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Potassium Bioavailability in a Tropical Kaolinitic Soil

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Abstract: Some plant species are able to acquire non-exchangeable forms of K, which improve K availability and cycling in cropping systems, and which may explain the lack of response to K. However, this would not be expected in soils dominated by kaolinite. The aim of this study was to assess non-exchangeable K (Kne) use by three selected plant species grown in a tropical Haplic Plinthosol with low exchangeable K (Ke). A greenhouse experiment was conducted with soybean (*Glycine max* L., Merr.), maize (*Zea mays* L.), and ruzigrass (*Urochloa ruziziensis*) with or without K fertilization for three growing cycles. The crop treatments were compared with a control without plants. In the absence of K fertilization, all the tested plants were able to use non-exchangeable K and non-exchangeable K contributed more than 80% of the K demand of the plants in the first growing cycle, even in this kaolinitic soil. In the first growing cycle, soybean and maize took up more non-exchangeable K than ruzigrass, concomitant with higher dry matter yields. Over the three crop cycles, as both biomass yield and K uptake decreased in the unfertilized systems, the dependence of plants on non-exchangeable K decreased. Unfertilized ruzigrass showed a strong ability to acquire non-exchangeable K from the soil. Over the course of three growing cycles, K application decreased the absolute uptake of non-exchangeable K as well as its fractional contribution to total K uptake by the crops.

Keywords: potassium balance; K in tropical soil; plant K availability; potassium cycle; exchangeable K; non-exchangeable K

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1. Introduction

The uptake of nutrient Potassium (K) is the second most, only behind nitrogen, and between the essential nutrients required by plants. K is found in large concentrations in the vacuoles and cytoplasm of plant cells and is a major enzyme activator, although it is not strongly bound by any cellular molecules [1]. In soil, K is transported to roots primarily by diffusion in the soil solution; however, under some conditions, mass flow may also be an important transport mechanism [2,3]. The K concentration in soil solution is primarily buffered by K ions adsorbed electrostatically at the surfaces of soil minerals and organic colloids. When these ions move into the soil solution and are taken up by plants, it is commonly assumed that they can be slowly replenished by K from interlayer sites in secondary layer silicates and possibly by structural K in primary minerals (micas and feldspars), where most soil K typically occurs [4–9]. Structural K in the minerals of silt and sand fractions of soils is usually discounted as a significant source of plant-available K during a growing season because of the slow K release and low surface area of these particles.

The potential bioavailability of soil K over a growing season is commonly estimated in standardized soil tests by extraction with 1 M ammonium acetate or Na-saturated anionic resin beads [10,11]. This fraction of soil K may include both ions electrostatically adsorbed at mineral surfaces and an indeterminate fraction of interlayer K. This fraction is often termed "exchangeable K," although the extraction is strongly driven by the carboxylate functional groups of the acetate or the resin, in addition to displacement of K by NH_4^+ or Na^+ [12]. By contrast, most interlayer K and structural K in feldspars is not readily extracted by typical soil tests and is often referred to as "non-exchangeable K", although a preferred term would be non-extractable K (since the soil test method involves more than simply cation exchange reactions) [13]. In soils, the movement of K ions between surface-adsorbed and interlayer fractions depends on coupled biological, chemical, and physical mechanisms in the rhizosphere [14]. Plant uptake of K generates a strong concentration gradient in the rhizosphere solution, leading to the release of electrostatically adsorbed K and some K from the interlayers of 2:1-layer silicate minerals. Release of interlayer K may also be accelerated by the presence of organic anions, root exudates and microorganisms that promote mineral weathering, and K dissolution [15]. It is usually assumed that charged sites near mineral edges (also called wedge sites) are the most likely locations of interlayer K release to the soil solution [16,17].

Although most tropical soils are low in soil-test K [3,18,19], the crop response to K fertilization can be inconsistent [20–24], perhaps because some added fertilizer K is adsorbed at interlayer sites or because some interlayer K can be accessed by plants. When surface-adsorbed K concentrations are very low, plants depend on interlayer K, and there is often a concomitant yield penalty [25,26]. The dynamics of surface-adsorbed, interlayer, and structural K in soil have primarily been studied in soils in temperate climates, where 2:1 clay minerals are often dominant. Potassium in tropical soils, often dominated by 1:1 clay minerals such as kaolinite as well as Fe or Al oxides, has received much less attention, and the importance of non-exchangeable forms of K to plant uptake and growth in these soils is not well understood.

Some plants, such as those of the genus *Urochloa* ssp. and pearl millet (*Pennisetum americanum*, L.), are able to take up K from both the surface-adsorbed fraction and non-exchangeable K [18,27]. Soybean is also able to take up non-exchangeable K [28], albeit less efficiently than *Urochloa* ssp. [29]. Uptake of non-exchangeable K has been observed mainly when fertilizer K is not applied, i.e., when exchangeable, surface-adsorbed K is not present [18]. The drivers and mechanisms of non-exchangeable K uptake vary from species to species and are related to root morphology [15], the composition of root exudates, and the concentration of soluble K. Hence, plants such as ruzigrass (*Urochloa ruziziensis*), maize, and soybean grown in soils with low soil-test K may exhibit different responses to K fertilizer. Therefore, we hypothesize that the use of these species in rotation in a crop system will affect the exploration of non-exchangeable soil K, affecting K cycling in the system, which could explain the lack of response to K in some circumstances.

The objectives of this study were to (i) evaluate the growth of ruzigrass, maize, and soybean in a highly weathered kaolinitic soil with low exchangeable K content and (ii) measure the capacity of these plants to take up and deplete non-exchangeable K over three successive crop cycles.

2. Materials and Methods

A pot experiment was carried out in a greenhouse in Botucatu, Sao Paulo, Brazil. The soil material was collected at a depth of 20–40 cm of a Haplic Plinthosol (FAO, 2014) under native forest in Nova Xavantina, Mato Grosso, Brazil. Samples were taken from this depth to provide a sample with exchangeable K lower than in the uppermost soil layer due to litter recycling. The soil was air-dried and passed through a 5-mm sieve. Selected initial soil physical and chemical properties [12] are shown in Table 1. Using thermogravimetric and x-ray diffraction analyses, we determined that the clay fraction in this material was dominated by kaolinite, with substantial amounts of goethite and biotite as well as a small amount of vermiculite [30].

Table 1. Selected initial soil chemical characteristics (before liming amendment).

Soil Properts	Value	Units
Clay	275	$g \cdot kg^{-1}$
Silt	175	$g \cdot kg^{-1}$
Sand	550	$g \cdot kg^{-1}$
Initial pH [1] $_{(CaCl2)}$	3.8	–
Soil organic carbon [5]	7.0	$g \cdot kg^{-1}$
Available phosphorus (P_{resin})	7.2	$mg \cdot kg^{-1}$
Calcium ($Ca^{2+}{}_{resin}$)	120	$mg \cdot kg^{-1}$
Mg ($Mg^{2+}{}_{resin}$)	30	$mg \cdot kg^{-1}$
Potassium [2] ($K^{+}{}_{resin}$)	72	$mg \cdot kg^{-1}$
Non-Exchangeable K [4]	230	$mg \cdot kg^{-1}$
NAE K [3] (HNO_3)	302	$mg \cdot kg^{-1}$
Cation exchange capacity ($CEC_{pH\ 7.0}$)	8.3	cmolc kg^{-1}

[1] In 1:1 0.01 mol L^{-1} $CaCl_2$; [2] extracted with pearl Na-saturated cation exchange resin coupled with bicarbonate anion exchange resin, 1:1 volume ratio, 16 h shaking with a previously disaggregated sample [12]; [3] NAE–nitric-acid-extractable K, extracted with boiling HNO_3; [4] Non-exchangeable K = NAE K–Exchangeable K; [5] Soil organic carbon. = Organic matter determined according to [31]. CEC = Cation exchange capacity at pH 7 (Ca + Mg + [H + Al] + Exch K) [32].

Plastic pots with a height of 26 cm and a diameter of 28 cm (12 L) were each filled with 14 kg of air-dried soil. pH (1:1 0.01 mol L^{-1} $CaCl_2$) was raised to pH 5.4 by applying dolomitic limestone [32]. Subsequently, the soil was fertilized with 175 mg kg^{-1} of P as triple superphosphate, 13 mg kg^{-1} of S as calcium sulfate, 1.75 mg kg^{-1} of Cu as copper sulfate, and 1.75 mg kg^{-1} Zn as zinc sulfate.

In this paper, we define exchangeable K as readily available, as K that is extractable by a Na-saturated exchange resin, and non-exchangeable K as the difference between K extracted by boiling 1 M HNO_3 and exchangeable K. Exchangeable K roughly corresponds to surface-adsorbed K, and non-exchangeable K is assumed to represent some but not all interlayer K. Before starting the experiment, soil exchangeable K was 72 mg kg^{-1} and non-exchangeable K 230 mg kg^{-1} (Table 1). To deplete soil K to a low level, ruzigrass was grown in all pots for up to 45 days after plant emergence. Then, all pots were sampled, and the samples were combined for analysis. The ruzigrass crop reduced the exchangeable K to 21 mg kg^{-1} and non-exchangeable K to 223 mg kg^{-1}, on average.

The experimental design was a randomized complete block with four replications. The treatments included three crop species, soybean, maize and ruzigrass, grown with or without K fertilization as described in Table 2. Control pots without plants but with K (control + K) or without K (control) were also included. The experiment was run for three successive growing cycles. Ruzigrass, a perennial forage crop, was chosen because it has been widely used in integrated cropping systems in Brazil, has a fine root system that allows for a higher exploration of the soil compared with maize [33] and is very efficient in taking up soil K [34].

Nitrogen supply varied with crop species. For soybean, nitrogen was supplied via biological fixation. Soybean seeds were inoculated with 5 mL kg^{-1} of *Bradyrhizobium japonicum* (strains SEMINA 5079-CPAC 15 and SEMINA 5080-CPAC7). For maize, nitrogen was applied as urea at a rate of 80 mg of N kg^{-1}, divided into two applications 15 and 21 days after sowing [35]. For ruzigrass, 25 mg of N kg^{-1} were applied [34] as urea 15 days after sowing.

Table 2. Potassium (K) application rates for three crop cycles.

Treatments	Rates (mg K kg^{-1} Soil) *		
	First Crop	Second Crop	Third Crop
Ruzigrass + K	70	115	70
Ruzigrass	0	0	0
Soy + K	70	130	70
Soy	0	0	0
Maize+ K	70	200	140
Maize	0	0	0
Control Soil + K	140	140	140
Control Soil	0	0	0

* To determine the need for application of K, the level of K in soil and plants was determined after each harvest. The rate applied was chosen to compensate for the K removed by the plants and to maintain the level of exchangeable K in the soil above 70 mg kg^{-1}. K applied (mg pot-1) = K exported in harvest (mg pot^{-1}) + ((Ke in soil (mg kg^{-1})–70 (mg kg^{-1})) * kg of soil pot^{-1}).

In the +K treatment potassium was applied on the surface as potassium chloride at the rates shown in Table 2 in each planting cycle 15 days after seeding. The total K accumulated by the plants in each cycle was calculated and was applied before the next crop cycle. This strategy ensured that the plants would not need to use K sources other than the applied fertilizer.

Applied K can migrate directly to non-exchangeable forms [3]. Therefore, to monitor the behavior of K among the soil fractions when plants were not extracting it, K was applied to the pots without plants at 140 mg kg^{-1} as potassium chloride in each cycle (control + K treatment).

Soil moisture was maintained at nearly 80% of field capacity by applying deionized water every other day. To avoid water loss by percolation, the bottoms of the pots were sealed. The greenhouse was maintained with 13 h of artificial light per day and a temperature between 23 °C and 35 °C.

Before planting, seeds of soybean and maize were germinated for 48 h on paper towels moistened with distilled water and then transplanted into the soil. For ruzigrass, sowing was performed only once, and the plants were allowed to regrow after cutting. Considering the size of the plant of each species, we based on previous studies and used these same species in pots, so, seven days after emergence soybean was thinned to two plants per pot [28], three ruzigrass plants [36], or one maize plant [35]. The peak accumulation of K occurs at approximately 90 days for soybean [37] and maize [38], and thus these crops were grown for 90 days in each of the three successive cycles. By contrast, ruzigrass was grown for three successive cycles of 45 days each [36].

The entire aboveground portions of the plants in each pot were harvested by cutting at the soil surface and dried to constant weight in a forced-air oven at 60 °C for 72 h. The dry plant tissues were digested using a double-acid solution (HNO_3 + $HClO_4$ at a ratio of 2:1, *v/v*) [39].

After shoot harvest, the soil in each pot was sampled with a small-core auger (1.27 cm diameter) of sufficient length to reach the bottom of the pot. Old roots were not taken out of the pots. Three soil samples were taken per pot and combined into one replication. Soil samples were air-dried and ground to pass a 2-mm mesh screen. Resin-extractable (i.e., exchangeable) K was extracted with an ion-exchange resin saturated with Na [12], and non-exchangeable K was calculated as the difference between the amount of K extracted with boiling 1.0 mol L^{-1} HNO_3 [40] and exchangeable K (extracted with resin).

The net changes in soil exchangeable and non-exchangeable K during each crop cycle were calculated using the following equations after transforming soil K concentrations (mg kg^{-1}) to K stocks (g pot^{-1}), as in [3,34]:

$$\Delta Ke = K_f - K_i \quad (1)$$

$$\Delta Kne = K_f - K_i, \quad (2)$$

where Ke represents exchangeable K, Kne represents non-exchangeable K, ΔK is the change in the amount of each fraction of soil K, K_f is the final Ke or Kne in the soil, and K_i is the initial Ke or Kne in the soil before starting the experiment. Kne was determined as the difference of K extracted with boiling 1.0 mol L^{-1} HNO_3 and K extracted with resin.

To estimate the K balance in the soil-plant system, Equation (3) was used, considering the total K accumulated in plants (g pot^{-1}):

$$K_{bal} = K_{fert} - K_{abs} - \Delta Ke, \quad (3)$$

where K_{bal} is the K balance, K_{fert} is the mass of fertilizer K applied per pot, and K_{abs} is the total mass of K absorbed by the plants per pot. A negative value was interpreted as release and uptake of non-exchangeable K (depletion of Kne or other sources that were not soluble in the nitric acid extraction), whereas a positive value indicated that K was retained by the soil and root residues. To estimate the contribution of nonexchangeable K to total plant uptake, we used Equation (4):

$$Contrib_{Kne} (\%) = |K_{bal\text{-}neg}/K_{abs}| \times 100 \quad (4)$$

where $Contrib_{Kne}$ represents the fractional contribution and $K_{bal\text{-}neg}$ represents those values of Equation (3) that were negative.

The data were subjected to homogeneity of variance (Levene test) and normality (Shapiro–Wilk) testing, and if appropriate, ANOVA was performed. When the effects were significant, means were compared by the least significant difference method (LSD, $p < 0.05$) using the statistical package SISVAR [41].

3. Results

3.1. Potassium in Soil and Plants

Without K application, the three species accumulated more K in the first crop cycle than in the second and third crop cycles (Figure 1A). In the presence of K fertilizer, the plants absorbed larger quantities of K, as expected. When K fertilizer was applied, potassium uptake was less in the third crop cycle than in the first for soybean and ruzigrass but not for maize.

When no K was added, maize and soybean aboveground dry matter yield (DMY) decreased from the first through third crop cycles, whereas for ruzigrass the decrease in DMY was significant only in the third crop (Figure 1B). Maize and soybean suffered greater decreases in DMY after successive cultivations without K than did ruzigrass; the DMY decreased 87%, 88%, and 41% respectively. After the second crop, ruzigrass without K was still able to maintain its DMY similar to the first crop, while maize and soybean showed a significant decrease.

After the first cycle, exchangeable K was 21 mg kg^{-1} in the unfertilized control without plants (Figure 2A). In the fertilized treatment without plants (control + K), soil exchangeable K increased after the first fertilizer amendment, decreased after the second amendment, and increased again after the third amendment. In contrast, non-exchangeable K in the control + K pots continued to increase with successive applications of K (Figure 2B). In the cropped pots, successive crops depleted soil exchangeable K in the absence of K application, leading to an exchangeable K concentration lower than the unfertilized control (Figure 2A).

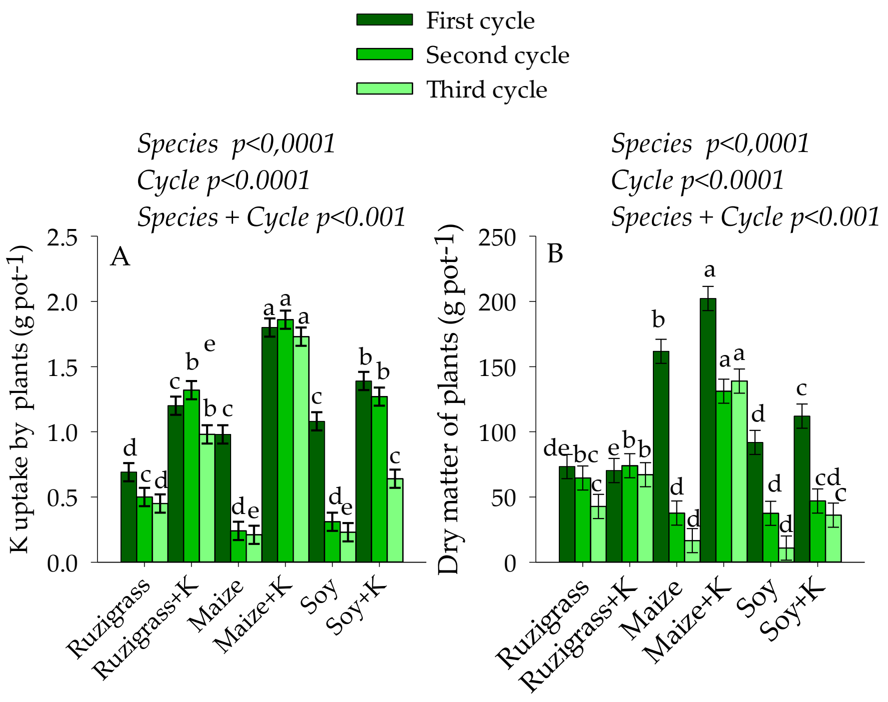

Figure 1. K uptake (**A**) and plant dry matter production (**B**) in three successive ruzigrass, maize, and soybean crop growth cycles, with and without application of K fertilizer. The absence of overlap by vertical bars shows significant differences among cycles in the same crop and fertility treatment. Lowercase letters indicate differences among species when crop cycle and fertility treatment were held constant (LSD, $p \leq 0.05$).

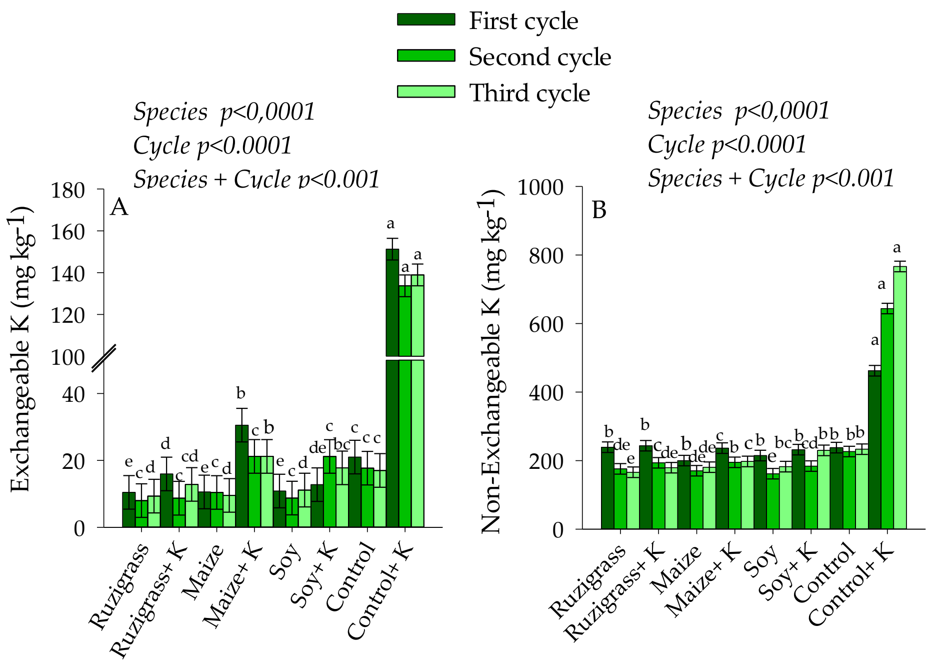

Figure 2. Soil exchangeable K (**A**), and nonexchangeable K (**B**), in three successive ruzigrass, maize, and soybean crop growth cycles with or without application of K fertilizer. The absence of overlap by vertical bars shows significant differences among cycles in the same crop and fertility treatment. Lowercase letters indicate differences among species when crop cycle and fertility treatment were held constant (LSD, $p \leq 0.05$).

Regardless of K application, non-exchangeable K decreased from the first to the second crop for all species. By the end of the first crop cycle, the non-exchangeable K concentration was similar to that of the non-fertilized control in all treatments (Figure 2B). After the first crop cycle, the largest decrease in soil non-exchangeable K occurred in the treatments with unfertilized ruzigrass. After the second crop cycle, non-exchangeable K concentrations were lower in all treatments without K than in the fertilized treatments. From the second to the third crop, the soil non-exchangeable K concentration did not change, except for an increase in the treatments with both K-fertilized and unfertilized soybean. By the end of the third cycle, depletion of non-exchangeable K was observed in most of the crop treatments, although in the fertilized soybean treatment non-exchangeable K had increased to its level after the first cycle. Non-exchangeable K increased over time in the control + K (Figure 2B).

Overall, even where fertilizer K was applied, there was a net decrease in both exchangeable and non-exchangeable K (as measured by extractions) over the three crop cycles of this study (Figure 3). Both ΔKe and the ΔKne were negative where plants were grown, and they were positive with no plants in the control + K treatment. The three unfertilized species and the fertilized ruzigrass led to greater net loss of soil-test exchangeable K, whereas the changes for fertilized maize and soybeans were statistically equivalent to that of the unfertilized control treatment (Figure 3A). The net change in soil-test, non-exchangeable K (ΔKne) over the three cycles was least in the fertilized soybean treatment, followed by the fertilized maize treatment. Unfertilized ruzigrass led to the greatest net loss of soil-test, non-exchangeable K (Figure 3B).

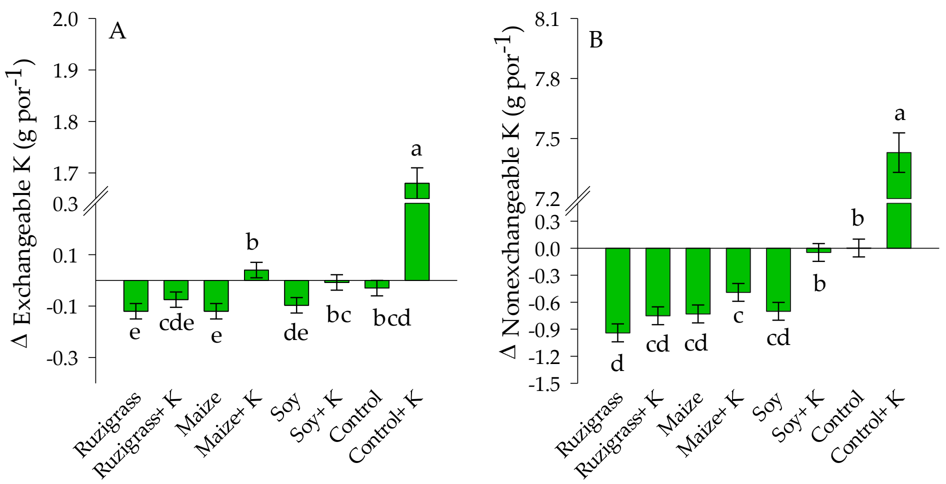

Figure 3. Net changes in soil-test, exchangeable K, ΔKe (**A**) and soil-test, non-exchangeable K, ΔKne (**B**) contents from before the first crop growth cycle to after the third crop growth cycle. The vertical bars represent standard error, and lowercase letters indicate difference among species (LSD, $p \leq 0.05$). Exchangeable K was extractable by a Na-saturated exchange resin, and non-exchangeable K is the difference between K extracted by boiling 1 M HNO_3 and exchangeable K.

In the first crop cycle all the unfertilized crops showed considerable uptake of non-exchangeable K (Figure 4A), but it decreased as the experiment progressed, following the decrease in total K uptake and dry matter yield (Figure 1A). In the first crop of fertilized maize, the uptake of non-exchangeable K was statistically equivalent to that of the unfertilized maize. The unfertilized maize and soybean took up more non-exchangeable K than did unfertilized ruzigrass only in the first cycle. From the first to the third cycle, the uptake of non-exchangeable K by unfertilized maize and soybean decreased around 80%, while non-exchangeable K uptake by unfertilized ruzigrass declined around 50% (Figure 4A).

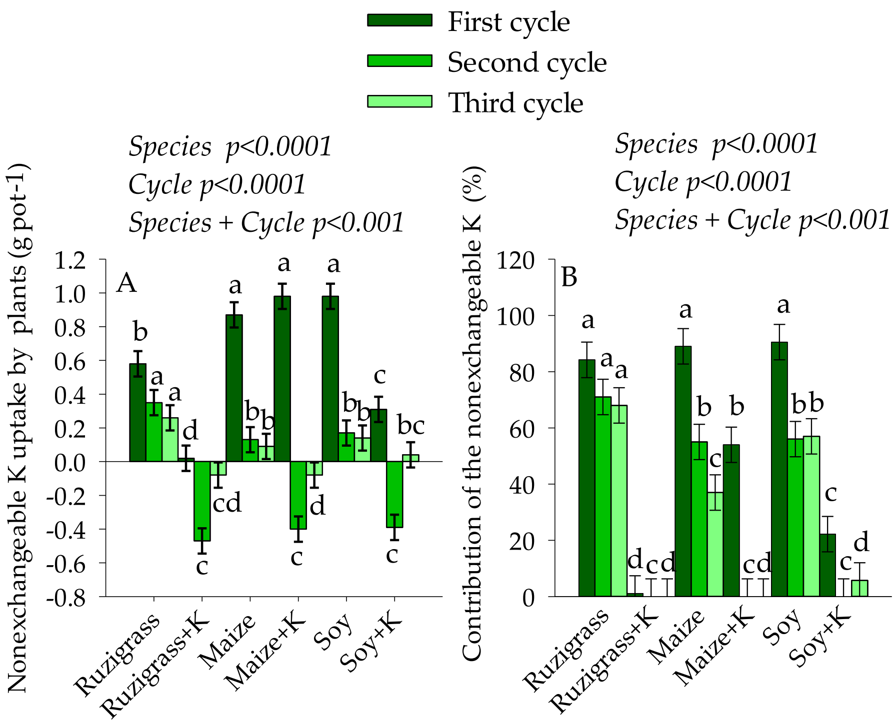

Figure 4. Nonexchangeable K uptake by plants (Kbal-neg) during each crop growth cycle (**A**), and the contribution of nonexchangeable K to total K uptake (**B**). Maize and soybean were grown for 90 days, and ruzigrass was grown for 45 days. The absence of overlap by vertical bars shows significant differences among the cycles, and lowercase letters indicate differences among species within given a fertility treatment and cycle (LSD, $p \leq 0.05$). Exchangeable K was extractable by a Na-saturated exchange resin, and non-exchangeable K is the difference between K extracted by boiling 1 M HNO_3 and exchangeable K.

Across all three species and crop cycles, the contribution of non-exchangeable K to the total uptake of K was greatest in the unfertilized treatments (Figure 4B). For soybeans and ruzigrass, the contribution of non-exchangeable K to plant demand decreased from the first to the second cycle, but there was no decrease from the second to the third cycle (Figure 4B). In contrast, there were successive decreases in the non-exchangeable contribution to uptake in each cycle of the unfertilized maize (Figure 4B).

3.2. Potassium Balance in the System

After three crop growth cycles without K application, the soil K balance was negative for all three species, and no difference was found between species. Conversely, when K was applied, a positive balance was always observed (Figure 5). The control + K treatment, where no crop was grown, showed the highest positive value. When maize and ruzigrass were fertilized, the balance was more positive than for fertilized soybean, which was similar to the unfertilized control.

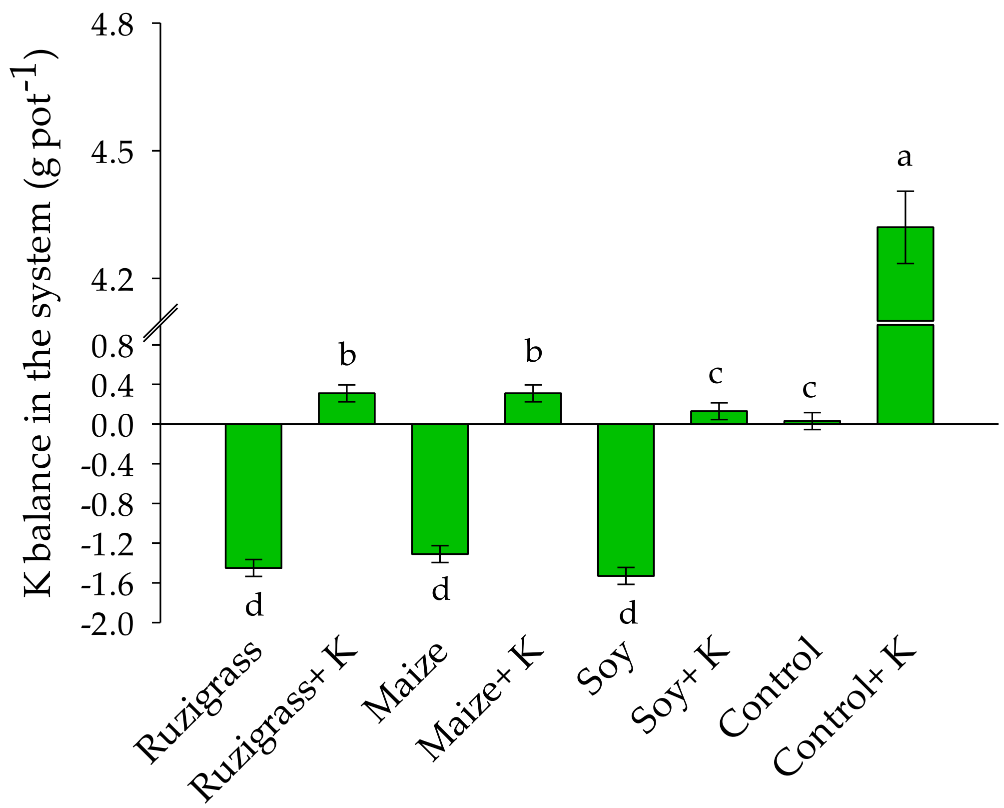

Figure 5. Potassium balance in the soil–plant system (($K_{bal} = K_{fert} - K_{abs} - \Delta Ke$) in relation to total K uptake after three crop growth cycles. Vertical bars represent standard error, and lowercase letters indicate difference between species (LSD, $p \leq 0.05$).

4. Discussion

In general, even when K fertilizer was applied, K uptake and DMY decreased as the experiment progressed, with the exceptions of the K uptake by maize and the DMY of ruzigrass (Figure 1B). Some studies have shown that successive monocropping, even with fertilizer application, can lead to a decrease in nutrient availability, including K, eventually compromising yields [42]. However, in this study, except for unfertilized pots, diagnostic leaf analysis did not reveal insufficient levels of any nutrient (data not shown) that could explain the decrease in dry matter production. Despite plant uptake of K from fractions that are less soluble than exchangeable K, uptake and removal of soil K over successive crop cycles can eventually lead to a decrease in K and dry matter production [43–45]. The use of ruzigrass to deplete soil exchangeable K was very effective (Figure 2A), as observed in previous studies [34]. Considering that exchangeable K had been significantly reduced before the first cropping cycle, it may be hypothesized that as plants extracted more native soil K with successive cycles, they had to scavenge for K that was bound more strongly to the soil minerals. For example, this K could be bound at interlayer sites near the edges of layer silicate minerals. It has been previously shown that K can be solubilized from minerals by the action of organic acids released in the plant rhizosphere, [17,46] found evidence of K deprivation decreasing the crystallinity of 2:1 phyllosilicates in a tropical soil. After depletion of this fraction the plants may have had more difficulty taking up non-exchangeable K from those interlayer or other structural positions where K is more tightly bound.

The responses of the three species to soil Ke and Kne depletion clearly demonstrated the differences in K usability among them and the importance of Kne for K supply in ruzigrass. Ruzigrass DMY responded to K application only in the third crop cycle and seemed not to be affected by the low exchangeable K levels in the first and second crop cycles

(Figures 1B and 2A). We infer that ruzigrass without added K was able to acquire K from soil pools less available than those utilized by soybean and maize [29,36,47]. The release of K from non-exchangeable pools by plants has been attributed to root exudates [48], but soil microbiota [49], including fungi [50], may also have a role. Soil K can be solubilized by a range of microbes such as *Acidithiobacillus*, *Agrobacterium*, *Arthrobacter*, *Aspergillus*, Bacillus, Burkholderia, Enterobacter Pantoea, Flectobacillus, Klebsiella, Microbacterium, Myroides, *Paenibacillus*, Pseudomonas, and Stenotrophomonas [51]. Several mechanisms of K solubilization have been reported so far, such as acidification, acidolysis, complexation, organic acids, auxins, siderophres, organic ligands, chelation, and exchange reactions [50,51]. Despite the increasing interest in K-solubilizing microbes, we could not find studies specifically with soybean or ruzigrass, and the plant species affects microbe colonization and efficiency [50,52]. Furthermore, in reports with a significant response to these microbes, the plants were inoculated, which was not the case in this experiment. Another uncertainty in assessing the actual importance of microbes in soil K solubilization is the survival of these microorganisms in unfavorable environments [50]. However, organic acid exudates may have had a considerable effect in the present experiment, since ruzigrass roots have been shown to release significant amounts of organic acids such as citrate, isocitrate, and oxalate [53]. Therefore, we infer that the ruzigrass DM yields without K fertilizer were, proportionally, less affected by successive crops than those of maize and soybean (Figure 1B) due to exudation of organic acids that promoted soil K release. Further, the contribution of non-exchangeable K to total K uptake by unfertilized ruzigrass was maintained over the three crop cycles, whereas it dropped for maize and soybean (Figure 4B).

Plant demand for K is an important driver of the uptake of non-exchangeable K [36,54]. Because the soil initially had low exchangeable K, i.e., below the minimal critical level [55], the unfertilized treatments had to rely on the release of non-exchangeable K to meet the demand in the first cropping cycle. Even when K fertilizer was applied, some non-exchangeable K may have been taken up, only to be replenished by added fertilizer K. The decrease in exchangeable K and the increase in soil non-exchangeable K between the second and third cycles of fertilized soybean may have been due to the conversion of exchangeable K to non-exchangeable K (Figure 2A,B). This suggests that not all exchangeable K was utilized by the plants, with conversion of the surplus to non-exchangeable K.

Recent works, to deplete the K fractions, show an increase in Ke through the application of K [42] which did not occur in our work, that even with the application of K, the Ke contents remained lesser the critical level. On the other hand, Kne decreases, over successive cultivations, by about 46% [42], our results also showed a decrease in this fraction even with K application (Figure 2).

Even after the three successive crops of maize and soybean cropping, K fertilization was sufficient to maintain soil-test Ke at levels similar to that of the control treatment with no fertilizer (Figure 3A). Over the entire experiment, ruzigrass depleted soil-test Ke, even with K fertilizer application. Furthermore, without K application, maize, and ruzigrass depleted soil-test Ke more than did soybean.

Depletion of Kne (negative ΔKne) was observed in all crop treatments except the fertilized soybean treatment (Figure 3B). Increased Kne was observed in the control + K treatment. The greatest depletion of Kne throughout the experiment was observed for the unfertilized treatments (Figure 3B).

In K-fertilized maize, which did not deplete Ke, Kne still decreased, perhaps due to the high K demand by maize. For fertilized soybean, however, the applied K was sufficient, and there was no need to use Kne. By contrast, ruzigrass depleted both soil Ke and Kne (Figure 3), even when fertilized with K, certainly due to its high cycling capacity [29]. Plants with more prolific root systems are more efficient in absorbing K from less soluble fractions, and root systems with a larger surface area, such as those of grasses [56], may exude organic anions into a larger volume of the soil [15,57] and thus remove more K from these fractions.

For maize and soybean, in the first cycle, there was a contribution of the soil non-exchangeable K fraction even with K application (Figure 4B). These crops showed higher DMY than ruzigrass (Figure 1A). High K demand of plants forces the use of non-exchangeable K [34,54], and maize and soybean have higher demand for K than does ruzigrass.

Although soil exchangeable K was low at the beginning of the experiment, the plants were able to take up K. Ruzigrass has been reported to have a higher capacity to acquire non-exchangeable K than maize or soybean [29]. Therefore, maize and soybean were able to access some of the K that is considered non-exchangeable according to routine chemical extractions, whereas ruzigrass root exudates may have been able to solubilize additional non-exchangeable K that was bound more tightly to soil minerals. We can speculate that most of the non-exchangeable K taken up initially came from the fraction with intermediate solubility and bound near layer silicate edges.

With the sequential application of K in the absence of plants (control + K), exchangeable K increased after the first application (first cycle), decreased in the second cycle, and increased again in the third cycle (Figure 2). Some of the K from the fertilizer applications was apparently converted to non-exchangeable K, which increased after each fertilization (Figure 2B). Conversion of applied K to non-exchangeable K is possible and may occur quickly [41,58]. This conversion may explain the decrease in exchangeable K (Figure 2A) and corresponding increase in non-exchangeable K between the first and second cycle of the K-amended control (Figure 2B). Increased non-exchangeable K after K application to soils without plants has been observed in tropical soils [4,41]. In soil with low exchangeable K, an equilibrium will be reached in the soil solution after K application, after which further K application may result in a linear increase in non-exchangeable K [59].

The uptake of non-exchangeable K was highest when K was not applied (Figure 4A). However, in the first cycle, even when K was applied, non-exchangeable K contributed considerably to the total K uptake of maize and soybean (Figure 4B). In that cycle, both dry matter production and K uptake were promoted by K fertilization, and they were higher for maize and soybean than for ruzigrass (Figure 1). Apparently, the high demand exceeded the supply of both added K and exchangeable K, leading to uptake of non-exchangeable K. As K is taken across root cell membranes, the rhizosphere becomes more acid due to the release of H+ by roots [1]. We speculate that K was released from non-exchangeable pools in response to this acidification.

The K balance in soil/plant systems depends on the different pools of soil K that plants may access as well as on the inputs, removals, and losses of K from the system. This balance will tend to be negative when K fertilizer is not applied and will be increasingly positive as the amount of applied K increases [42]. A negative balance implies that non-exchangeable K has been taken up, and a positive balance suggests that applied K has been converted to non-exchangeable K (including both K that is assessed in HNO_3- extraction as well as other forms of structural K). Non-exchangeable K may originate from trioctahedral phyllosilicates, such as biotite, or it may occur in hydroxy-interlayered vermiculite. While x-ray diffraction and thermal analysis studies of the soil in this study showed a predominance of kaolinite in the clay fraction (~65%), goethite, biotite, and vermiculite were also present (~15%, ~16%, and ~3%, respectively) [30]. Biotite is likely to have been a significant source of non-exchangeable K in this soil.

5. Conclusions

In a tropical kaolinitic soil with limited exchangeable K and in the absence of K fertilization, non-exchangeable K (HNO_3-extractable) contributed more than 80% of the K taken up by ruzigrass, maize, and soybean. Over three crop cycles, the proportion of total K taken up from non-exchangeable sources was greater for ruzigrass than for maize and soybean. The results of this study show that non-exchangeable K can be used by plants at the same time that the exchangeable K fraction is being used, therefore, soil nutrient pools determined by chemical extractions do not separate strictly into plant-available and plant-unavailable pools that are consistent for multiple plant species. This is an important point to be considered in developing K fertilizer recommendations for cropping systems where ruzigrass, maize, and soybean are included.

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