P6, exhibiting the lowest MACAs among the Oxisols (Table 4). In spite of having very similar aspects in terms of soil color, the greater differences in this profile can be related to the presence of a 2:1 mineral ratio and less pronounced amounts of gibbsite, which presented contents with a reduction of approximately 69 % (Table 2). The lower effectiveness in As adsorption in samples with a 2:1 clay minerals ratio and low gibbsite content have been reported by Mello et al. (2006). Studies in As adsorption using clay minerals suggested that the Si-OH edges are less effective than the Al-OH groups in adsorbing As (Manning and Goldberg, 1997). On the other hand, the presence of

**Table 6** – Correlation coefficient between a number of physical, chemical, and mineralogical attributes of the studied soils.

Attribute	CEC	TOC	Clay	Fe <sub>D</sub>	Fe <sub>ox</sub>	Fe <sub>ox</sub> /Fe <sub>D</sub>	pH	Gb	Kt
A horizon									
TOC	0.15°	1.00							
Clay	-0.31°	0.46**	1.00						
Fe <sub>D</sub>	0.13°	-0.01°	0.02°	1.00					
Fe <sub>ox</sub>	-0.03°	0.38°	0.02°	0.08°	1.00				
Fe <sub>ox</sub> /Fe <sub>D</sub>	-0.20°	0.04°	-0.26°	-0.55**	0.42°	1.00			
pH	0.40°	0.00°	-0.29°	-0.04°	-0.18°	-0.03°	1.00		
Gb	-0.35°	0.34°	0.46**	0.38°	-0.05°	-0.30°	-0.17°	1.00	
Kt	-0.01°	-0.31°	0.07°	-0.44**	-0.28°	0.25°	0.05°	-0.50**	1.00
B horizon									
TOC	0.62**	1.00							
Clay	-0.32	0.20	1.00						
Fe <sub>D</sub>	0.13	0.25	0.23	1.00					
Fe <sub>ox</sub>	0.16	0.33	0.03	0.30	1.00				
Fe <sub>ox</sub> /Fe <sub>D</sub>	0.12	-0.01	-0.28	-0.33	0.62	1.00			
pH	0.63**	0.26	-0.39	0.12	0.12	-0.09	1.00		
Gb	-0.14	0.40	0.46**	0.49**	0.21	-0.13	-0.38	1.00	
Kt	-0.06	-0.35	-0.32	-0.41	-0.29	0.10	0.01	-0.60**	1.00

\*\* and ° = Significant and non-significant at 1 and 5 %, respectively; CEC = total cation exchange capacity; TOC = total organic carbon; Clay = Natural clay; Fe<sub>D</sub> = dithionite-citrate; Fe<sub>ox</sub> = Fe ammonium oxalate; Gb = gibbsite; Kt = kaolinite.

gibbsite (Al-OH groups) in the soils favors the adsorption of As (Manning and Goldberg, 1997; Ladeira et al., 2001; Mello et al., 2006).

The lower MACAs values found in a number of soils can be explained by the  $Fe_{ox}/Fe_D$  ratio. The P3, for example, has a lower  $Fe_{ox}/Fe_D$  ratio in the Bw horizon (Table 2). This ratio is an appropriate indicator for the surface activity of the Fe oxides (Schwertmann, 1973). The interaction of As(V) and Fe oxy-hydroxides, including those with reduced crystallinity, is a function predominantly of inner-sphere surface complexes; these complexes contain no water molecules between the adsorbing ion and the surface functional group (Goldberg and Johnston, 2001).

The Oxisols, with their sandy loam texture (P3 and P10) (Table 2) and a predominantly kaolinitic mineralogy (Tables 2 and 3), showed a similar behavior for the As(V) adsorption (Table 4) compared to Inceptisols (P19 to P22).

As regards the Ultisols, the greatest differences between the A and B horizons were observed especially in the Bt horizon of P17, which presented the highest MACAs ( $3.25 \text{ mg g}^{-1}$ ), as shown in Table 4. In this case, an increase in clay content of 23 % was observed in the Bt horizon.

In general, Ultisols showed coarser granulometry and lower oxidic/gibbsitic contents than Oxisols, this possibly being the reason why the average MACAs of the former (2.16 in Bt) is slightly lower than that observed in the latter (2.46 in Bw). Due to the clay translocation, the A horizon of Ultisols often presented a sandy loam or silt loam texture. This situation tends to make soil pH slightly more alkaline, giving a lower MACAs to the soil with these characteristics compared to more acidic and dystrophic profiles of the Ultisol.

In Inceptisols, the average MACAs were  $1.63 \text{ mg g}^{-1}$  in the A horizon and  $1.69 \text{ mg g}^{-1}$  in the B horizon (Table 4), not substantially different from these values, except for P19. In this soil, the results of As(V) adsorption, considering the high Al content (Table 2), suggested the possibility of the existence of poorly crystallized Al forms, promoting an increase of 8 % in the MACAs. Increases in  $Fe_{ox}$  values with depth, together with the higher  $Fe_{ox}/Fe_D$  ratio in the B horizon, may also contribute to the higher adsorption of As in this horizon.

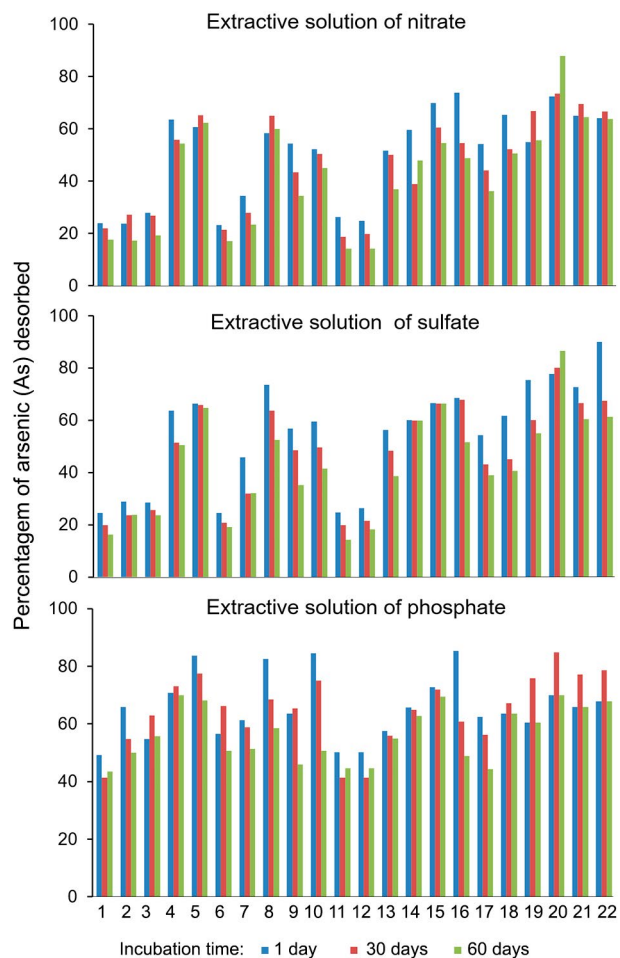
Out of all the Inceptisols, the profile P21 presented the highest MACAs, with a value of  $1.82 \text{ mg g}^{-1}$  of As. This soil, together with P22, presented a silty clay loam texture, with a finer particle size in relation to the others. In addition, the profiles P21 and P22 have the same textural class, but the presence of Fe oxides (Table 3) reveals their importance to studies of As adsorption.

The Entisol presented, as expected, the lowest value of MACAs due to the presence of a mineralogy composed essentially of quartz (Table 3) and kaolinite. Quartz is an inert material and thus the existing adsorption of As can be attributed to the structural Al-OH groups with kaolinite edges.

### Arsenic desorption

Arsenic ion chemical bonding to iron oxides and hydroxides are predominantly a product of inner-sphere complexes (Fendorf et al., 1997; Ona-Nguema et al., 2005), although an appreciable fraction is retained through physical forces as outer-sphere complexes (Catalano et al., 2008). According to the results shown in Figure 2, the percentage of remobilized or desorbed As differed from one studied profile to another, due to the set of chemical, physical, and mineralogical characteristics of the soils (Tables 1, 2, and 3), conferring a specific As retention capacity (Table 4).

Out of the solutions used to desorb the As, sodium phosphate presented a greater power of remobilization of As, followed by the sulfate and nitrate solutions. This is due to the chemical similarity between As and P, forming oxyanions (arsenate and phosphate) in the oxidation state +5 in soils whose environment is predominantly oxidant (Lytle et al., 2005). Even though As adsorption is not reversible, a large amount of sorbed



**Figure 2** – Percent of arsenic desorbed using extractive solutions of nitrate, sulfate and phosphate as a function of different incubation times.

As can be released by phosphate which has chemical properties similar to those of As(V) and can compete favorably with As(V) for adsorption sites (Zhang et al., 2011). Since phosphate fertilization is very frequent in different agricultural cultivations in tropical soils, attention must be paid to the ability of phosphorus to displace As by occupying the adsorption sites.

The release of As from tailings dams and other mining wastes constitute the major problem with regard to As contamination (Ladeira and Ciminelli, 2004). According to these authors, the mineral arsenopirita (FeAsS), when exposed to weathering, will oxidize, and produce sulfate, soluble As and acidity. Then, the sulfate can compete with As for adsorption sites. A number of authors point out that the mobility of toxic species, such as As, in the environment is a critical point in predicting contamination. For As(V),  $\text{H}_2\text{AsO}_4^-$  predominates pH values are between 2 and 7. When the pH are between 7-11  $\text{HAsO}_4^{2-}$  predominates. Both the  $\text{H}_3\text{AsO}_4^0$  and  $\text{AsO}_4^{3-}$  forms may be present under extremely acidic or alkaline conditions, respectively (Smedley and Kinniburgh, 2002). However, the methods applied in adsorption/desorption studies are not intended to simulate the exact conditions of arsenic release in the environment, but to predict the relative potential hazards of the samples when in contact with certain ions.

Sulfate, nitrate and phosphate are usually present in soils and possibly influence As mobility (Katsoyiannis and Zouboulis, 2002). Except for phosphate, both nitrate and sulfate are anionic species commonly found in sulfidic ore mines (Ladeira and Ciminelli, 2004). Even with soils presenting lower As desorption, when sulfate and nitrate are used, the presence of As is still high in the final solution.

In all soils, As continued to be desorbed over time. However, the percentage of remobilized As tended to decrease in most of them (Figure 2). Previous studies (Lin and Puls, 2000; Mello et al., 2006) have pointed out that the desorption of arsenite and arsenate in clay minerals diminishes the longer the time of residence.

According to the results obtained here, when comparing the percentage of As remobilized in the analysis involving the first (1 day), second (30 days), and third incubation time (60 days), As release over time was not reduced at a constant rate (Figure 2). One example is the As release using phosphate as extractor: the P18 (Ultissol), P19-21 (Inceptisols) and P22 (Entisols), are soils with lower clay content (Table 2) and are less oxidic. In these samples, the As remobilized in 60 days are similar to the first incubation period. In less weathered soils, such as Inceptisols and Entisols, there was no marked decrease in the rate of As release over time (after 60 days of incubation, approximately 60 % As was released using the three extractors).

Arsenic release (Figure 2) tended to be lower as the more clayey and oxidic the soils were (Table 3). The more weathered soils, such as Oxisols (P1-12) and Ultisols (P13-17) showed reductions in the percentage of

remobilization of As over time (Figure 2). Reduction in the percentage of remobilization of As over time occurs because As in the soil would be converted from the more labile to more recalcitrant forms with time (Mello et al., 2006).

Based on studies reported in the literature, a period of 24 h of contact between the mineral adsorbents and the As(V) solution ensures that the reaction has reached the equilibrium time. Many studies have commented that removal of As increased with the passing of time and the rate is initially quick, after, but subsequently declined as the point of equilibrium was approached (Lenoble et al., 2002; Lafferty and Loeppert, 2005; Jézéquel and Chu, 2006; Yadav et al., 2014). The effect of the contact time between adsorbate and sorbent on the sorption capacity of As indicates that the equilibrium time for As sorption occurred within 3 h (Yadav et al., 2014). With an increase in contact time of up to 6 h, the authors found no appreciable removal of As. For Al and Fe hydroxide, the equilibrium period for As(V) adsorption reported in the literature is 4 h after the initial reaction (Lenoble et al., 2002). Another study of As adsorption on Fe oxy-hydroxide yielded an equilibrium time equal to 12 h (Lafferty and Loeppert, 2005).

Considering the classes of the studied soils, among the Oxisols, the remobilization of As was highest in the P5 profile. This soil showed an As release ratio above 60 %, at 60 days of incubation (Figure 2). According to the characterization data of this soil as related to the mineralogy, this sample presents lower gibbsite and high kaolinite contents (> 68 %), as presented in Table 2. The presence of gibbsite (Al-OH groups) in the soils favors As adsorption (Manning and Goldberg, 1997; Ladeira et al., 2001; Mello et al., 2006). Consequently, a lower gibbsite content is unfavorable to the adsorption of As. Furthermore, kaolinite is a mineral that presents two surfaces: siloxane (Si-OH group) and gibbsitic (Al-OH group), and the Si-OH group is less effective in adsorbing anionic species (Manning and Goldberg, 1997). Because of their negative charged surface, clay minerals, such as kaolinite, generally have a low As adsorption capacity (Zhang et al., 2011).

As regards the Oxisols P1, P2 and P12, which are clayey and more gibbsitic (Tables 2 and 3), the results of As desorption were consistently low. The behavior of these soils, showed a high As adsorption capacity (Table 4). With the desorption of As, an average reduction of approximately 10 % was observed, pertaining to the three extractive solutions, when comparing the initial and the third run-through of the desorption experiment (Figure 2). The soil P10 presented the highest reduction of As release, comparing the first and third incubation times, with a considerably high percentage of desorption of As, which is probably due to the higher Fe and Al oxides of this soil (B horizon) compared to the other soils. Using phosphate as an extractor, for example, this soil showed a reduction of approximately 40 % in As release, decreasing from 84 % in the first time period (1



day), to 50 % at 60 days contact of the extractive solution with the soil.

The percentage of desorption of As in certain Inceptisols (P20 and P21) was higher than 80 % when using the phosphate as the extractive solution and 72 % with nitrate. This behavior may be explained by the coarser texture, presence of a 2:1 mineral ratio and especially the lower amount of gibbsite in these soils. This has environmental importance because gibbsite is thermodynamically more stable than Fe oxides and Al reduction does not occur in the environment. Therefore, a significant amount of As could be sequestered in a gibbsitic phase, (Mello et al., 2006) limiting the mobility of As.

As regards the adsorption of As, we observed that it was not necessarily the soils that obtained the highest MACAs that presented a lower desorption of the element over time. In studies on adsorption, MACAs was correlated mainly with soil texture. On the other hand, comparing the soils P1 and P5, which present the same proportion of clay (68 %) and similar adsorption capacity, we observed that the sample P1, with a mineralogy that was more gibbsitic, presented desorption of the element at a considerably lower rate, reaching a difference of 50 % using phosphate as an extractor. Studies reported in the literature (Lin and Puls, 2000; Zhang et al., 2011; Dias et al., 2019) mention that Al-hydroxides have a high specific surface. Dias et al. (2019) observed that adsorbents with higher values for specific surfaces have the highest adsorption capacity values. This fact is of great importance to the immobilization of As through adsorption and may explain the lower As desorption rate in P1.

The less weathered soils (P19 to P22), presented up to 70 % desorption of As after one day of contact (Figure 2). Subsequent to this period, As desorption continued to occur at a high rate even after two months of contact between the solution and soil. The Inceptisols (P19 to P22) showed low clay and oxide content, a higher  $Fe_{ox}/Fe_D$  ratio and a 2:1 mineral ratio. These attributes contributed to a higher release of As. The low As release in soils and sediments is related to the presence of gibbsite, a large amount of iron oxides and a lack of organic matter in the solid phase (Mello et al., 2006).

Soils and sediments in certain mining regions usually contain significant amounts of As and mining activity may promote an increase in As mobility, culminating in a potential risk of contamination of water sources (Mello et al., 2006). Thus, soils with lower desorption rates of As, such as Oxisols (P1, P2, P3, P6, P7, P11 and P12), are the most commonly recommended for use as geochemical barriers in the immobilization of As. For this purpose, more important than the high MACAs is a low desorption rate of contaminant over time. Soils P3 and P12, for example, have lower MACAs values when compared to the other Oxisols (Table 4), but have lower As desorption rates.

## Conclusions

The mobility of arsenic in the main soil classes in the state of Minas Gerais, Brazil, was attributed to factors such as the state of weathering of the soils, and to factors such as texture, PZSE, gibbsite, oxide contents. The release of As was controlled by the adsorption/desorption equilibrium in the solid phase. A low amount of oxidic clay in the soils, especially gibbsite, favors the release of As.

Oxisols presented the highest maximum adsorption capacity of arsenic (V), followed by Ultisols, Inceptisols and Entisols. The more oxidic the soils, especially gibbsitic, such as Oxisols and certain Ultisols, the greater the adsorption capacity of the As.

The percentage of remobilized As was different across the studied soils, which is due to the soil chemical, physical, and mineralogical characteristics, giving them a specific retention capacity of As. In general, when comparing the soil classes, the release of As was higher in Inceptisols and lower in the more oxidic Oxisols, especially into those that were more gibbsitic. The lower the release of As by soil, the higher the indication to act as a geochemical barrier to immobilize this element.

Among the extractors used to promote the desorption of the As retained in the soil, sodium phosphate showed the highest remobilization power of arsenic, due to the chemical similarity between arsenate and phosphate, followed by the sulfate and nitrate solutions. The presence of these ions in As-contaminated soils implies that in a natural environment it is plausible that they may cause As migration and, consequently, underground and surface water contamination.

Soils with a high MACAs would not necessarily be the most effective when used as a geochemical barrier in the immobilization of As. The soil should also exhibit a low desorption rate of As over time. For the development of a strong As geochemical barrier the soil has to be a clayey Oxisol, with relatively high amounts of Fe and Al oxides, especially gibbsite.

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## Authors' Contributions

**Conceptualization:** Fontes, M.P.F.; Almeida, C.C. Ker, J.C. **Data acquisition:** Almeida, C.C.; Pereira, T.T.C. **Data analysis:** Almeida, C.C.; Fontes, M.P.F.; Dias, A. C.; Pereira, T.T.C. **Design of methodology:** Fontes, M.P.F.; Almeida, C.C. **Writing and editing:** Dias, A.C.; Almeida, C.C.; Fontes, M.P.F.

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