Does Ferralsol Clay Mineralogy Maintain Potassium Long-Term Supply to Plants?

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ABSTRACT: Ferralsols (Latossolos) should contain few or no 2:1 clay minerals and have low potassium (K) contents, and consequently low levels of non-exchangeable K forms are expected. The aim of this study was to evaluate how the clay mineralogy of a Ferralsol affects the soil K dynamics in response to K fertilization during cropping and whether the clay mineralogy was altered due to successive crops and K fertilization. A tropical Brazilian Ferralsol under field conditions was sampled (0.00-0.20 m) in contrasting K fertilization plots: no K application (control plot) and 3,200 kg ha⁻¹ applied K₂O fertilizer. These two treatments were submitted at eight different crop cycles, performed in pots under greenhouse conditions, and fertilized with 0, 30, and 90 mg kg⁻¹ K₂O before each crop cycle. The biomass K, exchangeable K, non-exchangeable K, and structural K contents were determined after each crop cycle. At the end of the experiment, the presence of 2:1 clay minerals with hydroxy-aluminum interlayered in the soil clay fraction was verified, which ensured K adsorption in a form available to plants when K fertilizer was added. Cropping without K fertilization resulted in limited crop yields and exhausted the exchangeable and non-exchangeable K soil reserves. The previous K fertilization history influenced the soil K reserve and its availability to plants in the Ferralsol studied. The crops without K addition decreased the proportion of 2:1 hydroxy-Al interlayered clay minerals in the soil in relation to the kaolinite clay minerals.

Keywords: potassium forms, K fertilization, non-exchangeable K, 2:1 clay minerals, X-ray diffraction.
INTRODUCTION

Potassium (K) is an important nutrient worldwide (Sardans and Peñuelas, 2015). In agricultural lands, high K fertilization has been employed in Europe (Johnston, 2003) and in Brazil (Hurtado et al., 2008) to maintain crop production yield. Inadequate K fertilization frequently negatively affects growth (Andrist-Rangel et al., 2007). However, available K to plants is controlled by a complex exchange phenomenon between the solid and solution phases (Martin and Sparks, 1985). The most commonly used methods for estimating the content of available K for plants are those that determine exchangeable K, such as the ammonium acetate (NH₄OAc 1 mol L⁻¹), Mehlich-1 (HCl 0.05 mol L⁻¹ + H₂SO₄ 0.0125 mol L⁻¹) and cation exchange resin methods (Bortolon et al., 2010). However, assessing the exchangeable K form alone is not sufficient for estimating the total K uptake by crops, because some non-exchangeable K can be released from K-bearing clay minerals (Meurer and Anghinoni, 1993; Bortoluzzi et al., 2005; Darunsontaya et al., 2012; Moterle et al., 2016).

In this sense, soil K status is strongly influenced by the mineral soil constituents, and these depend on the soil weathering intensities and parent materials (Barré et al., 2008). Parent materials rich in K-bearing minerals may result in K-poor soils, depending on their weathering degree (Wilson, 1999). However, highly weathered soils can maintain small amounts of recalcitrant minerals as well as the 2:1 clay minerals, such as illite, which account for a large reserve of non-exchangeable K potentially available for plants (Silva et al., 1995; Melo et al., 2004; Darunsontaya et al., 2010, 2012; Moterle et al., 2016; Paola et al., 2016). The release of non-exchangeable K to the soil solution seems to adequately supply crop needs, regardless of K addition by fertilization (Darunsontaya et al., 2012). The 2:1 clay minerals act as either a K-sink or K-source, depending on the K fertilization regimen (Moterle et al., 2016).

In tropical and subtropical climates, large surface areas are covered by Ferralsols (Latossolos), which are highly weathered soils. The soil clay mineralogy is dominated by kaolinite as well as iron and aluminum oxy-hydroxides (i.e. goethite, hematite, and gibbsite), associated with the interstratified clay minerals and hydroxy-Al interlayered minerals (HIM) (Martins et al., 2004; Faria et al., 2012; Alves et al., 2013; Bortoluzzi et al., 2015). Although Ferralsols have low cation contents, previous studies have reported the presence of structural K and non-exchangeable K forms (Mielenzczuk, 1977; Goedert, 1983; Martins et al., 2004; Faria et al., 2012; Alves et al., 2013). Structural K is usually associated with the silt fraction of Ferralsols, in recalcitrant minerals such as mica and feldspars (Melo et al., 1995; Batista et al., 2016). The non-exchangeable K is linked to the presence of expandable 2:1 clay minerals (Silva et al., 1995). In this sense, small amounts of 2:1 clay minerals can affect the K dynamic, even in weathered soils. These premises reinforce that weathered soils can contain reactive clay minerals in their solid phase, which contribute non-exchangeable K to plant nutrition.

Evidence has been found in the literature concerning the capacity of weathered soils to release non-exchangeable K, but there are no specific reports on the clay minerals under fertilization and crop production. Our hypothesis is that 2:1 clay minerals, even when present in small amounts in weathered Ferralsols, contribute greatly to K dynamics, mainly as non-exchangeable K forms and supply K to plants. They also cause clay mineralogy changes following successive crops. Additionally, this discussion is important because K fertilization practices in large tropical agricultural areas worldwide have been carried out regardless of the soil clay mineralogy (van Raij, 1983; CQFS-RS/SC, 2004; Sousa and Lobato, 2004). The aim of this study was to evaluate how the clay mineralogy of a Ferralsol affects the soil K dynamics in response to K fertilization during successive cropping and whether the clay mineralogy was altered due to successive crops and K fertilization.
MATERIALS AND METHODS

This study was carried out using an existing long-term K-fertilization experiment that was started in 1983 by the Brazilian Agricultural Research Corporation - Embrapa Soybean, in Londrina (23° 11' 30.33" S and 51° 10' 57.80" W), Paraná State, Brazil. The altitude of the study site is 560 m a.s.l., and the relief is gently sloping. The geology of the area is basalt from the Serra Geral formation, which belongs to the São Bento Group. The climate is humid subtropical (Cfa), according to the Köppen classification system (Alvares et al., 2013), which is characterized by temperate humid conditions and well-defined seasons. The annual rainfall varies between 1,400-1,600 mm yr\(^{-1}\), the rainfall in the dry season is 190 mm (winter season), and the average annual temperature is 21 °C (Inmet, 2009). The natural vegetation is a semi-perennial tropical forest.

The soil at the study site is classified as a Ferralsol (WRB, 2015), which corresponds to a Latossolo Vermelho Eutrófico according to the Brazilian Soil Classification System (Santos et al., 2013). This soil type represents around 39 % of the whole country's surface, corresponding to 3,317,590.35 km\(^2\) (Manzatto et al., 2002). In summary, this Ferralsol has a deep profile with a Bw horizon (>0.50 m thick) and high cation leaching (Na\(^+\), K\(^+\), Ca\(^{2+}\), and Mg\(^{2+}\)), but it remains rich in Fe and Al contents. The soil profile is located on a relief with approximately 8 % slope and presents a clayed A horizon in the topsoil. The main soil properties are shown in table 1.

Our strategy was to use soil samples from a field experiment collected from plots with contrasting K application rates that was then submitted to successive cropping with different K fertilizers under greenhouse conditions.

Field experiment history

The K fertilization treatments consisted of applying 0, 40, 80, 120, 160, and 200 kg ha\(^{-1}\) K\(\text{2O}\) to summer crops. The field experiment consisted of six quantitative treatments with four replicates. From 1988–1993, no K fertilizer was applied. In 1994, 40 kg ha\(^{-1}\) K\(\text{2O}\) was applied at planting, except in the control treatment, and also applied on-site at different

| Table 1. Main soil properties of the Ferralsol from Paraná, Brazil, before cropping and after eight successive crops in a greenhouse experiment |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Soil properties                 | Soil in field conditions | After successive crops under greenhouse experiment |
|                                 | Horizons          | Treatments (K\(\text{2O}\) doses) |
|                                 | A\(^{(1)}\)       | B1\(^{(1)}\)     | F60T0           | F60T90          | F380T0          | F380T90         |
| Clay (g kg\(^{-1}\))           | 810.0            | 850.0            | -\(^{(2)}\)      | -               | -               | -               |
| Silt (g kg\(^{-1}\))           | 150.0            | 120.0            | -               | -               | -               | -               |
| Sand (g kg\(^{-1}\))           | 40.0             | 20.0             | -               | -               | -               | -               |
| Organic matter (g kg\(^{-1}\)) | 14.1             | 70.4             | -               | -               | -               | -               |
| Ca\(^{2+}\) (cmol kg\(^{-1}\)) | 40.2             | 30.3             | 7.5             | 7.8             | 7.4             | 7.6             |
| Mg\(^{2+}\) (cmol kg\(^{-1}\)) | 10.7             | 10.3             | 4.8             | 5.0             | 4.9             | 5.1             |
| Al\(^{3+}\) (cmol kg\(^{-1}\)) | 00.3             | 00.5             | 0.0             | 0.0             | 0.0             | 0.0             |
| K (mg kg\(^{-1}\))             | 320.0            | 74.0             | 11.0            | 86.0            | 16.0            | 253.0           |
| pH(H\(_{2}\)O)                  | 50.2             | 40.9             | 6.0             | 6.0             | 6.1             | 6.1             |
| CEC (cmolkg\(^{-1}\))          | 11.3             | 90.2             | 12.3            | 13.0            | 12.3            | 13.3            |

\(^{(1)}\) Data obtained from Silva (1994); \(^{(2)}\) not determined; F60T0 corresponds to a Ferralsol without K\(\text{2O}\) fertilization in the field experiment and no K\(\text{2O}\) fertilization in the greenhouse experiment; F60T90 is a Ferralsol without K\(\text{2O}\) fertilization in the field, but with K\(\text{2O}\) fertilization of 90 mg kg\(^{-1}\) per crop in the greenhouse experiment; F380T0 corresponds to a Ferralsol with K\(\text{2O}\) fertilization in the field experiment and no K\(\text{2O}\) fertilization in the greenhouse experiment; F380T90 corresponds to a Ferralsol with K\(\text{2O}\) fertilization in the field and K\(\text{2O}\) fertilization of 90 mg kg\(^{-1}\) per crop in the greenhouse experiment. Sand, silt, and clay fractions determined by the pipette method, described in Gee and Bauder (1986); organic matter determined by Walkley and Black method, modified by Tedesco et al. (1995); pH(H\(_{2}\)O) (soil:solution at a ratio of 1:1 v/v); Ca\(^{2+}\), Mg\(^{2+}\), and Al\(^{3+}\) (KCl 1 mol L\(^{-1}\)); K\(^{+}\) (H\(_{2}\)SO\(_{4}\) 0.05 mol L\(^{-1}\) and HCl 0.0125 mol L\(^{-1}\) - Mehlich-1); CEC = K\(^{+}\) + Ca\(^{2+}\) + Mg\(^{2+}\) + Al\(^{3+}\) + H.
rates (0, 40, 80, 120, and 160 kg ha\(^{-1}\) K\(_2\)O) 30 days after emergence. The following crops were planted: soybean (\textit{Glycine max} L. Merrill) in the 1983-1984 to 2000-2001 growing seasons, sunflower (\textit{Helianthus annuus}) in the 2001-2005 growing seasons, oats in the 1989 and 1990 growing seasons. Corn (\textit{Zea mays} L.) in the 2003 growing season, turnip (\textit{Raphanus sativus} L.) in the 2005 growing season, and wheat (\textit{Triticum aestivum} L.) in the 1984-1988, 1991-1993, 1995-1999, and 2004 growing seasons.

### Details of the greenhouse assay

For this stage, only two treatments were taken from the field experiment, representing the extreme K rates, i.e. the control treatment (F60) and the maximum K fertilized treatment (F380) that received 3,200 kg ha\(^{-1}\) K\(_2\)O. Approximately 60 kg of soil from each field treatment were collected at the layer of 0.00-0.20 m. Before starting the greenhouse assay, the soil clods were destroyed, and the soil mass was air-dried and passed through a 2 mm mesh sieve. The acidity was reduced to a pH of 6.0 by adding calcium carbonate and magnesium carbonate (2:1 ratio). For the greenhouse assay, 21 cm tall pots with 21 cm diameters were used. Each pot represented an experimental unit and received 3 kg of soil. The soil in the pots received a mix of nutrients using puriss p.a. reagents without K, and, during the cultivation sequence, three rates of K, using a KCl puriss p.a. solution, were added to each crop as shown in table 2. The rates were 0, 30, and 90 mg kg\(^{-1}\) K\(_2\)O per crop, except for the third and fourth crops which were not applied.

The greenhouse assay consisted of six treatments, representing two K levels from the field experiment (F60 and F380) that received three K rates (T0, T30, and T90) for the greenhouse experiment and four replications, totaling 24 experimental units in a completely randomized design. The schematic of the greenhouse assay is shown in figure 1. The following crop sequence was used: soybean (\textit{Glycine max} L. Merrill) and black oat (\textit{Avena strigosa} Scherb) three times, black bean (\textit{Phaseolus vulgaris} L.) twice, then sorghum (\textit{Sorghum bicolor} L. Moench), and millet (\textit{Pennisetum glaucum} L.). Eight successive cultivations were performed, and soil moisture was maintained at field capacity by weighing the pots daily.

### Plant and soil analysis

The aboveground plant biomass was collected approximately 30-60 days after emergence for each crop species and air-dried in a laboratory oven at 65 °C before storing for later chemical analyses.

Approximately 20 g of soil were collected at the end of each cropping season to determine the amounts of exchangeable K (Ke) using the Mehlich-1 extraction method (HCl 0.05 mol L\(^{-1}\) + H\(_2\)SO\(_4\) 0.0125 mol L\(^{-1}\)). Non-exchangeable K (Kne) was determined

### Table 2. Successive cultivation parameters used in the greenhouse study, including the crop species, growth period of each crop, number of plants per pot, and fertilizer type and quantity, in a Ferralsol from Paraná, Brazil

| Crops       | Species            | Crop time (day) | Plants per pot | K\(_2\)O added (mg kg\(^{-1}\)) | Other added nutrients |
|-------------|--------------------|-----------------|----------------|---------------------------------|----------------------|
| 1\(^{st}\)  | Sorghum            | 30              | 7              | 0, 30, and 90                   | N = 30, P = 150, S = 15, Zn = 7.5, Cu = 4.5, Mo = 0.15, B = 4.5 |
| 2\(^{nd}\)  | Black Oats         | 55              | 8              | 0, 30, and 90                   | N = 30               |
| 3\(^{rd}\)  | Black Oats         | 49              | 5              | -                               | N = 30               |
| 4\(^{th}\)  | Millet             | 41              | 5              | -                               | N = 22.5             |
| 5\(^{th}\)  | Black Beans        | 30              | 4              | 0, 30, and 90                   | N = 15, P = 150, S = 15, Zn = 7.5, Cu = 4.5, Mo = 0.15, B = 4.5 |
| 6\(^{th}\)  | Black Beans        | 38              | 3              | 0, 30, and 90                   | N = 30               |
| 7\(^{th}\)  | Soybean            | 32              | 5              | 0, 30, and 90                   | N = 15               |
| 8\(^{th}\)  | Black Oats         | 46              | 12             | 0, 30, and 90                   | N = 45               |
for extraction with HNO₃, 1 mol L⁻¹; the soil (2.5 g) was placed in a 100 mL Erlenmeyer flask, and 25 mL of HNO₃, 1 mol L⁻¹ were added. The Erlenmeyer flask was capped with a watch glass, placed on a hot plate in an open system at 110 °C, and heated for 10 min (Schimitz and Pratt, 1953). Structural potassium (Kₛ), representing the structural K in the minerals, was determined in the soil sampled before the greenhouse assay and after the fourth and eighth crops using concentrated HF (48 %) (Schimitz and Pratt, 1953). To determine the structural K, the soil (0.5 g) was placed in Teflon™ tubes with 50 mL concentrated HF in an open system. The samples were placed on a hot plate and heated to 105 °C until completely dry. Then, 5 mL of concentrated HClO₄ were added and heated at 105 °C until completely dry, and samples were diluted in 10 mL concentrated HCl (Schimitz and Pratt, 1953). The cumulative K in the plant dry matter was determined using the acid digestion procedure (Tedesco et al., 1995). All extracts were filtered through a Whatman™ Grade 42 filter paper, and K concentrations in solutions were determined using flame photometry. Standard and blank samples were included in each of the ten analyses to assess the quality of the chemical analysis. To build the calibration device, curves were made with a certified standard reference. For each soil parameter, means and standard deviations based on four replications were determined.

Soil samples from the contrasted K rate treatments were selected for the mineral analyses, both before the greenhouse assay (F60 Initial and F380 Initial) and after the greenhouse assay (F60T0, F60T90, F380T0, and F380T90). The intermediate treatments (T30) were not used for the mineralogical analyses. Aliquots from each replication were taken and mixed to form representative soil samples. Mineralogical analysis of the clay fraction was carried out according the methodology described by Bortoluzzi and Poleto (2006). In summary, the soil samples were treated with hydrogen peroxide (30 % at 40 °C) to eliminate organic matter, and the particles were dispersed using NaOH solution (6 %). The sand fraction (>53 μm) was sieved while the <53 μm fraction was separated into silt (2-53 μm) and clay (<2 μm) fractions by sedimentation using the pipette method (Gee and Bauder, 1986). One aliquot of the clay fraction was saturated with 1 mol L⁻¹ of magnesium chloride (Mg-saturation) and another with 1 mol L⁻¹ of potassium chloride (K-saturation). Excess ions in the samples were rinsed using distilled water. Magnesium-saturated clay suspensions were deposited onto glass slides and air-dried at room temperature (Mg-normal) to prepare oriented samples. The Mg-saturated clay fractions were also saturated with ethylene glycol (EG) for 7 days. The different K-saturated clay fractions were heated at 100 °C (K 100), 350 °C (K 350), and 550 °C (K 550) in a muffle furnace for 120 min each. The X-ray diffraction patterns (XRD) were obtained using a Shimadzu XD-7A diffractometer with Cu-Kα radiation, a voltage of 40 kV, and

Field experiment | Greenhouse crops
---|---
1983 | 2006 | 2007 | K doses (kg ha⁻¹ yr⁻¹) | Total K added (kg ha⁻¹) | K doses (mg kg⁻¹ per crop) | 0 (T0) | F60T0 | 30 (T30) | F60T30 | 90 (T90) | F60T90 | 0 (T0) | F380T0 | 30 (T30) | F380T30 | 90 (T90) | F380T90
0 | (0) F60 | 40 | 41 crops | 8 crops | 200 | (3,200) F380 |
40 | 80 | 120 | 160 | 200 |

**Figure 1.** Experimental design of the field and greenhouse K experiments regarding the K contents added to a Ferralsol from Paraná, Brazil.
a current of 20 mA. A diffraction range of 2-35° (2θ) was used, with steps of 0.02° (2θ) for normal conditions (air dried at room temperature), and steps of 2-14° (2θ) for EG conditions. The X-ray diffraction patterns from the sand and silt fractions were obtained from randomly oriented powders from 2-75° (2θ) using a step size of 0.05° 2θ (data not shown). The XRD patterns from the Mg-normal and K 350 samples were decomposed from 4-14° (2θ) using decomposition X-ray pattern software (Lanson, 1997), in which the 001 reflections were mathematically decomposed into elementary peaks. The XRD pattern decomposition was used to semi-quantitatively describe the patterns by estimating the relative peak intensities of each clay mineral over the sum of the intensities across the angular domain. The relative intensities of each elementary peak did not correspond to the relative proportions of the respective minerals (Lanson, 1997); however, the variation of the relative intensities was linked to variations in the mineral abundances. The surface area of each peak was determined and expressed as a relative proportion (percentage) of each peak in relation to the total surface area from all peaks.

**Statistical analysis**

The data were examined with an analysis of variance (ANOVA) in a completely randomized model. Analyses of variance were performed on the K levels of the soil and plant dry mass data, and the means were compared by the Tukey test with a statistical significance level of p<0.05. The mean content of the K forms in the soil as well as the initial content minus the final contents in the greenhouse assay for the three K rates were compared by the least significant difference (LSD) test at a 95 % significance level p<0.05.

**RESULTS**

**Mineralogy of the different soil fractions**

The sand fraction of the samples (53-2000 µm) contained predominantly quartz, maghemite, hematite, and gibbsite. The silt fraction (2-53 µm) was similar among the samples, but also contained kaolinite (data not shown).

All XRD patterns of the Mg-saturated clay fractions showed an intense peak at d = 1.42-1.45 nm in Mg-normal conditions (Figure 2) that was not displaced after EG solvation. The performance of 2:1 clay minerals after Mg saturation indicated an absence of expandable clay minerals, such as smectite. The absence of a peak at d = 1.00 nm in the XRD pattern (Mg-normal), indicated no illite presence. Kaolinite was dominant in the clay fraction, as was confirmed by the intense peaks at d = 0.72 nm and d = 0.36 nm (Mg-normal and EG solvation conditions), as was their absence after heating at 550 °C (Figure 2). After K saturation and heating at 350 °C (K 350) the peak at d = 1.42 nm (K-normal) was progressively collapsed at d = 1.26-1.39 nm and decreased its intensity after heating at 550 °C (K 550). Gibbsite was identified by peaks at d = 0.48 and 0.43 nm that disappeared after heating at 350 °C (F60 and F380; Figure 2).

Figure 3 displays the X-ray diffraction patterns of the clay fraction decomposed in the Mg-normal state and after K saturation and heating at 350 °C (K350). In all treatments, no-illite peak (d = 1.00 nm) was found. The relative proportion of diffracted intensity attributable to 2:1 clay minerals ranged between 12.0-21.4 %, while the surface area of the peak at d ~ 0.72 nm varied between 58.3-71.0 % (Figure 3). In addition, the peak decompositions centered at d = 0.72 nm showed that two kaolinite populations were present, one well crystallized with a high coherent scattering domain size (CSDS) at d = 0.72-0.73 nm, and one with a low CSDS (poorly crystallized) at d = 0.75 nm, which contributed to 11.8-21.0 % of the diffracted intensity (Figure 3). Interstratified kaolinite-smectite was not present because there was no peak at d = 0.72 nm displacement after EG solvation (Bortoluzzi et al., 2007).
After heating to 350 °C (Figure 3), the peak corresponding to the 2:1 clay minerals can be decomposed into two different peak behaviors. The peak at \( d = 1.45 \) nm (Mg-normal) displaced easily at \( d = 1.00 \) nm after heating to 350 °C, while another part of this peak collapsed at \( d = 1.26-1.30 \) nm. These results suggest that two vermiculite populations were present, one of vermiculite, wherever sheets of the aluminous chlorite were incomplete.
Figure 3. Modeled X-ray diffraction patterns from the Mg-saturated clay fraction and dried at room temperature (Mg-normal); K-saturated and heated to 350 °C (K 350) of a Ferralsol from Paraná, Brazil. (a) F60T0 - Mg-normal; (b) F60T0 - K350; (c) F60T90 - Mg-normal; (d) F60T90 - K350; (e) F380T0 - Mg-normal; (f) F380T0 - K350; (g) F380T90 - Mg-normal; F380T90 - K350. The patterns were decomposed between 4° and 14° (2θ), corresponding to the (001) clay mineral peaks.
that collapsed at $d = 1.00 \text{ nm}$ after heating to 350 °C (Meunier, 2007), and another vermiculite with interlayered hydroxy-Al (Chlorite-like) that did not completely collapse to $d = 1.00 \text{ nm}$ (Barnhisel and Bertsch, 1989; Meunier, 2007).

According to a semi-quantitative approach, the clay mineralogy changed with K fertilization rates (Figure 3). The relative surface area of XRD peaks, corresponding to 2:1 clay minerals, diminished compared to those of the poorly crystallized kaolinite ($d = 0.76 \text{ nm}$) at the high K rate (F380T90 in Mg-normal condition). This performance was also found by Moterle et al. (2016) studying an Acrisol from south Brazil. Furthermore, after heating to 350 °C, the peaks at $d = 1.30 \text{ nm}$ had a surface area that ranged between 7.8-17.9 % of the diffracted intensity, whereas the high K doses trended to produce a larger surface area, especially for the F380T90 treatment. For the F60 treatment, the surface area of this peak increased from 9.2 to 11.8 % with K rates of the T0 to T90 treatments (Figure 3). The surface area of the peak at $d = 1.00 \text{ nm}$ decreased from 3.3 to 1.6 % with the K rate (F380 treatment).

**Exchangeable (Ke), non-exchangeable (Kne), structural (Ks), and K in the plant dry mass**

In the F60 treatment without K addition, the Ke values decreased from 60.0 to 17.0 mg kg$^{-1}$ after eight successive crops. In samples collected following the addition of 3,200 kg ha$^{-1}$ K$_2$O in the field experiment (F380), and in samples from the eight greenhouse crops without K addition, the Ke decreased from 380.0 to 27.0 mg kg$^{-1}$ (Figure 4). After successive cropping, the exchangeable K content decreased in the treatments without added K. This result suggests that this soil does not contain enough non-exchangeable K (Kne) to maintain crop growth (Figure 4). However, a long history of K fertilization in the field ensured high initial K availability (F380) and the maintenance of an adequate K supply to crops, regardless of whether or not K was added in the soil (Figure 4).

The addition of 30 mg kg$^{-1}$ K$_2$O per crop during the greenhouse experiment was sufficient to maintain exchangeable K (Ke) values near the initial value in the F60 treatment. The exchangeable K contents in the F60 and F380 treatments, with the addition of 30 mg kg$^{-1}$ K$_2$O per crop, resulted in the Ke content decreasing from 60.0 to 35.5 mg kg$^{-1}$ and from 380.0 to 71.9 mg kg$^{-1}$, respectively (Figure 4). The addition of 90 mg kg$^{-1}$ K$_2$O per crop increased the Ke in the F60 treatment from 60.0 to 143.0 mg kg$^{-1}$, and decreased the exchangeable K in the F380 treatment from 380.0 to 251.0 mg kg$^{-1}$ (Figure 4).

The Kne content of the soils cultivated since 1983 without K fertilization (F60) decreased by approximately half, regardless of the K fertilization rate (Figure 4). In the treatment with 3,200 kg ha$^{-1}$ K$_2$O since 1983 (F380), the Kne content decreased from 178.8 to 49.5 mg kg$^{-1}$ after eight successive crops without K addition (Figure 4). In the high-K fertilization treatment, the Kne decreased from 178.0 to 133.2 kg ha$^{-1}$. The Ke and Kne values decreased intensively when the soil received K fertilizer in the field (F380).

The application of 30 mg kg$^{-1}$ K$_2$O before each crop was not sufficient to maintain the initial Kne levels in the soil, which decreased from 178.0 to 85.0 mg kg$^{-1}$ in the F380 treatment and from 51.0 to 54.0 mg kg$^{-1}$ in the F60 treatment. The addition of 90 mg kg$^{-1}$ K$_2$O per crop did not change the Kne contents after cropping in the F60 treatment, but it increased in the F380 treatment (Figure 4). The structural K (Ks) content was very low (approximately 300.0 mg kg$^{-1}$) in the F60 treatment before cropping and approximately 270.0 mg kg$^{-1}$ in the F380 treatment. These results reveal the low K reserves in the soil, according to the mineralogical constitution of the silt and sand fractions.

**Dry matter yield and the amount of potassium uptake by plants**

Cropping plants without K addition in the field experiment (F60) resulted in low plant dry matter production (by mass), independently of the K rates applied in the greenhouse assay (0, 30, and 90 mg kg$^{-1}$ K$_2$O per crop) compared to the F380 treatment (Table 3). In the
Figure 4. Potassium in plant dry matter. The initial K and final K contents were determined using different chemical extractors in an greenhouse experiment of a Ferralsol from Paraná, Brazil. (a) F60 - exchangeable K (Ke); (b) F60 - non-exchangeable K (Kne); (c) F60 - structural K (Ks); (d) F380 - exchangeable K (Ke); (e) F380 - non-exchangeable K (Kne); and (f) F380 - structural K (Ks). The treatments F60 and F380 represent the soil condition before beginning the greenhouse experiment; the K difference (Ke = exchangeable K; Kne = non-exchangeable K; and Ks = structural K) were determined by K content at the beginning experiment minus the K content at the end of the experiment for all K forms. The bars represent the Least Significant Difference (LSD) at p<0.05.

F60 treatment, only a rate of 90 mg kg\(^{-1}\) K\(_2\)O per crop applied in the greenhouse assay produced higher total dry matter than the control treatment (0 mg kg\(^{-1}\) K\(_2\)O per crop). Plant dry matter production in the F60 treatment was more dependent on K fertilization than in the F380 treatment; however, this production did not increase with the addition of K fertilizer in the greenhouse assay (Table 3).

Total K contents in the plant dry mass increased with K fertilization (Table 3). The plants accumulated 234.2, 482.6, and 708.2 mg K per pot in the F60 treatment when fertilized with 0, 30, and 90 mg kg\(^{-1}\) K\(_2\)O per pot, respectively (Table 3). In the F380 treatment, the plants accumulated 999.3, 1,187.1, and 1,215.7 mg K per pot in the F380 treatment when fertilized with 0, 30, and 90 mg kg\(^{-1}\) K\(_2\)O per crop, respectively (Table 3). These increases were amounted to 426.0, 245.0, and 174.0 % more K in the F380 treatment than in the
In the F60T0 treatment, the plants accumulated small K quantities in their aerial parts; however, in the F60T90 treatment, K uptake was approximately threefold (Table 3 and Figure 4). In the F380T0 treatment, the K uptake by the crop remained high, and was measured as twice as high as that of the F60T90 treatment (Table 3). The exchangeable K (Ke) was very sensitive to K fertilization, the difference in contents diminished (initial-final) when K was added (Figure 4). For the non-exchangeable K, the variation with the K doses was less important than for Ke, whereas Kne decreased with K addition, demonstrating a soil buffer capacity, i.e. great K fixation capacity in clay under non-exchangeable sites (Figure 4). The relationships of total K variations with the K application rates were not conclusive.

DISCUSSION

2:1 clay minerals in Ferralsol and their K-buffering capacities

In the clay fraction, the X-ray diffraction decomposition showed that the relative proportion of 2:1 clay minerals, such as vermiculite, was significant for a highly weathered soil (Figures 2 and 3). Furthermore, the XRD analyses made under different cation saturations and heating treatments allowed the identification of vermiculite with the hydroxy-Al interlayer (HIV), which was corroborated by previous studies on Brazilian weathered soils (Silva et al., 1995; Bortoluzzi et al., 2008; Inda et al., 2010; Caner et al., 2014; Cunha et al., 2014). In fact, the presence of hydroxy-aluminum minerals (HIMs) in variable proportions appears to be a main property of soils from sub-tropical areas in south Brazil (Kämpf and Klamt, 1978; Almeida et al., 2000; Marques et al., 2002, Bortoluzzi et al., 2008; Inda et al., 2010; Caner et al., 2014). The absence of K-bearing clay minerals in a soil, i.e. illite or feldspars, did not guarantee the K supply to plants when cropped without K addition by fertilizers (Figure 4). However, even when in very small quantities in the soil studied, the 2:1 clay mineral types controlled soil K reserves and K availability for plants (Figures 3 and 4).

The presence of the Al interlayer in this 2:1 clay mineral causes the low CEC of the soil due to Al occlusion in the clay interlayers; this neutralizes the permanent electrical

Table 3. Aerial plant dry matter and total K accumulated in the plant dry mass (Kdm) under greenhouse conditions in a Ferralsol from Paraná, Brazil

| Soil | K2O input | Successive crop sequence | mass of aerial plant dry matter | Kdm |
|------|-----------|--------------------------|-------------------|-----|
|      |           | 1st | 2nd | 3rd | 4th | 5th | 6th | 7th | 8th | Total | CV | mg per pot | % |
|      |           | g per pot | mg per pot |        |     |     |     |     |     |      |     |     |     |     |     |
| F60  | 0         | 1.3 ± 0.2 | 2.3 ± 0.2 | 2.7 ± 0.1 | 2.9 ± 0.6 | 5.7 ± 0.5 | 9.2 ± 0.2 | 4.1 ± 0.5 | 1.6 ± 0.6 | 29.7 bB(1) | 9.8 | 234.2 cB |
|      | 30        | 1.2 ± 0.3 | 2.4 ± 0.2 | 2.5 ± 0.2 | 3.6 ± 0.6 | 6.1 ± 0.5 | 10.3 ± 0.4 | 4.0 ± 0.4 | 2.3 ± 0.2 | 32.3 abB | 10.4 | 482.6 bB |
|      | 90        | 1.8 ± 0.2 | 2.6 ± 0.2 | 2.7 ± 0.3 | 3.0 ± 0.1 | 6.7 ± 0.3 | 10.3 ± 1.1 | 4.4 ± 0.2 | 2.4 ± 0.1 | 33.9 aB | 13.1 | 708.2 aB |
| F380 | 0         | 1.4 ± 0.2 | 2.9 ± 0.3 | 3.5 ± 0.3 | 3.8 ± 0.6 | 7.7 ± 0.4 | 9.9 ± 1.1 | 4.4 ± 0.2 | 2.3 ± 0.2 | 36.1 aA | 13.2 | 999.3 bA |
|      | 30        | 0.9 ± 0.1 | 2.5 ± 0.2 | 2.5 ± 0.2 | 4.5 ± 1.0 | 6.5 ± 0.5 | 11.0 ± 0.6 | 5.0 ± 0.4 | 2.6 ± 0.2 | 35.5 aA | 13.0 | 1,187.1 aA |
|      | 90        | 1.5 ± 0.2 | 2.9 ± 0.2 | 3.6 ± 0.3 | 3.6 ± 0.2 | 7.5 ± 0.1 | 11.7 ± 0.6 | 4.8 ± 0.5 | 2.3 ± 0.1 | 37.9 aA | 6.7 | 1,215.7 aA |

(1) Lowercase letters compare the K2O applications to each soil, F60 and F380 separate; uppercase letters compare the different initial levels of each soil (F60 and F380) and each K2O replacement rate (Tukey’s test p<0.05); CV is the ANOVA coefficient of variation. The values after ± sign represent the standard deviation of four replications from each mean.
charge (Janssen et al., 2003). The presence of Al in the interlayered vermiculite played a role in the soil chemical reactivity and the K-buffering capacity (Figures 2, 3, and 4). The reactive clay mineral contents are likely responsible for the non-exchangeable K reserve of 51.0 mg kg$^{-1}$ in the absence of K fertilization and 178.0 mg kg$^{-1}$ following K fertilization (Figure 4). In fact, when high K doses were applied to the soil, the exchangeable K soil contents increased, restoring the K in the siloxane cavities in interlayered 2:1 clay minerals. The K trapped by the interlayers of 2:1 clay minerals can be released to plants in future crops with no, or low, K supplies.

In general, non-exchangeable K contents in Brazilian Ferralsols are low, varying between 17.0 (Silva et al., 1995) and 231.0 mg kg$^{-1}$ (Meurer and Rosso, 1997), because of the absence of K-bearing clay minerals in the silt and clay fractions or the presence of hydroxy-Al minerals. However, clay contents in Ferralsols are normally high (Ghidin et al., 2006), and were 820.0 g kg$^{-1}$ for the soil studied (Table 1). In this sense, it was expected that the small quantities of 2:1 minerals observed in this soil contributed to the non-exchangeable K supply. Indeed, the non-exchangeable K content was 178.0 mg kg$^{-1}$ in the soil that received K by fertilization (F380T90) and only 51.0 mg kg$^{-1}$ in the soil without K fertilization (F60T0; Figure 4). This result demonstrates that the non-exchangeable K-buffering capacity varied between 51.0 (minimal K status) and 178.0 mg kg$^{-1}$ (maximum K status) and that the clay mineral responsible was the 2:1 clay mineral identified as HIV, which had a low degree of Al occlusion interlayer. Concerning K plant nutrition, our experiment showed that crop yields in a highly weathered soil were strongly dependent on K fertilization every year; however, the soil K-buffering abilities were guaranteed by the 2:1 clay minerals present. Vermiculite without, or having a low Al occlusion degree, had high K adsorption capacities, which can be very important for plant nutrition (Carey and Metherell, 2003; Simonsson et al., 2007; Öborn et al., 2010). Thus, a reversible K-fixation/release process controlled by the clay mineralogy, which was observed in this study, confers K-buffer capacities on the soils, as was also determined by Velde and Peck (2002), Darunsontaya et al. (2010), and Moterle et al. (2016).

**K dynamics following K application and crop cultivation**

The absence of K fertilization during the eight crop cycles under greenhouse conditions resulted in low crop yields (Table 3) and decreased the exchangeable and non-exchangeable K (Figure 4). However, if there was K fertilization, the exchangeable and non-exchangeable K increased. The supplementary K added to the crops appeared to restore, at least partially, the soil K reserves with K application (F60T90; Figure 4). Applying high K contents (F380) resulted in the accumulation of non-exchangeable K, which ensured plant productivity until the fifth crop cycle under greenhouse conditions (Table 3). When exchangeable K was added at rates greater than the plant K demand (F380T90), the K reserves increased slightly (Table 3 and Figure 4). The rate of 30.0 mg kg$^{-1}$ K$_2$O per crop (F380T30) seems to be the critical dose for this Ferralsol, because K reached sufficient contents in the soil for successive plant yield and the non-exchangeable K content was maintained (Table 3 and Figure 4).

The Ke was easily exhausted by plant uptake (Figure 4), because of its low binding energy, and this damaged plant productivity under greenhouse conditions (Table 3), and K could be displaced from the interlayers of the 2:1 clays. When the K status of the soil was high (F380T90), the K linked to the low energy (Ke) constituents was easily taken up by plants, and part of the K surplus was displaced toward the interlayer positions of the 2:1 clays. In addition, when plant nutrition is the only consideration, K can be applied before each crop to provide appropriate amounts of K and high exchangeable K, regardless of the soil K status. However, when K fertilization reaches a K surplus due to the clay mineral buffer capacity, exchangeable K favors K leaching, as verified in agricultural lands by Bortoluzzi et al. (2013). The challenge for adequate K fertilization is to know the K soil buffer capacity, including the clay soil mineralogy composition (Rao et al., 2000;
Castilhos and Meurer, 2002; Bortoluzzi et al., 2005, 2008; Britzke et al., 2012). In this sense, the K fertilization system can precisely match the K reserves (Rao et al., 2000; Pal et al., 2001), at the same time that non-exchangeable K forms can be released for plants (Rosolem et al., 1993; Moody and Bell, 2006; Kaminski et al., 2007).

**Effect of greenhouse crops on soil mineralogy**

The clay mineral changes due to cropping under restricted K fertilization are well described in the literature. Studying weak weathered soils under K-restriction, the vermiculitization process is easily observed, where the illite loss of K transforms into the vermiculite clay mineral (Bortoluzzi et al., 2005; Barré et al., 2008; Hinsinger et al., 2009; Bortoluzzi et al., 2012; Moterle et al., 2016).

In the case of this study, a highly weathered soil that does not contain illite, the vermiculitization process was not expected. However, here, the abundance between kaolinite and HIV clay minerals changed with K application and successive crop cycle greenhouse conditions (F380T90 and F60T90), decreasing the HIV proportion relative to kaolinite increase (Figure 3). Then, the high K application (F380T90) seemed to promote modification in soil mineralogy (Figure 3).

The increasing contribution of the HIV peak (d = 1.30 nm) attributed to clay dissolution and releasing of Al ions that can be incorporated into the 2:1 clay minerals interlayer (Moterle et al., 2016). In fact, kaolinite tends to increase in highly weathered soils due to favorable conditions for its formation (Bortoluzzi et al., 2008). This change was associated with long-term cropping (25 years) and eight successive crops under greenhouse conditions, because the conditions were different from the original non-anthropogenic environment. High cation absorption by plants results in a net efflux of protons and thus rhizosphere acidification, the same as under high pH conditions (Hinsinger et al., 2009). In this case, it was possible that dissolved Al$^{3+}$ in the soil solution near the roots (rhizosphere zone) was occluded by the 2:1 clay minerals interlayer, increasing the HIV proportion (Viennet et al., 2015). In weathered soils, such as Ferralsols, cropping causes K depletion from the siloxane cavity of the 2:1 clay minerals, and under an acid environment, the Al$^{3+}$ availability and the aluminization process increases in interlayers of 2:1 clay minerals, negatively affecting the K dynamics in soils. Finally, the crops without the addition of K had accelerated non-exchangeable K depletion, implying an increase in weathering intensity, but this phenomenon was not detected by the XRD analyses because there was no illite in this soil.

**CONCLUSION**

The Ferralsol clay fraction mineralogy was dominated by kaolinite, but 2:1 clay minerals, identified as vermiculite and hydroxy-Al interlayered vermiculite (HIV), ensured soil K-buffering capacity.

The K fertilization history influenced the soil K dynamics among the different K forms in the soil. With high K fertilization as part of the field experiment, the Ferralsol clay mineralogy allowed K fixation in non-exchangeable K sites. However, a lack of K fertilization limited the crop yield, compromising the exchangeable and non-exchangeable K forms.

The magnitude of Ferralsol K reserve/release could be controlled by the 2:1 clay minerals. Thus, the occurrence of 2:1 clay minerals in weathered soils, even in small amounts, can play an important role as soil K buffers, guaranteeing K adsorption or release from non-exchangeable K positions.

The crops in soils without K addition decreased the proportion of 2:1 hydroxy-Al interlayer minerals in relation to the kaolinite minerals.
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