



## POTASSIUM RESERVES IN THE CLAY FRACTION OF A TROPICAL SOIL FERTILIZED FOR THREE DECADES

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**Abstract**—Highly weathered soils of the humid tropics generally provide a poor mineral reserve of potassium (K), but evidence has been found which indicates that even in such soils non-exchangeable forms of K can be made plant available and this warrants further investigation. The objective of this study was, therefore, to determine the extent to which K can be released from poorly available reserves over a long period of time. The focus was on an Oxisol in southern Brazil cultivated for 32 years with a rotation of soybeans (*Glycine max* L.), maize (*Zea mays* L.), wheat (*Triticum aestivum* L.), and oats (*Avena strigosa* L.) with and without K fertilization. Mineral sources of K were identified by X-ray diffraction and by sequential chemical extraction from the clay fraction. The amounts of K-bearing mineral species and the amounts of total and plant-available K were quantified, then the effects of the long-term K-fertilization regime on these values were evaluated. The clay fraction was dominated by hematite, gibbsite, and phyllosilicates such as kaolinite. These minerals were unaffected by the K deprivation in the cropping systems, but in the clay fraction the absence of K fertilization for 32 years reduced the structural order of the 2:1 phyllosilicates associated with K reserves. This effect was most prominent in the root zone of the soil. Deprivation of K for more than three decades decreased the crystallinity of 2:1 phyllosilicates, which could be better evaluated from XRD patterns after the removal of kaolinite and Fe (oxyhydr)oxides. The K-free cultivation reduced the amounts of total soil K by increasing the depletion of K from pools that typically are poorly accessible to plants.

**Keywords**—Clay mineralogy · Extraction procedures · Soybeans · X-ray diffraction

### INTRODUCTION

Potassium (K) is the 7<sup>th</sup> most abundant element in the Earth's crust, forming 2.2% of its composition. In the lithosphere, igneous rocks and shale have the highest concentrations of K, while limestone and sandstones have lower concentrations (Zörb et al. 2014). Brazil is the 4<sup>th</sup> largest consumer of K-fertilizers in the world and imports ~90% of its demand, which grows annually.

In rainy years, high yields can be achieved by the crops with either inadequate or no K-fertilizer inputs. However, under negative K balance agricultural areas may experience continuous declines in yield over time (Calonego and Rosolem 2013). Cultivation without K fertilization or with insufficient amounts to uphold the nutrient reserve tends to reduce the contents of soluble and exchangeable K<sup>+</sup> in soils. A release gradient of K<sup>+</sup> from K-bearing mineral species is maintained when K fertilization is restricted. After K release, sites of K<sup>+</sup> retention can be replaced by Al<sup>3+</sup> or its polymers (Meunier 2007).

Potassium fertilization can affect the amount of reserved K and the mineralogy of the clay fraction in the soil over both the short (Norouzi and Khademi 2010; Adamo et al. 2016) and long (Calvaruso et al. 2009; Darunsontaya et al. 2012) terms. Most K in soils is held within the structure of minerals. The

percentage that such structural K forms in soil is usually >90% of total K. In some phyllosilicates, the K is usually located between 2:1 phyllosilicate layers or, to a lesser extent, in planar fractures and edge positions (Darunsontaya et al. 2010; Britzke et al. 2012; Vetterlein et al. 2013).

The mineral reserves of K in tropical Oxisols tend to be low in comparison to less developed soils of temperate regions. Highly weathered soils typically contain from 300 to 2000 mg kg<sup>-1</sup> of total K (Zörb et al. 2014). In such soils, Fe and Al (oxyhydr)oxides, kaolinite, and quartz prevail (Schaefer et al. 2008). However, clayey Oxisols may contain small to moderate amounts of hydroxy-Al interlayered minerals and interstratified kaolinite-2:1 clay minerals (Beinroth 1982; Bortoluzzi et al. 2005; Britzke et al. 2012; Testoni et al. 2017), which gives them a larger cation exchange capacity (CEC) than if they were strictly oxidic and/or kaolinitic Oxisols (Meunier 2007; Darunsontaya et al. 2012).

Even when developed in tropical or humid conditions with low K contents in the parent material, highly weathered soils may have mineral sources of K that contribute to crop nutrition. High yields of crops in very weathered soils originated from basaltic rocks, even without K-fertilization, were reported by Adamo et al. (2016) and Qiu et al. (2014). These soils may have Al-hydroxy layers or interstratified minerals that display high resistance to weathering, as is seen in the chlorite group (Meunier 2007). For immediate plant-availability, K<sup>+</sup>

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exchangeable forms can be associated with 2:1 phyllosilicates with or without Al-hydroxy interlayers, or any mineral with a low surface-charge density.

To access structural and non-exchangeable K pools of highly weathered soils, such as Oxisols, Melo et al. (2002) adapted some of the methods of Jackson et al. (1986) to create a sequence of selective extractions from soil clay minerals to estimate the contribution of each mineral species to the total K content of the clay fraction. In the adapted method, the amount of K and the sample mass loss (initial and final dry sample weight) were determined before and after each sequential treatment.

With the association of chemically selective extractions and X-ray diffractometry, the examination of how management practices can affect K reserves in the soil is possible. With this information, new management recommendations can be implemented so that cropping in highly weathered soils becomes more sustainable. The overall hypothesis of the present study was that long-term K-fertilization management promotes changes in the amount of K in the various pools and in the soil clay minerals. Hence, the objective was to quantify changes in K mineralogy and mineral reserves of K in the clay fraction of an Oxisol after 32 years of cropping with and without K fertilization.

## MATERIALS AND METHODS

### Study Area

A field experiment has been carried out since 1983 in a region of basaltic spills. The region (51° 10' W and 23° 11' S, 590 m a.s.l.) is located in the state of Paraná, Brazil. The region has a Köppen type Cfa climate (subtropical humid), with rain in all seasons (~1800 mm annually) and possible drought in the winter. The soil is a Rhodic Hapludox (Soil Survey Staff 2014). The soil chemical attributes (Mehlich 1953; van Raij et al. 1986) and texture distribution (Gee and Bauder 1986) of samples collected randomly in the experimental area in July 2015 are presented in Table 1. The experiment was carried out to evaluate the effect on the soil K forms and grain yields of cycles without (1989–1994; 2008–2014) and with (1983–1988; 1995–2008) K fertilization. The experiment was a randomized complete block design with four replicates and treatments containing one control and a K rate of 130 kg ha<sup>-1</sup> year<sup>-1</sup> (K-supplemented) applied as KCl (60% K<sub>2</sub>O) in plots of 40 m<sup>2</sup> (8 m×5 m).

The experiment was 0.4 km from a native semideciduous seasonal alluvial forest, belonging to the Brazilian Atlantic Forest biome. In general, these forests occupy environments between semiarid and coastal wetland. The tree stratum can have a size of ~25 m with a small proportion of leaf loss in the dry period. The experimental areas were cultivated with soybeans in all summer crops since 1983, and wheat (*Triticum aestivum* L.), corn (*Zea mays* L.), sunflower (*Helianthus annuus* L.), or black oat (*Avena strigosa* Schreb.) as winter crops. Seeding, pesticide application, weeding, and harvesting were done mechanically. In the control treatment, the plants usually manifested K deficiency, whereas the highest yields were observed when 130 kg K ha<sup>-1</sup> year<sup>-1</sup> was applied. The

only induced variation was the K rate. Climatic conditions or cultivated species were the same throughout the experiment period, with natural variations over the years.

### Soil Sampling and Preparation

Four composite soil samples (equal masses of five sampling points per plot) were collected with an 80 mm-diameter auger in December 2015: two were in the control treatment (1: 0.0–0.2 m; 2: 0.2–0.4 m soil layers), and the other two in the K-supplemented treatment (3: 0.0–0.2 m; 4: 0.2–0.4 m soil layers). For the forest soil, four rectangular areas of 8 m×5 m were demarcated in the portion of the forest at a similar altitude to that of the experiment (~590 m above sea level), with sides 2 m apart from each other. In each area, five random sampling points were made to form composite samples from 0.0–0.2 m and 0.2–0.4 m.

After air-drying (45°C) and sieving (2 mm), parts of the samples were used to determine the chemical attributes and particle-size distribution, and the other parts were treated with 30% (v/v) H<sub>2</sub>O<sub>2</sub> to remove organic components (Jackson 2014). The inorganic matrices obtained were dispersed with 0.01 M sodium hexametaphosphate and 0.01 M sodium hydroxide for 16 h (Gee and Or 2002). The sand fraction was retained on a 0.05 mm sieve, placed in porcelain capsules, and oven dried at 50°C. The remaining fractions, clay (<2 µm) and silt (2–50 µm), were separated by sedimentation according to Stokes' Law (Gee and Bauder 1986).

The air-dried clay fraction was ground with an agate mortar and pestle. To evaluate samples from the 0.0–0.4 m depth, equal masses of samples from the 0.0–0.2 m and 0.2–0.4 m depths were mixed. The choice of the 0.0–0.2 m and 0.2–0.4 m depths was due to the fact that these are the layers collected for soil fertility assessment in most agricultural areas in Brazil. In addition, >86% of the dry-weight soybean roots is usually concentrated in the 0.0 to 0.2 m layer (Coale and Grove 1986). The amount of organic matter and the effect of roots are both reduced in the 0.2 and 0.4 m layer. In this layer, minerals are less altered due to the smaller effect of root acids, weathering, and microorganisms, thus representing a less altered microenvironment but one that still influences plant nutrition.

### Chemical and Mineralogical Analyses

Analytical reagent-grade chemicals with high purity and ultra-pure water (UW) (~18.2 MΩ cm) were used to prepare all solutions. The plant-available K was extracted by both Mehlich-1 and ion exchange resin extractants (Mehlich 1953; van Raij et al. 1986) in the experimental treatments (control and K-supplemented) and the native forest soil samples. To obtain the total K contents, 0.5 g of air-dried and sieved (0.149 mm) soil sample was digested in a microwave oven with concentrated HCl, HNO<sub>3</sub>, and HF (method EPA 3052) (United States Environmental Protection Agency [USEPA] 1996), and the contents were determined by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). After the granulometric fraction separation by the method of Gee and Or (2002), air-dried and sieved (0.149 mm) clay, silt,

**Table 1.** Soil chemical and textural attributes of the Oxisol

Layer depth (m)	pH (0.01 M CaCl <sub>2</sub> )	OC (g kg <sup>-1</sup> )	K <sub>M</sub>	K <sub>R</sub>	Al	H + Al
			mmol <sub>c</sub> kg <sup>-1</sup>			
0.0–0.2	4.4±0.1	16±0.5	1.2±0.1	1.5±0.1	9±1.7	66±4.6
0.2–0.4	4.3±0.0	8±0.4	0.9±0.1	1. ±0.1	9±1.1	6±2.8
	CEC pH 7.0	Ca	Mg	Clay	Silt	Sand
	(mmol <sub>c</sub> kg <sup>-1</sup> )	(mmol <sub>c</sub> kg <sup>-1</sup> )			(g kg <sup>-1</sup> )	
0.0–0.2	104±4.3	24±2.2	13±0.8	715±12	202±5	56±4
0.2–0.4	107±2.9	19±1.0	11±0.8	712±8	214±3	60±2

OC = Organic carbon (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) – (Walkley and Black 1934); Ca, Mg, and Al (1 M KCl) - (Bertsch and Bloom 1996); K<sub>M</sub> (Mehlich-1) - (Mehlich 1953); K<sub>R</sub> (ion exchange resin) - (van Raij 1998); H+Al = (SMP – Schoemaker-McLean-Pratt buffer solution) - Shoemaker et al. (1961)

and sand samples were analyzed to determine the total K contents in each individual fraction. The equipment (iCAP 6200 – Thermo Fisher Scientific®, Waltham, Massachusetts, USA) was operated at 1150 W, with 500 and 700 mL min<sup>-1</sup> of auxiliary and nebulizer gas flow, with yttrium (Y) as an internal standard. All analyses were performed with four replicates.

X-ray diffraction (XRD) patterns were obtained from powdered and parallel-oriented clay fractions using a Philips PW 1877 (Eindhoven, North Brabant, The Netherlands) diffractometer with CuK $\alpha$  radiation (0.1542 nm, 40 kV, and 40 mA) and a graphite diffracted-beam monochromator. In order to study phyllosilicates, one aliquot of the clay fraction sample (from control and K-supplemented treatments) was saturated with 1 M KCl and the other with 1 M MgCl<sub>2</sub>. Samples mounted onto a porous ceramic plate by vacuum filtration were analyzed by XRD as follows: K-saturated samples at 25°C (25K), 110°C (110K), 350°C (350K), and 550°C (550K); the Mg-saturated sample at 25°C (25Mg); and the ethylene-glycol saturated sample at 25°C (eg-Mg), all at a speed of 0.02°2 $\theta$  s<sup>-1</sup>, over the range 3 to 90°2 $\theta$ . The diffraction pattern was interpreted based on the 00l peak positions according to Brindley and Brown (1980).

Two crystallographic parameters of kaolinite were obtained: (1) the width at half height (WHH) of its peaks at  $d = 0.725$  nm; and (2) the crystallinity index according to Hughes and Brown (1979). For this, XRD patterns were obtained over the range 3–28°2 $\theta$  at a scan rate of 0.01°2 $\theta$  s<sup>-1</sup> from deferrated clay samples, with Fe oxides removed with sodium citrate-bicarbonate-dithionite (CBD).

The sequential selective extraction of minerals proposed by Melo et al. (2002) was carried out, with adaptations, to determine the contribution of mineral species to the total K content of the clay fraction. The analysis was based on two identical sub-samples of the clay fraction, which received the same treatments, one of which was used to determine the elemental composition of the extracts by ICP-AES, while the other was used for the mineralogical study of residues by XRD with parallel-oriented

samples (0.01°2 $\theta$  s<sup>-1</sup>, range of 3–60°2 $\theta$ ). The order of extraction was:

- (1) 2.5 g of Na-saturated clay was treated with sodium CBD for the extraction of pedogenetic Fe oxides (Mehra and Jackson 1958). The procedure was repeated five times, until a change in coloration from red to whitish gray, indicating the removal of the high levels of Fe oxides in the clay. The amounts of K, Fe, and Al were measured in the extract by ICP-AES.
- (2) 1.2 g of deferrated clay (previously treated with CBD) was treated with 5 M NaOH (Norris and Taylor 1961; Jackson et al. 1986) for the extraction of kaolinite and gibbsite. In the process, the milled clay was added to Teflon beakers containing 100 mL of 5 M NaOH (2 h at 250°C), then centrifuged at 2700 $\times$ g to obtain the first extract. The first extract process formed sodalite, which was then removed in the second extract (Singh and Gilkes 1991) by shaking and centrifuging (2700 $\times$ g) the material with 45 mL of 0.5 M HCl twice, totaling 90 mL of extract. The K content extracted by this treatment was given by the sum of the contents determined in the two extracts.
- (3) 0.4 g of deferrated clay, without kaolinite or gibbsite (previously treated with 5 M NaOH), was treated with crystalline NaHSO<sub>4</sub> for the extraction of 2:1 phyllosilicates (Jackson et al. 1986) modified by Melo et al. (2002). The sample was maintained at 250°C for the first 0.5 h of heating and followed at 270°C for a further 2 h. At the end of the reaction, the residue hardened and was digested with 3 M HCl. The K content then was measured in the extract.
- (4) 0.1 g of clay without Fe oxides, kaolinite, gibbsite, and 2:1 phyllosilicates was digested with HF, HNO<sub>3</sub>, and HCl (USEPA 1996) for digestion of feldspars and other more resistant minerals. After digestion, the K content was determined in the extract.

General procedures for all extractions were: (a) drying of the samples at 80°C for 16 h before and after each extraction;

(b) washing (shaking and centrifuging the suspension at  $2700\times g$  for 10 min with 80 mL of 0.5 M  $(\text{NH}_4)_2\text{CO}_3$  and 40 mL of UW to remove excess salts); (c) the sample mass was weighed before and after the extractions (initial and final weight, respectively); (d) after each extraction part of the mass obtained was used for the preparation of parallel-oriented layers (XRD) and the other part for subsequent sequential extraction; and (e) the determination of elements in the extracts was done by ICP-AES. For treatments 2 and 3, teflon beakers were used in a sand bath, as proposed by Melo et al. (2002), rather than in vitreous silica crucibles with heated screw caps on Bunsen's nozzle, proposed by Jackson et al. (1986).

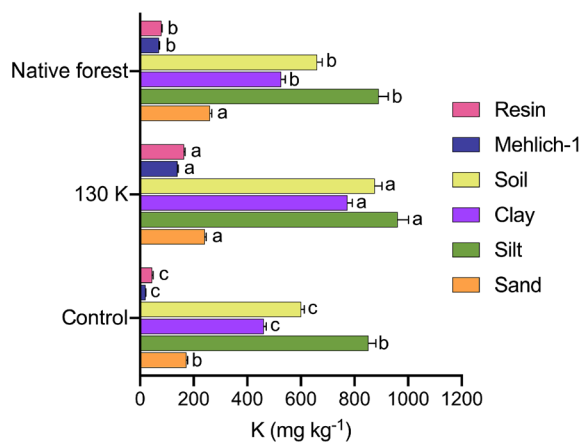
### Statistical Analyses

The data were submitted to the tests of homoscedasticity and residues normality of Hartley and Shapiro-Wilk, respectively. After, the analysis of variance (ANOVA) was performed and, in case of sufficiently low  $P$ -value of ANOVA's assumptions ( $<0.05$ ), the data were analyzed by the Tukey test.

## RESULTS AND DISCUSSION

### Structural and Plant-available K in Soil

The K-supplemented treatment yielded a total soil K content larger than the control and the native forest (Fig. 1). As expected, the sand fraction contained the least K at  $\leq 200 \text{ mg kg}^{-1}$ . The largest total K content was found in the silt fraction, ranging from 780 to  $900 \text{ mg kg}^{-1}$ , in which the 130 K treatment exhibited the highest K contents. In the sand fraction, the control treatment contained the smallest amount of total K (Fig. 1). The clay fraction had a total K content ranging from  $450 \text{ mg kg}^{-1}$  (control) to  $750 \text{ mg kg}^{-1}$  for the K-supplemented treatment, which also had the largest K content in the clay fractions compared to the control treatment and the native forest. In



**Fig. 1.** Total K contents in soil (yellow), sand fraction (orange), silt fraction (green), clay fraction (purple), and plant-available K extracted with Mehlich-1 (blue) and ion-exchange resin (pink) as a function of treatments and a reference site (native forest) in the 0–0.4 m layer. The means are presented with their respective standard errors ( $n = 4$ ). The comparisons of means (Tukey: 5%) were performed between the same variables (bars with the same color) in the three conditions evaluated

addition, considering that the soil consisted of  $>71\%$  clay, it accounted for  $\sim 62$ – $71\%$  of the K reserves in the soil.

The K-availability to plants was also affected by the treatments (Fig. 1). These plant-available pools are the outcome of complex relationships and fluxes between the K forms, soil phases, K-application regime, rhizosphere types, uptake by plants, and losses (leaching and K removal with the harvest) (Zörb et al. 2014). The same differences were observed with the two plant-available K extractants, with the highest plant-available K contents in the K-supplemented treatment, as expected because of K-fertilizer inputs. The CEC of the soil of  $\sim 100 \text{ mmol}_c \text{ dm}^{-3}$  is consistent with the advanced weathering. Despite the distinct extraction nature of the plant-available K extractants examined, the same differences were observed in the conditions evaluated (Fig. 1). The smallest K contents in the control treatment compared to the amount of K found in native forest soil suggest that the absence of K fertilization can affect plant-available K in long-term cultivated soils, while K rates of  $\sim 130 \text{ kg of K ha}^{-1}$  can increase K contents above the values found in native forest soils.

In addition to K removal caused by crops, the smaller K contents in the clay fraction of the control treatment, in relation to the native forest, may be associated with the smaller amounts of organic acids released by roots being in contact with minerals that may release K. The large volume of decomposing litter on the soil surface is also a factor linked to the highest solution- and exchangeable-K contents in forest soils when compared to cultivated soils (Tripler et al. 2006).

In clayey soils located in humid tropic regions with high rainfall, the K-leaching flux promotes movement from structural and non-exchangeable forms to exchangeable forms, rather than the opposite (Sparks and Huang 1985). Structural K forms become available to plants only after years under accelerated depletion of exchangeable K by crops. Therefore, the contribution of the structural K forms to short-cycle nutrient species is little or nothing, as found by Kaminski et al. (2007) in Alfisols and by Moterle et al. (2016) in Oxisols. In the absence of K-fertilization (Csathó 2007) and especially in soil micro-regions that suffer from the action of organic acids (Basak and Biswas 2009), e.g. in the rhizosphere, the release of K from clay minerals is higher. The greater vertical distribution and the morphological diversity of roots means that forest soils have profiles with more pores and greater movement of water, thus favoring mineral hydrolysis.

### Soil- and Clay-fraction Mineralogy

The clay fraction of the experimental site had kaolinite ( $d$  values: 0.725, 0.444, 0.356, 0.234, 0.169, 0.149 nm), hematite ( $d$  values: 0.296, 0.250, 0.220, 0.183, 0.169, 0.145 nm), and gibbsite ( $d$  value: 0.483 nm) as dominant minerals and traces of maghemite ( $d$  value: 0.293 nm) (Fig. 2). The presence of kaolinite was predictable as it is a phyllosilicate found widely in Oxisols of the humid tropics (Schaefer et al. 2008). Goethite and hematite ( $\alpha\text{-FeOOH}$  and  $\alpha\text{-Fe}_2\text{O}_3$ ) are dominant in well-developed soils (Mehmood et al. 2015).

The presence of hematite in the clay fraction (Fig. 2) was expected due to the pedoenvironmental conditions: e.g. large Fe contents in the parent material (basalt), high temperatures, rapid mineralization of organic matter, and a pH close to neutrality (Inda et al. 2013). The presence of gibbsite, the most representative aluminum hydroxide in tropical humid soils, is also to be expected (Camargo et al. 2014). The results are consistent with the mineralogy of other South American Oxisols (Schaefer et al. 2008).

Analyses of the soil fractions without iron oxides allowed the identification of peaks at 1.4 nm (Fig. 3); treatments with MgCl and MgCl+ethylene glycol (Mg+EG) suggested that the peaks close to 1.4 nm were probably caused by Al hydroxyinterlayered (HI) 2:1 phyllosilicate (Fig. 4). This conclusion was based on the absence of an increase in the basal spacing after solvation with ethylene glycol, the collapse of this mineral at temperatures equal to or greater than 350°C, and the gradual asymmetric enlargement and loss of intensity of the reflection at 1.4 nm after KCl saturation and thermal treatments (Fig. 3), as reported by Kämpf and Curi (2003). Traces of 2:1 phyllosilicates in a highly weathered gibbsitic Oxisol were only identified by Rodrigues Netto (1996) after removal of iron oxides and treatment with KCl at 25, 135, 300, and 500°C, and Mg+EG in the clay fraction. Potassium may be associated with illite and HI 2:1 phyllosilicates in Brazilian Oxisols, either enclosed within kaolinite laths or as a discrete mineral (Melo et al. 2002).

The HI 2:1 phyllosilicate identified by the reflection at 1.4 nm in the soil clay fraction did not expand after solvation, but suffered contraction followed by collapse with increasing temperature in the K-saturated samples (Fig. 3). The contraction after thermal treatments and expansion after solvation with ethylene glycol rely on the degree of intercalation of Al-OH

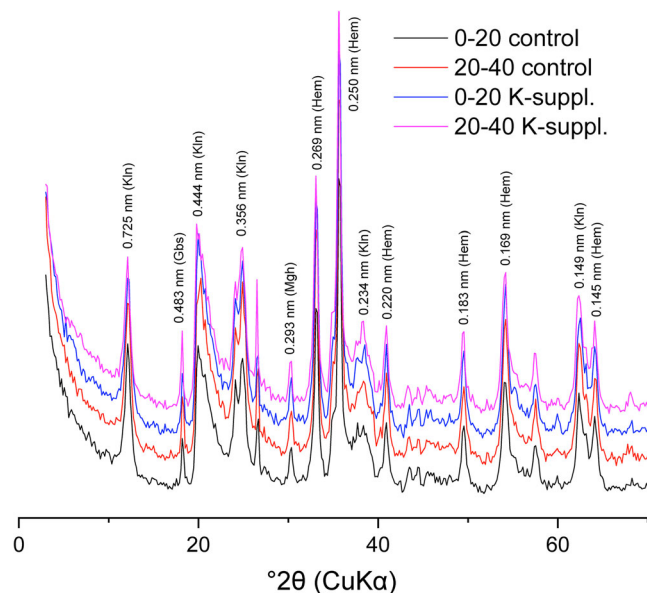
polymers in the interlayers (Kämpf et al. 1995; Castilhos et al. 2002; Meunier 2007). Although stable under tropical conditions, the Al hydroxide polymers may be partially removed from the interlayer HI 2:1 phyllosilicates due to management practices (Kämpf and Curi 2003; Simonsson et al. 2009).

No changes were observed in collapse pattern of the HI 2:1 phyllosilicate between treatments (control or K-supplemented) (Fig. 3). After solvation with Mg and Mg+EG, however, the control samples collected from 0–0.2 m depth exhibited slightly less well defined peaks relative to the other conditions evaluated (Fig. 4). Decrease in peak definition for the control treatment was not observed from 0.2 to 0.4 m, probably because of weaker action of the roots extracting K in this layer during the years of cultivation. Illite and hydroxy-aluminum interlayered vermiculite (HIV) were observed by Moterle et al. (2016) to be sensitive to K fertilization in an Ultisol after 15 years.

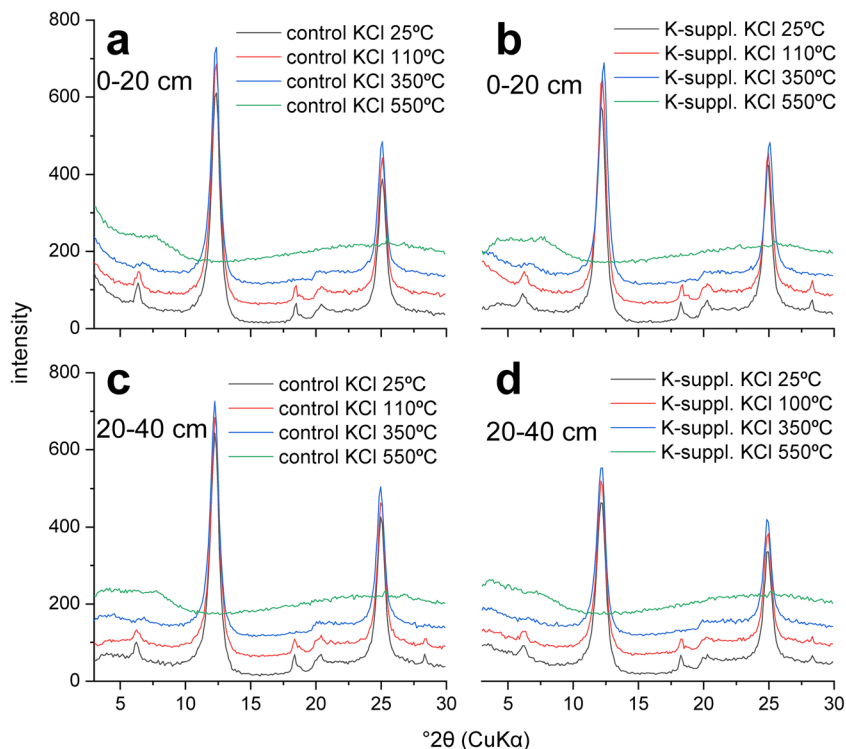
The structural K fraction plays a buffer role for K in the soil, supplying K for plants over time (Moterle et al. 2016). Changes in the mineralogy of HI 2:1 phyllosilicates in an untilted acidic Oxisol were noted by Inda et al. (2010). Those authors also attributed the 2:1 mineralogy changes to destabilization caused by larger organic matter contents and higher pH values in surface layers (0–0.2 m). Based on the present study, however, the absence of a K-fertilizer regime reduces the stability of HI 2:1 phyllosilicates in long-term cultivated Oxisols.

#### K Reserve in Sequentially Extracted Minerals

The effective removal of hematite from the clay fraction after treatment with CBD was confirmed by the absence of reflections at 0.250 nm, as well as the effective removal of kaolinite and gibbsite after treatment with 5 M NaOH, due to



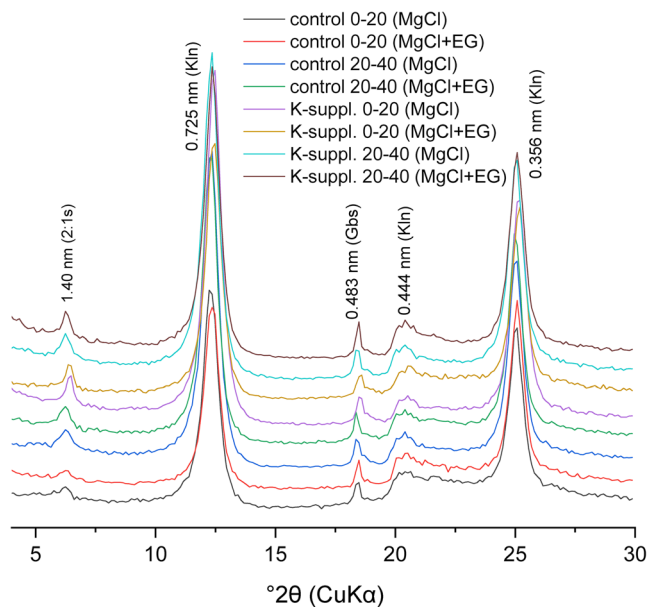
**Fig. 2.** XRD patterns of the soil-clay fraction. Samples 01-black (0.0–0.2 m) and 02-red (0.2–0.4 m) of the control treatment and samples 03-blue (0.0–0.2 m) and 04-pink (0.2–0.4 m) of the 130 kg ha<sup>-1</sup> K treatment (K-supplemented). Kaolinite (Kln); gibbsite (Gbs); maghemite (Mgh); hematite (Hem); quartz (Qz)



**Fig. 3.** XRD patterns of the soil-clay fraction without Fe oxides and saturated with KCl in 25, 110, 350, and 550°C. Control treatment in 0.0–0.2 m **a** and 0.2–0.4 m **c**, and the K-supplemented treatment (K-suppl.) in 0.0–0.2 m **b** and 0.2–0.4 m **d**. 2:1 phyllosilicates (2:1s); kaolinite (Kln); gibbsite (Gbs)

the absence of reflections at 0.720 and 0.484 nm (Fig. 5). The clay fractions contained, on average,  $185 \text{ g kg}^{-1}$  of  $\text{Fe}_2\text{O}_3$  and  $15 \text{ g kg}^{-1}$   $\text{Al}_2\text{O}_3$ , estimated from the Fe and Al contents obtained by extraction with CBD, possibly associated with

hematite and gibbsite. The presence of Fe oxides was confirmed by the reduction of ~24% in the clay fraction mass after treatment with CBD (Table 2) and by the hematite reflections identified by XRD (Fig. 2).



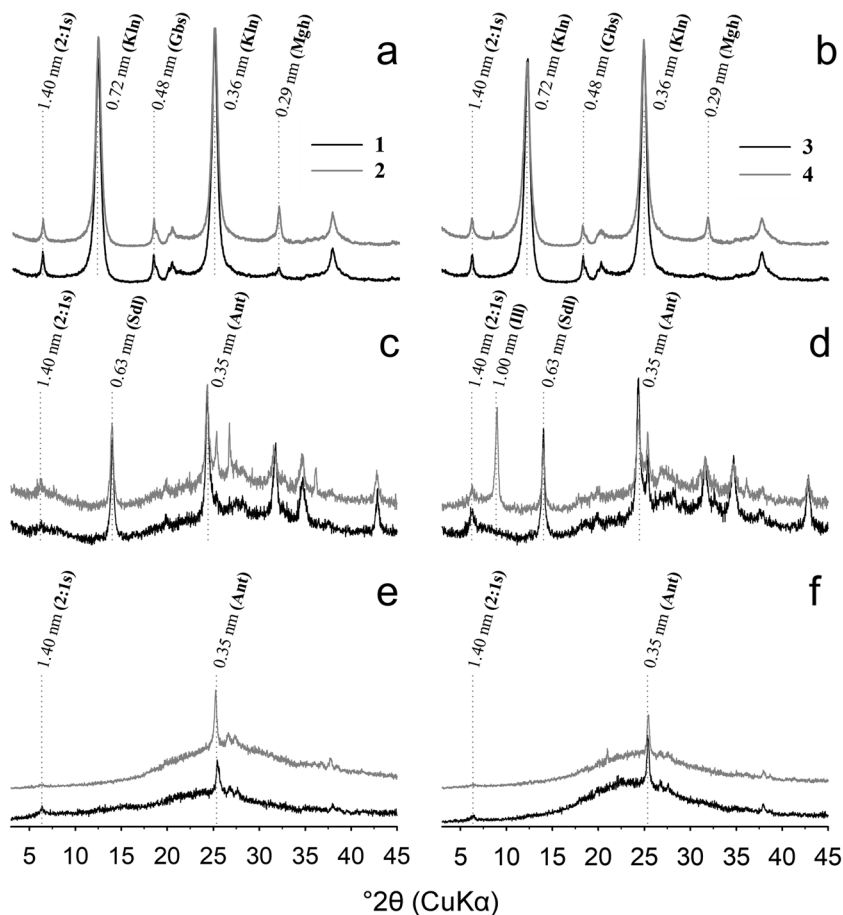
**Fig. 4.** XRD patterns of the soil-clay fraction from 0.0–0.2 and 0.2–0.4 m layers without Fe oxides and saturated with MgCl and MgCl+Ethylene glycol (EG) in 25°C. Control (without K fertilization) and K-suppl (K-supplemented treatment). 2:1 phyllosilicates (2:1s); kaolinite (Kln); gibbsite (Gbs)

The presence of illite ( $d$ : 1.00 nm) was observed in samples from K-supplemented plots (Fig. 5). Failure to detect illite reflections by XRD in the control treatment may have occurred due to lower concentrations, the presence of small and weathered particles, or the presence of expanded layers inside the mineral. In the control conditions, the deprivation of K promoted the release of exchangeable K and the reduction of total K in the clay fraction (Fig. 1). The K deprivation thus affected the mineral reserve of K associated with clay minerals.

The release gradient from the solid phase was necessary to balance the K buffering power in the soil. The continuous K depletion reduced the amount and crystallinity of K minerals, to the point where they could no longer be identified by conventional XRD (Darunsontaya et al. 2010). The release of structural and non-exchangeable K from clay minerals is a very slow process dependent on mineral stability (Sparks and Huang 1985). For instance, the larger rate constant for  $K^+$  release in trioctahedral micas compared to dioctahedral micas observed by Milford and Jackson (1960) and by Reed and Scott (1962) confirmed the importance of mineral stability in the K-release process.

The good stability of Al-hydroxy 2:1 clay minerals corroborates their low susceptibility to the effects of K deprivation observed in the present study. Although illite has a greater K concentration, its structure is less stable than that of Al-hydroxy 2:1 clay minerals. Over time, therefore, improper K management affects more intensely the less stable minerals such as illite. These effects can be observed in the total K contents in the clay fraction (Fig. 1) and in XRD reflections (Fig. 5).

No further reflections were observed at 1.00 nm after treatment with  $\text{NaHSO}_4$ , which indicates the removal of illite; reduction in the intensity of the reflections at 1.40 nm denotes a decrease in the crystallinity of 2:1 phyllosilicates (Fig. 5). An artifact containing Si and S was identified on some of the clay-oriented slides after extraction with  $\text{NaHSO}_4$  (Fig. 5c, d). The formation of the same artifact was reported by Melo et al. (2003) who reported that its presence made it difficult to identify reflections of micaceous minerals which resisted  $\text{NaHSO}_4$  treatment. As their reflections occur at  $20\text{--}27^\circ 2\theta$ , the presence of the artifact was not taken into account in Fig. 5. In addition to ill-defined reflections of 2:1 phyllosilicates,



**Fig. 5.** XRD patterns of the clay fraction: (a, b: parallel-oriented samples after CBD treatment); (c, d: parallel-oriented samples after 5 M NaOH treatment); (e, f: parallel-oriented samples after  $\text{NaHSO}_4$  treatment). Samples 1 and 2 (control: 0.0–0.2 and 0.2–0.4 m, respectively); 3, and 4 (K-supplemented: 130 kg K  $\text{ha}^{-1}$ , 0.0–0.2 and 0.2–0.4 m, respectively). (Kln) kaolinite; (Gbs) gibbsite; (Ant) anatase; (Mgh) maghemite; (2:1s) 2:1 phyllosilicates; (Ill) illite; (Sdl) sodalite

**Table 2.** Reduction of clay mass by sequential treatments for extraction of mineral phases in the soil clay fractions

Sample <sup>1</sup>	Fraction <sup>2</sup>				Illite <sup>3</sup>	K-feldspar <sup>4</sup>
	Fe Ox	Kln+Gbs	2:1	Resd		
	..... g kg <sup>-1</sup> .....					
1 (control)	245±6	638±17	30±2	55±5	0.41±0.04	0.63±0.08
2 (control)	247±4	637±21	28±1	57±3	0.45±0.03	0.66±0.06
3 (K-supplemented)	249±10	636±17	31±2	51±4	0.66±0.06	0.59±0.06
4 (K-supplemented)	230±9	643±19	30±2	52±7	0.65±0.07	0.62±0.09

<sup>1</sup> Samples 1 (0.0–0.2 m) and 2 (0.2–0.4 m) of the control treatment and samples 3 (0.0–0.2 m) and 4 (0.2–0.4 m) of the 130 kg K ha<sup>-1</sup> treatment (K-supplemented).

<sup>2</sup> Fraction = mass reduction of the sample by the treatments in relation to the initial mass [(mass removed\*1000)/initial mass], being: Fe Ox (crystalline iron oxides removed with CBD); Kln+Gbs (kaolinite and gibbsite removed with 5 M NaOH); 2:1 (2:1 phyllosilicates removed with NaHSO<sub>4</sub> crystals); and Resd (residual fraction).

<sup>3</sup> Illite contents in the clay fraction estimated from K extracted with NaHSO<sub>4</sub>, considering the average concentration of 77 g kg<sup>-1</sup> of K in the mineral.

<sup>4</sup> K-feldspar content in the clay fraction estimated from K extracted with HF, considering the average concentration of 129 g kg<sup>-1</sup> of K in the mineral (Melo et al. 2003).

anatase (*d* value: 0.350 nm) was identified after NaHSO<sub>4</sub> treatment; this was expected due to the significant resistance of this mineral to dissolution. The presence of anatase and other titanium minerals in the extraction system with NaHSO<sub>4</sub> in clayey soils was also noted by Melo et al. (2003).

The presence of HI 2:1 phyllosilicates in the clay fraction of Oxisols was also reported by Ghidin et al. (2006) and by Castro et al. (2014). The 2:1 primary and secondary clay minerals contained in the finer fractions in the soil indicate a strong relationship with the availability of exchangeable K, and the presence of more stable forms of K as non-exchangeable and structural K over time in agricultural areas. In highly weathered soils, these stable forms (non-exchangeable and structural K) tend to be more homogeneous among different classes of aggregates (Mitton et al. 2019). The presence of HI 2:1 in the clay fractions of the plots that received potassium fertilization may be related to less depletion of non-exchangeable and structural K forms. In this sense, potassium fertilization has proved to be an important tool in the balance of the buffering power of highly weathered tropical soils and in the maintenance of a mineral reserve of K.

In an assessment of clay minerals over time in the Morrow Plots (Illinois, USA), Velde and Peck (2002) observed a significant loss of illitic material in the continuous-corn cultivation plots. Those authors concluded that illite-smectite clay minerals are very important for K buffering and can become K-poor or K-rich depending on the supply potential of the mineral K reserve in the soil during growing seasons. Specifically, if the soil does not contain mineral reserves that can become available during high K-removal phases during crop growth, a continuous decrease of K contents in 2:1 clay minerals will follow. The opposite will occur when the soil contains sufficient K content to nurture the cultivated plants and to penetrate the 2:1 clay mineral structures, increasing their stability and permanence in soil over time (Velde and Peck 2002).

In a more recent study of the Morrow Plots, Bakker et al. (2019) highlighted that dissolution of coarse clay-mineral phases, rather than alteration, plays an important role in K supplementation for plant nutrition and indicated that some of the K used by plants is obtained from subsoil in a non-K limited context, and it was related to the resilience of K-bearing minerals in the long term.

Small amounts of clay fraction (2:1 phyllosilicates) were removed by NaHSO<sub>4</sub>, on average 31 g kg<sup>-1</sup>, and by HF (Residual pool or fraction - Resd), on average 53 g kg<sup>-1</sup>, with little variation among samples. Moreover, the amounts estimated for micas and feldspars were small (Table 2) when compared with the results obtained by Melo et al. (2003) from less weathered soils. This behavior was predictable, being based on soil parent material, soil drainage, and the climate of the region, all of which favor weathering and the formation of kaolinite and oxides (Rebertus et al. 1986; Mehmood et al. 2015). Despite the small contribution of these mineral species in terms of mass to the K reserve of the clay fraction was significant (Table 2; Table 3), with total mean contents of 1494 mg kg<sup>-1</sup> K in the 2:1 phyllosilicate fraction and 1512 mg kg<sup>-1</sup> K in the residual fraction. The release of up to 3173 mg kg<sup>-1</sup> K in NaHSO<sub>4</sub> treatment (2:1 phyllosilicate pool), and the total nutrient reserve of 4276 mg kg<sup>-1</sup>, obtained by extraction with HF (Resd) in an Oxisol with 780 g kg<sup>-1</sup> of clay was quantified by Martins et al. (2004).

Release of K by CBD was not expected, due to the small probability of association of the cation with more crystalline Fe oxides. The small amounts released (Table 3) can be attributed to the dissolution of some particles of Al-silicates in the process, as observed by Melo et al. (2002), or even illite particles, as reported by Jackson et al. (1986). The abundance of Kln in soil clay fractions was confirmed by the large mass reduction (640 g kg<sup>-1</sup> on average) observed during sequential extractions (Table 2). These levels were close to those found by Melo et al. (2003) in a Rhodic Hapludox developed in the same rocky



formation of the soil used in the present study and are in accord with the kaolinite and gibbsite reflections in the clay fraction (Fig. 2; Fig. 3). These minerals had little association with K, with a mean content of 243 mg kg<sup>-1</sup> K and little variation among samples (Table 2). The release of K associated with Kln was very significant when considering the K content and the amount of mass removed by 5 M NaOH treatment (Table 4), with almost half of all total K associated with this pool.

An average difference of ~30% between the control and the K-supplemented treatments was verified for the total K contents in the 0.0–0.4 m samples (Table 4) and this can be attributed to the considerable export of K for >60 crops during the 32 years without K fertilization. Samples of the clay fraction of native forest soils close to the experiment have a total K content of 803 mg kg<sup>-1</sup>. This implies that even using high rates such as K-supplemented, cumulative and residual K cycles are inefficient at maintaining the natural K reserve in the clay fraction of highly weathered soils.

The Kln crystallinity indexes in the 0–0.2 m soil layer were lower (5.1: control; 4.9: K-supplemented; 4.7: native forest) than the indexes obtained in the 0.2–0.4 m soil layer (7.8: control; 7.2: K-supplemented; 6.5: native forest). Melo et al. (2002) and Darunsontaya et al. (2012) demonstrated that K associated with less crystalline kaolinite formed in many weathered soils. The release of K can be attributed to the occurrence of residual occluded layers of mica within the crystalline structure of the mineral (Singh and Gilkes 1991), or even to the presence of 2:1–1:1 interstratified clay minerals which were solubilized by the 5 M NaOH solution (Trakoonyingcharoen et al. 2006). Melo et al. (2002) also observed lower crystalline indices in Kln of an Oxisol with depth. The indices found in the current study, however, represented poorly crystalline Kln, according to the standards proposed by Hughes and Brown (1979). The association between K and the unordered Kln structure in the soil, therefore, is more propitious (Lee et al. 1975; Brindley et al. 1986). Similar results were reported by Darunsontaya et al. (2012) who evaluated the crystallinity and presence of K in kaolinite crystals from Thai Oxisols derived from basaltic rocks compared to

soils derived from clastic rocks. The clay fraction of certain Oxisols can contain illite, even if it may be undetectable by XRD techniques, i.e. not present within the kaolinite structure but in small illite crystals associated with dominant kaolinite crystals (Darunsontaya et al. 2012).

The hypothesis that kaolinite may be associated with 2:1 phyllosilicates is reinforced by some of the kaolinite reflections found between 0.720 and 0.730 nm (Fig. 4). The presence of interlayer kaolinite-vermiculite in Italian soils which originated from basalt was verified by Righi et al. (1999), and its formation was attributed to the relief of the area studied and the internal drainage. In tropical regions, kaolinite associated with interstratified 2:1 phyllosilicates in the 0.720–0.730 nm basal spacings of an Alfisol clay fraction were identified by Bortoluzzi et al. (2005). Similar findings were reported by Delvaux et al. (1990), who described strong associations between halloysite and smectite in six deferrated clay samples from B horizons derived from tropical basaltic pyroclasts in Cameroon. A tropical chronosequence (lateritic Alfisols) was examined by Ryan et al. (2016) who found that halloysite and kaolinite derived from smectite alteration can preserve interstratified smectite layers and large Fe contents. Interstratified Fe-rich kaolinite with smectite layers were reported by Pincus et al. (2017) to become progressively more illite-like and vermiculite-like in soil samples from the Pacific coast of Costa Rica. The transmission electron microscopy (TEM) results of Pincus et al. (2017) indicated that K<sup>+</sup> is fixed in interlayers with local charge close to illite-like values.

The smallest amount of K in the extraction of 2:1 phyllosilicates with NaHSO<sub>4</sub> in the clay fraction of the control treatment in relation to the other samples is an indicator that the absence of K fertilization may have increased the release of K from 2:1 phyllosilicates of the clay fraction (Table 3). This suggests that the release of K from the mineral phase was more related to these 2:1 phyllosilicates than with kaolinites and possible feldspars, as seen by the small variation in these pools. The alteration of the clay-fraction mineralogy as a consequence of absorption by plants was observed either under laboratory conditions, where alfalfa (*Medicago sativa* L.)

**Table 3.** Amounts of K obtained in mineral species of the soil-clay fraction

Sample <sup>1</sup>	Fraction <sup>2</sup>				HIPM <sup>3</sup>
	Fe Ox	Kln+Gbs	2:1	Resd	
	.....(mg kg <sup>-1</sup> ).....				
1 (control)	9±1	130±5	1048±17	1488±39	2536±56
2 (control)	9±1	169±9	1245±24	1494±48	2739±72
3 (K-supplemented)	7±1	145±7	1652±36	1504±55	3156±91
4 (K-supplemented)	8±1	154±8	1680±38	1533±62	3213±100

<sup>1</sup> Samples 1 (0.0–0.2 m) and 2 (0.2–0.4 m) of the control treatment and samples 3 (0.0–0.2 m) and 4 (0.2–0.4 m) of the 130 kg ha<sup>-1</sup> K treatment (K-supplemented).

<sup>2</sup> Iron oxides (Fe Ox); kaolinite and gibbsite (Kln+Gbs); 2:1 phyllosilicates (2:1); residual fraction (Resd).

<sup>3</sup> Highly Weathered Primary Minerals (HIPM), represents the sum of 2:1 and Resd fraction. The K contents were calculated based on the release of the nutrient by each treatment in the sample concentrated by the previous extraction.

**Table 4.** Percentage of the total K reserve of soil-clay fraction associated with mineral species

Sample <sup>1</sup>	Total K (mg kg <sup>-1</sup> )	Fraction <sup>2</sup>			
		Fe Ox	Kln+Gbs	2:1	Resd
		.....(%).....			
1 (control)	462±12	1	40	15	40
2 (control)	455±15	1	45	15	36
3 (K-supplemented)	682±23	1	40	22	33
4 (K-supplemented)	630±19	1	41	21	33

<sup>1</sup> Samples 1 (0.0–0.2 m) and 2 (0.2–0.4 m) of the control treatment and samples 3 (0.0–0.2 m) and 4 (0.2–0.4 m) of the 130 kg ha<sup>-1</sup> K treatment (K-supplemented).

<sup>2</sup> Iron oxides (Fe Ox); kaolinite and gibbsite (Kln+Gbs); 2:1 phyllosilicates (2:1); residual fraction (Resd). The calculation of the percentages was done as follows: [(amount of mineral fraction (g kg<sup>-1</sup>)\*total K content in the specific fraction (mg kg<sup>-1</sup>))/10000].

induced the release of interlayer K (Norouzi and Khademi 2010), or field conditions, where Norway spruce (*Picea abies* L.) and oak (*Quercus sessiliflora* Smith.) decreased the less crystalline phases of illite-like minerals (Calvaruso et al. 2009), usually in the rhizospheric soil (Bourbia et al. 2013; Khormali et al. 2015).

Adamo et al. (2016) studied the release of K in illite layers of the soil clay fraction in the Campania region of Italy and concluded that mineral changes due to corn-root extraction may occur during a cropping period. Potassium fertilization did not influence the composition or structure of the 2:1 phyllosilicates during the crop period, with the majority of the K ions added to the system being rapidly absorbed by the plants, according to Adamo et al. (2016). The current study showed that over the long term (>30 y), however, K fertilization maintained large total K contents in the clay fraction and illite-like minerals, identifiable by XRD compared to the situation where K is absent (control).

The variation in K contents between control and K-supplemented treatment after HF digestion (Table 3) was probably related to the high resistance of K-containing minerals that resisted NaHSO<sub>4</sub> treatment and the low roots-accessibility of K contained in these minerals, as verified by Kaminski et al. (2007) in Alfisols and by Moterle et al. (2016) in Oxisols. As feldspars are not affected by this treatment, most of the K content extracted with HF after the use of NaHSO<sub>4</sub> were presumed to be associated with feldspars. Reflections of the 2:1 phyllosilicates persisted after NaHSO<sub>4</sub> treatment, however, indicating that some of the K released during HF extraction was associated with 2:1 phyllosilicates in order to account for the overestimate of K-feldspar concentrations (Table 2). In addition, the mass contribution of the fraction extracted with HF did not reach 6%, and in this mass were minerals such as anatase, which do not have K linked in the crystalline structure.

Minerals such as biotite and K-feldspars were not identified by conventional XRD in the soil parent material of the present study (data not shown). Conversely, the presence of traces of K (from 6 to 10 g kg<sup>-1</sup>) is common in basalts from southern Brazil (Peate et al. 1992; Torres et al. 2008). These residual amounts of K can be attributed to traces of amphiboles (Mayer et al. 2014), biotites (Haldar 2017), or K-feldspars (Dana and

Hurlbut 1981). Chemical and mineralogical properties of different sizes of aggregates in two soil classes (Acrustox: 8.0–4.0 mm; 4.0–2.0 mm; 2.0–0.5 mm; 0.5–0.2 mm; and <0.2 mm; and Ustrochrept: 8.0–4.0 mm; 4.0–2.0 mm; 2.0–0.5 mm; and 0.5–0.2 mm) were evaluated by Mitton et al. (2019) who observed that the distribution of exchangeable K in the different aggregate classes was random, but with significant differences. The smallest aggregates (0.5–0.2 mm) contained more K because of their smaller pores, limiting water flow and nutrient loss. These chemically rich microenvironments (smaller aggregates) were considered by Melo et al. (2002) to be responsible for the maintenance of biotite particles in the clay fraction of Oxisols from various regions of Brazil.

Another complementary hypothesis that should be considered for the origin of K-minerals in the soil is wind deposition. Saltation can result in local redistribution of nutrients in samples, as shown in a Nigerian Psammentic Paleustalf according to Sterk et al. (1996), while suspension may transport dust over thousands of kilometers, causing a regional transport of nutrients including K. According to Sterk et al. (1996) these events are accentuated during storms and may have an impact on soil fertility. Based on wind patterns from the Atlantic Ocean into the continent (García 1994), the probable source of these K minerals is less weathered soils located to the east and southeast of the State of Paraná, formed from Paleozoic sedimentary materials (Bigarella and Salamuni 1961).

In conclusion, one of the worst environmental implications of the imbalanced long-term K fertilization is the degradation of K-mineral pools. Greater rates of K fertilization will be necessary to achieve high crop yields. This will lead to reduced efficiency in the use of K fertilizers and higher nutrient losses. In addition, the results from the present study suggest that further studies on K concentrations in aggregates of different sizes and wind deposition of K-bearing minerals will help to clarify the dynamics of the K-mineral reserves in highly weathered soils over time. The comparison between native forest soils and intensively managed soils can also be a good way to improve nutrient reserve variations over time.

## CONCLUSIONS

Long-term K-fertilization promoted changes in K pools associated with the nutrient mineral reserve in the soil. The presence of 2:1 phyllosilicates, even in very small proportions, can be affected by K deprivation throughout three decades of cultivation. The reduction of total K contents and the contents associated with 2:1 phyllosilicates after 32 years of cropping without K addition confirm the greater mineral buffering capacity of plant-accessible K pools and the decrease in resistance to weathering of these 2:1 phyllosilicates.

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## Compliance with Ethical Standards

## Conflict of Interest

The authors declare that they have no conflict of interest.

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