



# **Research Findings**



Potassium deficiency symptoms in upper soybean leaves. Photo by R.F. Firmano.

## Long-Term Potassium Administration/Deprivation Cycles on Tropical Oxisol: Effects on Soil Fertility and Soybean Performance

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## Abstract

Highly weathered soils in the humid tropics generally present low potassium (K) mineral reserves. When K fertilization is restricted, exchangeable K forms tend to run out quickly, hampering crop yield. Furthermore, in the long-term, soil mineral reserves may be affected. A field experiment carried out from 1983 to 2016 at Londrina (Paraná state), evaluated the effect of potassium chloride (KCl) fertilizer rates (0, 40, 80, 120, 160 and 200 kg K<sub>2</sub>O ha<sup>-1</sup> year<sup>-1</sup>) on soybean yield under long cycles of K application (1983-1988; 1995-2008) and K deprivation (1988-1994; 2008-2014). In October 2015, each plot was divided into two, and K fertilizer was reapplied to one half, whilst the second half remained K deprived. The objectives of the present study were to explore soybean nutrition under long-term withheld K

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fertilization to study the dynamics of K forms in the soil, and to identify an optimum K fertilization rate that would also maintain K reserves in a highly weathered soil. Soil exchangeable K contents (evaluated using the Mehlich-1 and the ion exchange resin methods) corresponded highly with previous K application rates, whilst non-exchangeable K and soil total K were much less affected by treatments.

Soybean responded dramatically to exchangeable K levels at the lower K range and according to Mehlich-1 and the ion exchange resin method, was saturated already above 70 and 110 mg kg<sup>-1</sup>, respectively. This K residue level was stored in the soil 8 years after an application rate of 120 kg K<sub>2</sub>O ha<sup>-1</sup> and, with no additional fertilizer, was sufficient to support 90% of the maximum yield obtained from the plots where K had been reapplied.

The results indicate that the role of non-exchangeable and structural K forms has been underestimated. Also, a large proportion of the applied K reaches and is stored in the structural K forms, where it remains accessible to plant roots in the long-term. In conclusion, a K application range of 80-120 kg  $K_2O$  ha<sup>-1</sup> is expected to support reasonable growth, development, and yield of soybean on humid tropical Oxisols, whilst preserving future soil fertility. Lower rates would allow sufficient yields in the short-term, but soil fertility might decline with time. Higher application rates would be partially wasted and could even lead to a reduction in yields.

*Keywords: Glycine max* L.; highly weathered soil; Mehlich-1; non-exchangeable K.

## Introduction

Brazil is the fourth largest potassium (K) fertilizer consumer in the world, importing 90-95% of its annually rising demand. Potassium fertilizer demand increased by 10% from 2015 to 2016, translating to 700,000 tonnes of potassium oxide (K<sub>2</sub>O). Highly weathered soils typically contain 300-2,000 mg K kg<sup>-1</sup> (Silva et al., 2000), a relatively low mineral reserve in comparison to temperate climate soils in Brazil, which may have up to 30,000 mg kg<sup>-1</sup>. Interestingly, though born from a poor-K parent rock material and developed under humid tropical conditions, highly weathered soils may encompass mineral K sources sufficient to support crop nutrition. Indeed, species cultivated on soils rich with ferric and aluminum oxides with prevalent kaolinite and quartz, and under restricted K fertilization, often display deficiency symptoms and low tissue K contents (Lalitha and Dhakshinamoorthy, 2014; Darunsontaya et al. 2010). Still, high crop yields have frequently been reported over the years in spite of the humid tropical climate and soils originating from basaltic rocks, and even without K fertilization (Adamo et al., 2016; Qiu et al., 2014).

In Brazil, plant available soil K is measured using acidic solutions, such as with the Mehlich-1 or the ion-exchange resin methods. Nevertheless, the exchangeable phase is not the sole K source for plant nutrition (Rosolem *et al.*, 2012). For instance, soybean (*Glycine max* L.) crops exhibit a very rapid response to small changes at the lower range of exchangeable K content in the soil, however, this response diminishes at the higher range (Fig. 1). Crop response to K application is also quite often negligible, even on highly weathered acidic soils of the humid tropics and subtropics (Rosolem *et al.*, 2001). Such a phenomenon has been attributed to K reserves ingrained in the mineral soil fraction, mainly in ditrigonal positions in the phyllosilicate structure, or edge and fracture positions of these minerals in intermediate stages of weathering (Sharpley and Smith, 1988).



Fig. 1. Soybeans cultivar yields as a function of exchangeable K contents (Mehlich-1) in soil. Oliveira Jr. *et al.*, 2013.

Potassium deficiency symptoms often occur in plants grown on soils where the exchangeable K forms have gradually been exhausted overtime, and not adequately replenished via fertilization. In this scenario, the estimated K losses from agricultural systems may have serious economic consequences. Modern and high-yielding soybean cultivars occupy 33.9 million ha in Brazil (Brazilian Supply Company, 2017) and demand higher K inputs than traditional cultivars. The absence of such levels can lead to the exhaustion of soil exchangeable K forms, whereas the impact on other soil K reserves is unclear. The objectives of the present study were to explore soybean nutrition under long-term withheld K fertilization to study the dynamics of K forms in the soil, and to identify an optimum K fertilization rate that would also maintain K reserves in a highly weathered soil.

## **Materials and methods**

## Study area

A long-term field experiment started in 1983 in a region of basaltic spills where the vegetation is classified as semi-deciduous seasonal forest. The region (51° 10' W and 23° 11' S, 590 m above sea level) is located in the Paraná State Basin (Fig. 2). The northern part of



Fig. 2. Location map of the study area.

| Table 1. Soil chemical and textural attributes. |                        |                                    |                  |       |       |                    |          |
|---|------------------------|------------------------------------|------------------|-------|-------|--------------------|----------|
| Soil layer                                      | pН                     | Calcium                            | Magnesium        | $K_1$ | $K_2$ | Aluminum           | $H^++Al$ |
| m   | 0.01 CaCl <sub>2</sub> | cmol <sub>c</sub> kg <sup>-1</sup> |                  |       |       |                    |          |
| 0.0-0.2   | 4.4                    | 2.4                                | 1.3              | 0.12  | 0.15  | 0.9                | 6.6      |
| 0.2-0.4   | 4.3                    | 1.9                                | 1.1              | 0.09  | 0.13  | 0.9                | 6.7      |
|   |                        |                                    |                  |       |       |                    |          |
|   | OC                     | Phosphorus                         | CEC              | V     | Clay  | Silt               | Sand     |
|   | $g kg^{-3}$            | mg kg <sup>-3</sup>                | $cmol_c kg^{-l}$ | %     |       | g kg <sup>-1</sup> |          |
| 0.0-0.2   | 16                     | 31                                 | 10.4             | 37    | 715   | 229                | 56       |
| 0.2-0.4   | 8                      | 18                                 | 10.7             | 32    | 712   | 228                | 60       |

Note:  $OC = Organic carbon (K_2Cr_2O_7)$ ; Ca, Mg and Al (KCl 1 mol L<sup>-1</sup>); P and K<sub>1</sub> (Mehlich-1); K<sub>2</sub> (ion exchange resin); H<sup>+</sup>+Al = (SMP - Schoemaker-McLean-Pratt buffer solution); CEC = cation exchange capacity; V represents the percentage of saturation by basic character cations (Ca<sup>2+</sup>, Mg<sup>2+</sup> and K<sup>+</sup>) in relation to the CEC of the soil, which is obtained by the sum of these cations with H<sup>+</sup> and Al<sup>3+</sup>.



**Fig. 3.** A schematic description of the multi-annual K application (1983-1988; 1995-2008) and deprivation (1988-1994; 2008-2014) cycles. Soil and crop examinations took place during 2015-2016 (black arrow), when each plot was divided into two for new treatments: K reapplication vs. K deprived control.

the 3<sup>rd</sup> plateau in Paraná State, Brazil, is characterized as a Cfa Köppen type climate (subtropical humid), with rains throughout all seasons (1,800 mm annually) and possible droughts in the winter. The soil is a Rhodic Hapludox (Soil Survey Staff, 2010). The chemical attributes and textural characterization (Mehlich, 1953; Raij, 1998) of soil samples collected in July 2015, are listed in Table 1.

The experiment aimed to evaluate the long-term effects of restricted and unrestricted K fertilization cycles on soil K forms and on grain yields. The experiment design consisted of randomized complete blocks arranged in 24 plots ( $40 \text{ m}^2$ , 8 x 5 m), with four replicates and six treatments, consisting of one control and five K rates (40, 80, 120, 160 and 200 kg K<sub>2</sub>O ha<sup>-1</sup> year<sup>-1</sup>) applied as KCl (60% K<sub>2</sub>O).

Potassium applications took place from 1983 to 1988 and again from 1995 to 2008, but not from 1989 to 1994 or 2008 to 2014. During the rounds of application, K was applied annually for the summer crops, with 40 kg  $K_2$ O ha<sup>-1</sup> year<sup>-1</sup> applied at sowing, and the remaining amounts as a side dressing. In October 2015, the

plots were divided in two to receive new treatments: one half would be reapplied with K fertilizer and the other half would continue not to receive K - for the eighth consecutive year (2015-2016).

The area was predominantly cultivated with soybean in the summer and with wheat (*Triticum aestivum* L.), maize (*Zea* mays L.), sunflower (*Helianthus annuus* L.) or black oat (*Avena strigosa* L.) in winter. Yield and plant nutritional status assessments were made for soybean, which is the only species cultivated every year in the area, and the one with the highest amount of K per unit mass in its tissues. Seeding, pesticide application, weeding and harvesting were done mechanically.

## Soil sampling and preparation

Composite soil samples derived from five subsamples, randomly collected in each experimental unit from 0.0-0.2 and 0.2-0.4 m deep, were collected in July 2015 - before the K reapplication - and in December 2015 - two months after the K reapplication. The samples were dried (50°C) and sieved (2 mm mesh). Native soil samples near the experiment were also collected from the same soil depths as mentioned above to compare the effect of cultivation and treatments on soil chemical and mineralogical attributes.

## K forms

The exchangeable soil K was extracted separately using two different methods: Mehlich-1 solution (Mehlich, 1953), and the ion exchange resin (van Raij, 1998).

The non-exchangeable K phase was extracted using boiling nitric acid (HNO<sub>3</sub>) (Knudsen *et al.*, 1986; Pratt, 1997). Since K availability varied as per the previously applied K rates, concentrations of 0.25, 0.5, 2.0, and 4.0 mol L<sup>-1</sup> were used in addition to the reference concentration - 1 mol L<sup>-1</sup> HNO<sub>3</sub>, thus calibrating the HNO<sub>3</sub> technique to the low K range expected under extended periods of withheld K. Non-exchangeable K contents were calculated based on the difference between the total K contents obtained by the HNO<sub>3</sub> extraction, and the exchangeable K contents obtained by the Mehlich-1 or the ion exchange resin methods.

For total K determination, 5 g of soil samples were digested by the EPA 3052 method (USEPA, 1996), in the presence of 2 ml of HCl, 9 ml of  $HNO_3$  and 3 ml of HF (hydro-fluoric acid). Moist digestion was carried out in a microwave oven under the following conditions: 5.5 min of heating to, and then maintenance at 180°C under 2 MPa pressure for 9.5 min, and 10 min of cooling to room temperature. The extract was filtered on quantitative filter paper and transferred to 100 ml flasks. The K contents were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES).

## **Mineralogical analyses**

Powdered and parallel-oriented soil fraction samples, separated according to Gee and Or (2002), were evaluated by X-ray diffraction (XRD) in order to characterize the soil mineralogy. Analyses were performed on a computer-controlled X-ray diffractometer using a copper tube graphite monochromator. The velocity of the goniometer was  $0.02^{\circ}2\theta$  s<sup>-1</sup>, with a range of 3 to 90°20.

## Plant sampling and preparation

At the full bloom stage (R2) of the soybean, with a relatively high rate of K absorption (Zobiole *et al.*, 2012), trifolia diagnostic leaves (third from the apex of the plant and without petiole) were collected randomly from each subplot. Mechanical harvesting was performed at full soybean maturity (R8), and 6 m of the three central lines of each subplot (9 m<sup>2</sup>) were sampled. All plant tissues were dried at 50°C, milled, and sieved in 35 sieves (mesh size 0.5 mm). The fresh and dry aerial parts were taken to calculate the biomass produced in each subplot.

### K contents in leaves

The plant tissue (0.25 g per sample) was digested in 6 ml of  $HNO_3$  (65% v/v  $HNO_3$ ) and 2 ml of hydrogen peroxide ( $H_2O_2$ ). The nutrient content was determined using ICP-AES. Moist digestion was carried out in a microwave oven under the following conditions: 10 min of heating to, and then maintenance at 170°C for 15 min under 2 MPa pressure, and cooling for 20 min to room temperature.

## Yield

Yield was determined based on the grain mass per sampled plot  $(9 \text{ m}^2)$ , adjusted to 13% water content, and converted into kg ha<sup>-1</sup>.

### Statistical analyses

Regression analyses were carried out to determine K rates of the subplots with and without K reapplication. The data on soil chemical attributes and K forms underwent analysis of variance and Tukey's comparison (5%). Simple linear correlations were applied to verify the presence of significant correlations between the K contents extracted from the soil, by different methods, with the soybean yield attributes and K contents in plant organs.

## Results

XRD examination revealed that the clay mineralogy of the experimental site is composed of kaolinite (d: 0.725, 0.444, 0.356, 0.234, 0.169, 0.149 nm); hematite (d: 0.296, 0.250, 0.220, 0.183, 0.163, 0.145 nm); gibssite (d: 0.483 nm); quartz (0.334 nm); maghemite (0.293 nm) as the dominant minerals (Firmano, 2017). No differences could be observed between selected treatments, in spite of the significant contrast in their K application regime.

Soil sampling took place at the end of the eighth year, in which K application was readministered, or not, following seven years of K deprivation. Generally, all soil samples displayed low total K contents, ranging from 500 to 700 mg kg<sup>-1</sup> soil, with only minor differences between the two soil layers (0-0.2 and 0.2-0.4 m. The highest total K content was found after the 80 kg K<sub>2</sub>O ha<sup>-1</sup> rate had been reapplied, followed by the content of the native forest soil. The unfertilized control had the lowest total K content. Interestingly, the highest K reapplication rate (+K<sub>160</sub>) displayed a relatively low K content, equivalent to that of its non-fertilized control (-K<sub>160</sub>).

The sand soil fraction had the lowest total K contents, ranging from 193 to 168 mg kg<sup>-1</sup>. It contributed less than 2.5% of the total soil K - less than its relative portion in the soil texture (Table 1). The silt fraction displayed the highest total K contents, ranging from 775 to 900 mg kg<sup>-1</sup> soil, with no remarkable differences between treatments (Fig. 4). The clay fraction exhibited lower total K contents, from 450 mg kg<sup>-1</sup> at the control up to 680 mg kg<sup>-1</sup> at the +K<sub>80</sub> treatment. Nevertheless, since clay is the dominant fraction (>71%) in the soil texture, it contributed 62-71% of

the soil's K reserve. Furthermore, changes occurring in the clay fraction determined the total and available soil K status. Cultivation seemed to not have much influence on the mean total K distribution in soil fractions, which was 65, 33, and 2% for the clay, silt, and sand fractions, respectively vs. 61, 36, and 3% for the same fractions in the native forest (Fig. 4).

In contrast, total soil K contents were significantly affected by interactions between cultivation and the various nutrition treatments (Figs. 5 and 6). On average, total K contents were quite similar in the experimental area and the native forest - 781 and 803 mg kg<sup>-1</sup>, respectively, however, content was significantly lower under K rates below or equal to 80 kg K<sub>2</sub>O ha<sup>-1</sup>, and particularly under no K fertilization. On the other hand, rates equal to or greater than 120 kg K<sub>2</sub>O ha<sup>-1</sup> meant that K reserves were maintained in the soil over time (Fig. 5).

Non-exchangeable K content was lowest in plots that had received the lowest K doses throughout the 33 years of the experiment.

However, it increased linearly from 40 to 60 mg kg<sup>-1</sup> soil depending on prior K application rates. After seven years of deprivation, the effect of K reapplication on the non-exchangeable K contents was marginal, irrespective of dosage (Fig. 5). The non-exchangeable K content was however significantly dependent on the HNO<sub>3</sub> concentration used for sample extraction, as well as on the method used to determine the exchangeable K contents – Mehlich-1 or ion exchange resin. In the cases where total soil K was higher than 800 mg kg<sup>-1</sup>, the lower HNO<sub>3</sub> concentrations (0.25-0.5 mol L<sup>-1</sup>) were sufficient to yield most of the non-exchangeable K fraction. However, below this threshold, more rigorous concentrations were needed (Fig. 5). Furthermore, where the non-exchangeable K fraction was calculated using the resin-determined exchangeable K, non-exchangeable K forms of the relatively K-poor soils were detectable solely using the higher HNO<sub>3</sub> concentration range.

Following seven years of K deprivation, in July 2015, the soil exchangeable K contents followed the pattern of past K doses, especially where doses had been higher than 80 kg K<sub>2</sub>O ha<sup>-1</sup>



Fig. 4. Total K content in soil fractions from representative samples taken from plots in 2016 following 7 years of K deprivation (-K) and K reapplication carried out in the eighth year at two rates - 80 and 160 kg K<sub>2</sub>O ha<sup>-1</sup>. The control sample from a nearby non-cultivated native forest never received K application.



**Fig. 5.** Total (extracted using HNO<sub>3</sub> + HF) and non-exchangeable soil K (extracted with five concentrations of HNO<sub>3</sub>: 0.25; 0.5; 1; 2; and 4 mol L<sup>-1</sup>) following seven years of K deprivation and as a function of past and reapplied K rates: A and B - the last year of K deprivation in July 2015; C and D - shortly after reapplication in Dec 2015 of the eight years; E and F - after reapplication at the end of eight years in 2016. Non-exchangeable K contents were calculated by subtracting exchangeable K, extracted using either Mehlich-1 (A, C, E) or ion exchange resin (B, D, F), from the total K contents.

year<sup>-1</sup> (Fig. 6). Where K deprivation continued for half of the plots, this situation remained the same 6 months later in December 2015. Nonetheless,  $K_2O$  reapplication to the other half of the plots brought about a significant increase in exchangeable

K contents, which was proportional to the dose applied (Fig. 6). Although the response pattern of the exchangeable K levels to the reapplied nutrient was similar for the two extraction methods, the ion exchange resin technique obtained consistently higher levels.



Fig. 6. Mean values of exchangeable K, extracted using the Mehlich-1 or the ion exchange resin method, to measure the effects of residual K before nutrient reapplication (July 2015), and soon after K had been reapplied (+K) or not (-K), (Dec 2015).

The difference varied from 22 to 42 mg kg<sup>-1</sup> soil, being smaller but significant at the smaller K doses (0-80 kg  $K_2O$  ha<sup>-1</sup>), where the resin's results were 2-fold greater.

Soybean yield was highly responsive to very slight changes in the lower range of soil exchangeable K (Fig. 7A and B). Maximum grain yields were obtained at the low range of 60-80 mg kg<sup>-1</sup> of soil exchangeable K - determined using the Mehlich-1 method. Any further increase in exchangeable K failed to produce higher yields. A similar pattern, but at a significantly higher range of exchangeable K (above 100 mg kg<sup>-1</sup>) was observed where the ion exchange resin method was employed. The yields obtained under

the reapplied K treatment at the lower doses of 40 and 80 kg ha<sup>-1</sup> were significantly higher, by 25 and 12.5%, respectively, than the corresponding non-fertilized control. At this responsive range, the difference in K availability between the reapplied and control treatments surged dramatically by 25-30 mg kg<sup>-1</sup> (Fig. 6). At the higher application rates, the difference in yields was much smaller, ranging from 5-7.5 mg kg<sup>-1</sup> (Fig. 7A and B), in spite of the consistently higher soil K availability (Fig. 6).

A similar but more gradual response pattern was observed for leaf K content (Fig. 7C and D). Here, saturation was reached above soil exchangeable K contents of 120 mg kg<sup>-1</sup> at the



Photo 1. K deficiency symptoms in soybean and maize in the northern state of Paraná. Photo by R.F. Firmano.

reapplied K treatments, as compared to above 100 mg kg<sup>-1</sup> for the corresponding control samples (Mehlich-1). Again, the ion exchange resin method gave rise to a similar response pattern but at higher ranges of exchangeable K. Leaf K contents were 40% greater in plants grown with 80 kg K<sub>2</sub>O ha<sup>-1</sup> reapplied K, as compared to the corresponding control. The differences at the other K application rates were much smaller or none (Fig. 7C and D). Also, K reapplication significantly enhanced soybean grain size and quality, particularly at a dose range of 40-120 kg K<sub>2</sub>O ha<sup>-1</sup> (Fig. 8).

## Discussion

Soil fertility, in the sense of K availability, can be analyzed by the instantaneous  $K^+$ concentration in the soil solution at the roots vicinity. This instantaneous  $K^+$ 



Fig. 7. Soybean yield (A, B) and leaf K contents (C, D) as functions of actual levels of soil exchangeable K, determined using the Mehlich-1 or ion exchange resin methods. Measurements took place in 2016, with soybean crops reapplied with 0, 40, 80, 120, 160, and 200 kg K<sub>2</sub>O ha<sup>-1</sup> (A, C) vs. non-fertilized control (B, D) after seven years of K deprivation.

concentration is the momentary outcome of complex relationships and fluxes between the different K forms, soil phases, uptake by plants, fertilizer application regime, and loss due to leaching (Fig. 9).

Under the extensive precipitation characteristic of humid tropic regions, outward K fluxes (leaching) might dominate the system, thus promoting K movement from structural and nonexchangeable forms to the exchangeable fraction, rather than the opposite. However, fluxes replenishing the exchangeable K phase are assumed to be much slower than the outward fluxes (K removal by plants and leaching).

The clay mineral profile at the experimental site was comprised mainly by kaolinite, a 1:1 class mineral with low CEC (cation exchange capacity) values (about 10 meq 100 g<sup>-1</sup>), while 2:1 class clay minerals with substantially higher CEC values were scarce. The significant presence of kaolinite ( $[Al_2Si_2O_5(OH)_4]$ ) was expected, as this phyllosilicate can be found in higher

amounts in well-developed soils of the humid tropics (Fontes et al., 2001). Goethite and hematite ( $\alpha$ -FeOOH and  $\alpha$ -Fe<sub>2</sub>O<sub>2</sub>) are dominant iron oxides in Oxisols (Childs, 1981). The presence of quartz and hematite was expected due to the pedoenvironmental conditions, such as high iron (Fe) content in the parent material, high temperatures, rapid mineralization of organic matter and pH close to neutrality (Schwertmann and Murad, 1983). Gibssite ([Al(OH),]), the most representative aluminum hydroxide in tropical humid soils, was also expected (Fontes et al., 2001). Thus, in spite of comprising 72% clay (Table 1), the local clay mineral profile can establish relatively low CEC, insufficient to retain considerable levels of exchangeable K. This was the major reason why the control plants manifested K deficiency symptoms; after 34 years of K deprivation, the exchangeable K phase was almost depleted (Fig. 6) and unable to support even a minimum yield level (Fig. 7).

It may be postulated that the depletion of exchangeable K, under continuous conditions of crop cultivation with insufficient K



Fig. 8. Soybean grain quality for different K reapplication rates (A) vs. control samples with no K reapplication (B), in subplots deprived of K for seven years but demonstrating the residual effects of prior K fertilization.



Fig. 9. A simplified diagram describing the dynamics among K forms in agricultural systems.

replenishment, accelerated the release of exchangeable, and subsequently non-exchangeable K forms, from the total K reserves. This assumption is partially supported by the degradation of 2:1-type clay minerals, and the very poor crystallinity which did not allow sufficient detectability in the XRD tests. Under accelerated depletion of exchangeable K, the rates of K release from the structural phase of the clay minerals are too high, and hence those structures are loosened and disappear.

Nevertheless, the contribution of the structural K forms to short-cycle nutrient species is low, given the small amounts of K released over time (Figs. 4 and 5). Kaminski *et al.* (2007) observed little participation of structural K from Alfisol under successive crops cultivation. Similar results were obtained for Oxisols (Moterle *et al.*, 2016). Therefore, although comprising the major part of soil K reserves, structural K forms only become bioavailable after more available forms are intensely removed by crops, especially under deprived K fertilization (Csathó, 2002), or due to a direct action of microorganisms and organic acids (Basak and Biswas, 2009).

The reduction in non-exchangeable forms was possibly influenced by the low soluble K<sup>+</sup> levels in plots with a history of low K application rates - 80 kg K<sub>2</sub>O ha<sup>-1</sup> or less (Fig. 5). Here, the balance between K input and output was negative; K loss due to leaching and take-up by crops was higher than K application. The continuous K<sup>+</sup> depletion disturbed the balance between K forms and to reestablish the cation chemical equilibrium, K was released from non-exchangeable fractions (Simonsson *et al.*, 2007). Plant roots have an active role in this process, excreting both protons and organic acids to their microenvironment (Paola *et al.*, 2016), thus accelerating K release from the non-exchangeable phase (Bortoluzzi *et al.*, 2005; Melo *et al.*, 2005).

Two methods were employed in the present study to quantify the exchangeable K in the soil: Mehlich-1, and the ion exchange resin. The Mehlich-1 mechanism of extracting exchangeable K uses a double acid solution to enrich the soil sample with protons, and exchange them for  $K^+$  ions adsorbed to the electronegative surface of mineral or organic colloidal particles (Mehlich, 1953). The ion exchange resin approach challenges the soil particles with a substantially higher CEC, thus competing for cations. Generally, the response patterns to both methods for prior and current K application rates were similar, excluding some deviations at the extremely low and high levels (Fig. 6). This confirms van Raij's (1998) remarks, ascribing similar results to both methods, on tropical soils. However, considerable quantitative differences occurred between the methods, indicating that the ion exchange resin method is more efficient at extracting  $K^+$  ions, as it



Photo 2. Phenological stages and symptoms of K deficiency in selected time and locations at the experiment site throughout soybean cycle. Photo by R.F. Firmano.

consistently obtained values higher than those of the Mehlich-1 method (Fig. 6). Some of the difficulties of the Mehlich-1 method to accurately extract exchangeable K from relatively poor soils are reflected by the non-exchangeable K results (Fig. 5). The higher levels obtained using Mehlich-1, especially when higher acid concentrations were employed, may again suggest that the ion exchange resin is more efficient at accessing hard-to-get K<sup>+</sup> ions. Alternatively, it may be questionable whether that 'hidden' exchangeable K is accessible by plant roots. However, the establishment of a standard and reliable method to quantify the exchangeable K phase in soils has not yet been reached.

The principal aim of K application regimes is to construct and replenish sufficient levels of available K during crop growth and development, avoiding nutrient shortage as well as saturation. In the present study, the response of soybean plants to relatively small increases in K availability was very sharp, particularly at the lower range of nutrient availability (Fig. 7). Potassium content in leaves upsurged from 9.1 to 25.6 g kg<sup>-1</sup> and yields reached their maximum levels following a relatively small change in available K. While reapplication at low rates - 40 kg K<sub>2</sub>O ha<sup>-1</sup> - was insufficient to increase nutrient saturation in the exchangeable K phase, plant response was significant. Clover and Mallarino (2013) identified the critical K concentrations for several modern soybean cultivars, below which, yield losses range between 20 to 23 g kg<sup>-1</sup> K. On the other hand, in the present study, when rates of 160 and 200 kg K<sub>2</sub>O ha<sup>-1</sup> were reapplied, the levels of available K exceeded plant demand and uptake, and even caused a slight yield reduction (Fig. 7).

The most striking finding of the present study is the ability of the soil to preserve considerable levels of fertility over long periods of K deprivation. After 8 years without K fertilization, where prior application rates were equal to or greater than 120 kg  $K_2O$  ha<sup>-1</sup>, K exchangeable content was higher than 71 mg kg<sup>-1</sup> (Mehlich-1) or 112 mg kg<sup>-1</sup> (ion exchange resin) (Fig. 6). These levels, with no additional K application, produced 90% of the maximum yield obtained from corresponding plots reapplied with K (Fig. 7A and B). Thus, the rapid response phase of soybean to available K occurs at

the lower range of soil K contents for soybean grown on Oxisols at K exchangeable levels less than 40 mg dm<sup>-3</sup> (Mehlich-1), as observed by Rosolem and Nakagawa (2001). Furthermore, in the plots that were not applied with K fertilizer for 34 years, soil exchangeable K content was 22 (Mehlich-1) or 45 (ion exchange resin) mg kg<sup>-1</sup> (control, Fig. 6), and soybean yield levels reached 2,000 kg ha<sup>-1</sup> - about 60% of the maximum (Fig. 7). These results provide strong indications that the role of the non-exchangeable and the structural K forms has been underestimated. Moreover, they shed new light on the actual role of K fertilizer application on humid tropic Oxisols; a large proportion of the applied K reaches and is stored in the structural K forms, where it remains accessible to plant roots in the long-term (Fig. 9).

In conclusion, a K application range of 80-120 kg  $K_2O$  ha<sup>-1</sup> is expected to support reasonable growth, development, and yield of soybean on humid tropical Oxisols, whilst preserving future soil fertility. Lower rates would allow sufficient yields in the short-term, but soil fertility might decline over time. Higher application rates will be partially wasted and even lead to a slight reduction in yields.

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Photo 3. Difference in soybean maturation speed in the subplots that received K (+K) and in those that did not receive K (-K) after the last restriction cycle of the experiment. Photo by R.F. Firmano.

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## References

- Basak, B.B., and D.R. Biswas. 2009. Influence of Potassium Solubilizing Microorganism (*Bacillus mucilaginosus*) and Waste Mica on Potassium Uptake Dynamics by Sudan Grass (*Sorghum vulgare* Pers.) Grown under Two Alfisols. Plant and Soil 317(1-2):235-255.
- Bortoluzzi, E.C., D.R. Santos, J. Kaminski, L.C. Gatiboni, and D. Tessier. 2005. Potassium Fertilization Affecting the Mineralogy of a Acrisol in Rio Grande do Sul, Brazil. Revista Brasileira de Ciência do Solo 29(5):327-335.
- Brazilian Supply Company. Brazilian Grain Harvest 2017: Grains, Tenth Survey. Available at: <u>https://www.conab.gov.</u> <u>br/</u>. Accessed on 8 Dec 2017.
- Calonego, J.C., and C.A. Rosolem. 2013. Phosphorus and Potassium Balance in a Corn-Soybean Rotation under No-Till and Chiseling. Nutrient Cycling in Agroecosystems 96(1):123-131.
- Childs, C.W. 1981. Field Tests for Ferrous Iron and Ferric-Organic Complexes (on Exchange Sites or in Water-Solubre Forms) in Soils. Australian Journal of Soil Research 19(2):175-180.
- Clover, M.W., and A.P. Mallarino. 2013. Corn and Soybean Tissue Potassium Content Responses to Potassium Fertilization and Relationships with Grain Yield. Soil Sci. Soc. Am. J. 77(2):630-642.
- Csathó, P. 2002. The Residual Effect of K Fertilization in a Hungarian Corn Monoculture Long-Term Field Trial, 1990-1999. Communications in Soil Science and Plant Analysis 33(15-18):3105-3119.

- Darunsontaya. T., A. Suddhiprakarn, I. Kheoruenromne, N. Prakongkep, and R.J. Gilkes. 2012. The Forms and Availability to Plants of Soil Potassium as Related to Mineralogy for Upland Oxisols and Ultisols from Thailand. Geoderma 170:11-24. DOI: 10.1016/j.geoderma.2011.10.002
- Firmano, R.F. 2017. Residual Effect of Potassium Fertilization on the Nutrient Forms in Soil. Dissertation. 120 p. (Soil and Plant Nutrition Program), University of Sao Paulo, Piracicaba, Brazil.
- Fontes, M.P.F., O.A. de Camargo, and G. Sposito. 2001. Electrochemistry of Colloidal Particles and their Relationship with the Mineralogy of Highly Weathered Soils. Scientia Agricola 58(3):627-646.
- Gee, G.W., and D. Or. 2002. Particle-Size Analysis. p. 255-293. *In:* Dane, J.H., and G.C. Toop (eds.). Methods of Soil Analysis: Physical Methods. Soil Science Society of America.
- Kaminski, J., G. Brunetto, D.F. Moterle, and D.S. Rheinheimer. 2007. Depletion of Soil Potassium as Affected by Successive Cultivation. Revista Brasileira de Ciencia do Solo 31(5):1003-1010.
- Knudsen, D., G.A. Peterson, and P.F. Pratt. 1986. Lithium, Sodium and Potassium. p. 1358. *In:* Page, A.L. (ed.). Methods of Soil Analysis. 1<sup>st</sup> ed. American Society of Agronomy, Madison.
- Lalitha, M., and M. Dhakshinamoorthy. 2014. Forms of Soil Potassium: A Review. Agri Reviews 35:64-68. DOI: 10.5958/ j.0976-0741.35.1.008.
- Mehlich, A. 1953. Determination of P, Ca, Mg, K, Na and NH<sub>4</sub> by North Carolina Soil Testing Laboratoris. Raleigh: University of North Carolina: 8.
- Melo V.F., G.F. Corrêa, A.N. Ribeiro, and P.A. Maschio. 2005. Kinetics of Potassium and Magnesium Release from Clay

Minerals of Soils in the Triângulo Mineiro Region, Minas Gerais State, Brazil. Revista Brasileira de Ciencia do Solo 29:533-545. DOI: 10.1590/S0100-06832005000400006.

- Moterle, D.F., J. Kaminski, D. Santos Rheinheimer, L. Caner, and E.C. Bortoluzzi. 2016. Impact of Potassium Fertilization and Potassium Uptake by Plants on Soil Clay Mineral Assemblage in South Brazil. Plant and Soil 406(1-2):157-172.
- Oliveira, A. Jr., C. Castro, F.A. Oliveira, and L.T. Jordão. 2013. Potassium Fertilization in Soybean: Nutrient Balance Care. IPNI Agronomic Informations 143:1-10.
- Paola, A., B. Pierre, C. Vincenza, D.M. Vincenzo, and V. Bruce. 2016. Short-Term Clay Mineral Release and Re-Capture of Potassium in a Zea mays Field Experiment. Geoderma 264:54-60.
- Pratt, P.F. 1997. Potassium. p. 1143. In: Black, C. (ed.). Methods of Soil Analysis. 3<sup>rd</sup> ed. American Society of Agronomy, Madison.
- Qiu, S., J. Xie, S. Zhao, X. Xu, Y. Hou, X. Wang, W. Zhou, P. He, A.M. Johnston, P. Christie, and J. Jin. 2014. Long-Term Effects of Potassium Fertilization on Yield, Efficiency, and Soil Fertility Status in a Rain-Fed Maize System in Northeast China. Field Crops Research 163:1-9.
- Van Raij, B. 1998. Bioavailable Tests: Alternatives to Standard Soil Extractions. Communications in Soil Science and Plant Analysis 29(11-14):-1553-1570.
- Rosolem, C.A., and J.C. Calonego. 2013. Phosphorus and Potassium Budget in the Soil-Plant System in Crop Rotations under No-Till. Soil and Tillage Research 126:127-133.
- Rosolem, C.A., and J. Nakagawa. 2001. Residual and Annual Potassic Fertilization for Soybeans. Nutrient Cycling in Agroecosystems 59(2):143-149.
- Schulze, D.G. 1981. Identification of Soil Iron Oxide Minerals by Differential X-Ray Diffraction. Soil Science Society of America Journal 45:437-440.

- Schwertmann, U., and E. Murad. 1983. Effect of pH on the Formation of Goethite and Hematite from Ferrihydrite. Clays and Clay Minerals 31(4):277-284. DOI: 10.1346/ CCMN.1983.0310405.
- Sharpley, A.N., and S.J. Smith. 1988. Distribution of Potassium Forms in Virgin and Cultivated Soils of the USA. Geoderma 42(3-4):317-329.
- Silva, I.R. da, A.E.F. Neto, L.A. Fernandes, N. Curi, and F.R. do Vale. 2000. Forms, Quantity/Intensity Ratio and Bioavailability of Potassium in Different Latosols (oxisols). Pesquisa Agropecuaria Brasileira 35(10):2065-2073.
- Simonsson, M., S. Andersson, Y. Andrist-Rangel, S. Hillier, L. Mattsson, and I. Born. 2007. Potassium Release and Fixation as a Function of Fertilizer Application Rate and Soil Parent Material. Geoderma 140(1-2):188-198.
- Soil Survey Staff. 2010. Keys to Soil Taxonomy. 11th Edition. United States Department of Agriculture, NRCS.
- USEPA. 1996. Soil Screening Guidance: Technical Background Document. 2<sup>nd</sup> ed. United States Government Publishing Office, Washington, USA.
- Zobiole, L.H.S., R.S. Oliveira Jr., J. Constantin, A. Oliveira Jr., C. Castro, F.A. Oliveira, R.J. Kremer, A. Moreira, and L. Romagnoli. 2012. Nutrient Accumulation in Conventional and Glyphosate-Resistant Soybean under Different Types of Weed Control. Planta Daninha 30(1):75-85.

The paper "Long-Term Potassium Administration/Deprivation Cycles on Tropical Oxisol: Effects on Soil Fertility and Soybean Performance" also appears on the IPI website at:

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