

Changes in potassium pools in Paraná soils under successive cropping and potassium fertilization

Alterações das formas de potássio em solos do Estado do Paraná submetidos à cultivos sucessivos e adubação potássica

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Abstract

The changes in soil potassium pools under intense cropping and fertilized with potash fertilizer are still little known to the soils of Paraná State. The effects of potassium fertilization and successive cropping on changes in K pools in different soils of Paraná, Brazil, were investigated in this study. Twelve soil samples, collected from the upper layer 0–0.20 m, were fertilized or not with K and subjected to six successive cropping (i.e., soybean, pearl millet, wheat, common beans, soybean and maize). All the crops were grown for 45 days, and at the end of the second, fourth and sixth cropping, the soil from each pot was sampled to determination of the total K, non-exchangeable K, exchangeable K and solution K. The result showed that the soil potassium pools varied widely. Total K concentration ranged from 547 to 15,563 mg kg⁻¹ (4,714 mg kg⁻¹, on average). On the average, structural K, non-exchangeable K, exchangeable K and solution K of the soils constituted 84.0, 11.3, 4.6 and 0.1% of the total K, respectively. Soils differ in the ability to supply potassium to the plants in the short to medium term, due to the wide range of parent material and the degree of soil weathering. When the soils were not fertilized with K, the successive cropping of plants resulted in a continuous process of depletion of non-exchangeable K and exchangeable K pools; however, this depletion was less pronounced in soils with higher potential buffer capacity of K. The concentrations of K non-exchangeable and exchangeable K were increased with the addition of potassium fertilizers, indicating the occurrence of K fixation in soil. After the second cropping, the soil exchangeable K levels remained constant with values of 141 and 36 mg kg⁻¹, respectively, with and without the addition of K fertilizer, reflecting in establishing of a new dynamic equilibrium of K in the soil.

Key words: Potassium availability, non-exchangeable K, exchangeable K, potassium supply power, intense cropping

Resumo

As alterações nas formas químicas de potássio (K) em solos cultivados e submetidos à fertilização potássica, ainda, são pouco conhecidas para os solos do Estado do Paraná. Neste estudo, os efeitos de cultivos sucessivos e da fertilização potássica nas alterações das formas de K foram estudados em solos com diferentes características físico-químicas do Estado do Paraná. Amostras de 12 solos coletadas da camada de 0–20 cm de profundidade, foram submetidas à adição ou não de fertilizante potássico e a seis cultivos sucessivos de plantas (soja, milheto, trigo, feijão, soja e milho). Em todos os cultivos as plantas foram cultivadas por um período de 40 dias. Após o segundo, quarto e sexto cultivo foram coletadas

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amostras de solos para a determinação dos teores de K total, K não-trocável, K trocável e K na solução. Os solos diferenciaram-se na capacidade de suprir K às plantas a curto e médio prazo. A absorção de K pelas plantas em cultivos sucessivos, sem a adição de fertilizante potássico, desencadeou um processo contínuo de exaustão de formas não-trocáveis e trocáveis de K no solo, sendo menos acentuada nos solos com maior poder tampão de potássio. Os teores de K não-trocável e K trocável aumentaram com a adição de fertilizantes potássicos, indicando fixação de K pelo solo. Após o segundo cultivo de plantas os teores de K trocável mantiveram-se constantes com valores médios de 141 mg kg^{-1} (com a adição de K) e 36 mg kg^{-1} (sem adição de K), expressando um novo equilíbrio dinâmico do K no solo.

Palavras-chave: Disponibilidade de potássio, K não-trocável, K trocável, poder tampão de potássio, cultivo intensivo

Introduction

Soil potassium (K) reserves constitute an important factor for crop yields. In general, most soils contain between 600 and 19,000 mg kg^{-1} of K, however, the major portion of these K (90 to 98%) is tied up as a structure component of primary and secondary minerals (structural K), and only 0.1 to 2% is readily available for use by plants (SPARKS, 2000). According to Sparks and Huang (1985), soil potassium includes the solution K, exchangeable K, non-exchangeable K and structural K, and these pools are in equilibrium, following a gradient in which its availability decreases. Understanding the mechanisms that involve release and fixation of K in soil is important because soils may contain widely variable pools of K that are potentially mobilized by chemical weathering of soil minerals (SIMONSSON et al., 2009).

In tropical soils, with predominance of low activity clay minerals as kaolinite and, iron and aluminum (hydr)oxides, the solution and exchangeable K are the most important pools of this nutrient in the soil and known as the readily available K pool to plants (SHAIKH et al., 2007). However, the available K pool is relatively low and corresponds to crop demand during only a few years of intense cropping and the release of K from non-exchangeable sources can contribute significantly to plant K nutrition in some soils in the short and medium term (SIMONSSON et al., 2007; STEINER et al., 2012; ROSOLEM et al., 2012). When solution and exchangeable K are reduced to low levels by plant uptake, non-exchangeable K can be released

from clay interlayers (BORTOLUZZI et al., 2005). Therefore, for sustainable crop production, the available K must be continually replenished through non-exchangeable and mineral K reserves.

For the appropriate management of K fertilization is important assess the availability of different soil K pools and their influences on K dynamic in the soil profile. This is because the insufficient fertilizer application may lead to depletion of the soil K reserves (SINGH et al., 2002; BORTOLUZZI et al., 2005; ROSOLEM et al., 2012; STEINER et al., 2012). On the other hand, the excessive fertilizer rates may result in low nutrient use efficiency (BALIGAR et al., 2001), as well as intensify K losses by erosion and leaching (ERNANI et al., 2007; WERLE et al., 2008; ROSOLEM et al., 2010). Soil K dynamic depends on type and quality of clay, soil texture, pH, soil cation exchange capacity (CEC), and the ratio of calcium (Ca^{+2}) + magnesium (Mg^{+2}) / K^{+} (ROSOLEM et al., 2010). These factors regulate the exchangeable/solution K ratio and K availability. Thus, the K availability depends of soil K pools and the amount of K stored in each pool (ROSOLEM et al., 1988).

The intense cropping of K-demanding crops and/or potash fertilizer application may affect the relation between soil K pools and its availability, leading to changes in clay mineral composition (VELDE; PECK, 2002; PERNES-DEBUYSER et al., 2003; BORTOLUZZI et al., 2005; ROSOLEM et al., 2012). Borkert et al. (1997) observed a marked decrease in soil exchangeable K concentration during successive years of soybean

crops and reported that it would be necessary to apply at least 80 kg ha⁻¹ yr⁻¹ of K₂O to maintain soil exchangeable K concentrations and avoid depletion of the soil K reserves. Rosolem et al. (1988) found that when the soil exchangeable K concentration is less than 60 mg kg⁻¹ there is release of K from non-exchangeable sources, and these sources would be responsible for the K nutrition of plants, and the maintenance of appropriate levels of soil K. In a sandy clay soil of southern Brazil, Brunetto et al. (2005) found that the soil non-exchangeable K concentration increased with the use of high rates of potash fertilizer and decreased in the lower rates or when there was no addition of fertilizers. Therefore, knowledge of the balance of soil K pools serves as support to understand the factors related to the supply of this nutrient to plants, contributing to the understanding of K dynamics in the soil.

This study was designed to investigate the effects of potassium fertilization and successive cropping on the changes of potassium pools in

different soils of Paraná, Brazil.

Material and Methods

Two pot experiments were carried out in a greenhouse at the West Paraná State University in Marechal Cândido Rondon, Paraná, Brazil (24° 31' S, 54° 01' W, and altitude of 420 m) to study the effect of K fertilization and successive cropping on the changes of different soil potassium pools.

Surface samples (0–0.20 m) from 12 non-cultivated soils were collected in areas under native vegetation or ancient reforestation in the State of Paraná, Brazil. The selection of sites for soil sampling was defined based in the different soil parent materials occurring in the State of Paraná (Table 1). Soils were classified according to the Brazilian System of Soil Classification (EMBRAPA, 2013) and Keys to Soil Taxonomy (SOIL SURVEY STAFF, 2010). Properties of the soils were determined by adopting standard procedures, and some characteristics are shown in Table 2.

Table 1. Classification, parent material and sampling site of the 12 soils used in the experiments.

Soil	Brazilian soil classification [†]	USDA soil taxonomy ^{††}	Parent material	Municipality
Ox1	Red Latosol	Rhodic Acrudox	Basalt ⁽¹⁾	Marechal Cândido Rondon
Ox2	Red Latosol	Rhodic Hapludox	Shale ⁽²⁾	Ponta Grossa
Ox3	Red-Yellow Latosol	Typic Hapludox	Caiuá sandstone ⁽³⁾	Umuarama
Ox4	Red-Yellow Latosol	Typic Hapludox	Furnas sandstone ⁽⁴⁾	Ponta Grossa
Alf1	Red Nitosol	Typic Hapludalf	Basalt ⁽¹⁾	Marechal Cândido Rondon
Alf2	Red Nitosol	Typic Hapludalf	Shale ⁽²⁾	Ponta Grossa
Alf3	Haplic Plinthosol	Typic Plinthaqualf	Shale ⁽²⁾	Ponta Grossa
Ult1	Red-Yellow Argisol	Arenic Hapludult	Caiuá sandstone ⁽³⁾	Umuarama
Ult2	Red-Yellow Argisol	Arenic Hapludult	Basalt ⁽¹⁾	Mercedes
Ent	Regolithic Neosol	Typic Usthorthent	Basalt ⁽¹⁾	Marechal Cândido Rondon
Ert	Haplic Gleysol	Typic Endoaquert	Alluvial sediments	Marechal Cândido Rondon
Ept	Haplic Cambisol	Typic Fragiudept	Furnas sandstone ⁽⁴⁾	Ponta Grossa

[†] Brazilian soil classification (EMBRAPA, 2013). ^{††} Approximate equivalence to USDA soil taxonomy (Soil Survey Staff, 2010).

⁽¹⁾ Basaltic lava flows. Between two consecutive lava flows, there is usually interbedded sedimentary material - sandstones and siltstones.

⁽²⁾ Shales and siltstones dark gray, very micaceous, laminated, with intercalated sandstones.

⁽³⁾ Continental sedimentary deposits predominantly of sandstone, quartz, feldspar, chalcedony and opaque.

⁽⁴⁾ White sandstones, micaceous, feldspathic, with kaolinitic matrix and cross bedding with conglomeratic levels.

Lime (CaO 25%, MgO 12% and EEC 96%) was applied before of the experiments to raise base saturation up to 70% for clayey soils, 50% for sandy soils and 60% for medium texture soils. The soils

were then moistened to reach 70% water retention capacity and incubated for 25 days. Afterwards, 7.5 kg subsamples of each soil were transferred to 8-L plastic pots with sealed bottoms.

Table 2. Some properties⁽¹⁾ of the soils used in the experiments.

Soil	pH	OM	P	K ⁺	Ca ²⁺	Mg ²⁺	Al ³⁺	CEC	V	K _s	PBC ^K
		g dm ⁻³	mg dm ⁻³	----- cmol _c dm ⁻³ -----					---- % ----		
Ox1	4.6	22.7	9.1	0.38	3.1	1.8	0.6	14.9	35	2.6	7.8
Ox2	3.8	21.3	2.2	0.18	2.6	0.6	0.8	14.1	25	1.3	3.5
Ox3	4.9	20.3	15.4	0.16	3.9	2.2	0.2	12.9	64	1.2	4.1
Ox4	4.2	29.4	13.1	0.16	3.0	1.0	0.4	13.1	31	1.2	4.7
Alf1	5.2	32.7	7.6	0.30	5.6	1.9	0.2	15.7	49	1.9	9.2
Alf2	3.9	31.8	9.8	0.21	2.3	0.6	1.1	16.1	19	1.3	5.8
Alf3	3.8	31.2	3.1	0.19	1.2	0.4	1.2	14.2	12	1.3	2.1
Ult1	5.2	9.1	20.3	0.15	2.1	0.4	0.2	6.4	43	2.3	1.3
Ult2	3.7	30.0	10.7	0.34	6.1	1.7	3.4	16.6	49	2.0	12.8
Ent	5.1	15.7	11.8	0.37	5.9	2.3	0.2	15.3	56	2.4	10.9
Ert	3.6	20.7	2.8	0.12	4.4	1.4	3.5	17.5	34	0.7	6.7
Ept	5.2	16.2	9.5	0.26	2.8	1.2	0.1	9.8	41	2.6	2.6

Soil	Soil particle size			BD	PD	θ _v	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	TiO ₂	Ki	Kr
	Sand	Silt	Clay									
	----- g kg ⁻¹ -----			kg dm ⁻³		----- g kg ⁻¹ -----						
Ox1	90	10	900	1.05	2.31	386	234	198	223	394	1.79	1.14
Ox2	90	125	785	0.94	2.33	262	101	97	264	101	0.65	0.53
Ox3	690	60	250	1.21	2.69	314	65	38	75	107	1.47	1.12
Ox4	675	10	315	1.30	2.68	206	41	33	109	44	0.64	0.54
Alf1	240	210	550	1.05	2.44	406	209	169	179	437	1.98	1.24
Alf2	80	140	780	0.92	2.42	450	117	78	220	114	0.90	0.74
Alf3	215	170	615	0.94	2.65	250	114	103	289	120	0.67	0.55
Ult1	895	20	85	1.52	2.69	204	18	24	28	67	1.11	0.71
Ult2	155	145	700	1.09	2.62	318	206	162	197	34	1.78	1.16
Ent	180	185	635	1.11	2.63	420	221	196	153	289	2.46	1.35
Ert	110	440	450	1.16	2.43	256	161	66	83	345	3.29	2.19
Ept	755	10	235	1.21	2.62	254	43	25	137	49	0.54	0.48

⁽¹⁾ pH in 0.01 mol L⁻¹ CaCl₂, soil:solution ratio (1:2.5). OM: Organic matter, Walkley-Black method. P and K were extracted by Mehlich-1 solution. Ca, Mg and Al were extracted by 1 mol L⁻¹ KCl solution. CEC: cationic exchange capacity was estimated by the summation method (CEC = Ca + Mg + K). V: soil base saturation. K_s: percent K saturation of soil. PBC^K: potential buffering capacity of K [in (mmol_c kg⁻¹)/(mmol L⁻¹)^{1/2}] determined as described by Mielniczuk (1978). Particle size analysis was performed by the pipette method (Embrapa, 1997). BD: bulk density measured by the graduated cylinder method (Embrapa, 1997). PD: Particle density (Embrapa, 1997). θ_v: soil volumetric moisture content at field capacity measured as described by Luchese et al. (2001). The Fe and Al contents, associated to the secondary minerals, were extracted with 9 mol L⁻¹ H₂SO₄ solution, and Si was removed with NaOH from the residue of the acid attack, and values expressed in the form of oxides (Embrapa, 1997). Ki: weathering index calculated by the molar ratio SiO₂/Al₂O₃. Kr: molar ratio SiO₂/Al₂O₃+Fe₂O₃.

In greenhouse conditions, the soils were subjected to six successive cropping of plants: (1st) soybean, (2nd) pearl millet (3rd) wheat, (4th) common beans, (5th) soybeans, and (6th) maize and two K fertilization levels [no fertilized or fertilized with potash fertilizer]. The treatments consisted of 12 soils and the addition (+K) or not (-K) of potassium fertilizer, arranged in a randomized block design in a factorial design with four replications. Potassium fertilization was performed with potassium chloride (KCl) in amounts equivalent to raise the percent K saturation up to 6%.

Before sowing of crops, the soils were fertilized with 80 mg kg⁻¹ of N as ammonium nitrate, 120 mg kg⁻¹ of P as simple superphosphate, 5 mg kg⁻¹ of S as calcium sulfate, 5 mg kg⁻¹ of Cu as copper sulfate, 5 mg kg⁻¹ of Zn zinc sulfate, 1 mg kg⁻¹ of Mo as ammonium molybdate and 2 mg kg⁻¹ of B as boric acid. At 15 and 30 days after plant emergence were also applied 40 mg kg⁻¹ of N as urea solution. Soil moisture was monitored daily and adjusted to 80% of the water retention capacity of soils.

All the crops were grown for 45 days, and at the end of the 2nd, 4th and 6th cropping, the soil from each pot was sampled, air-dried and ground to pass through a 2.0 mm mesh screen. Soil total K was determined via wet digestion with concentrated acid [hydrofluoric acid (HF), perchloric acid (HClO₄) and nitric acid (HNO₃)] as described by Embrapa (1997). Exchangeable K was extracted by the 1.0 mol L⁻¹ ammonium acetate solution (CH₃COONH₄) buffered to pH 7.0 (SANZONOWICZ; MIELNICZUK, 1985). Non-exchangeable K was obtained by the difference between amount of K extracted with boiling 1.0 mol L⁻¹ HNO₃ and K extracted with ammonium acetate solution (KNUDSEN et al., 1982). The amount of available K was extracted by Mehlich-1 (0.05 mol L⁻¹ HCl + 0.0125 mol L⁻¹ H₂SO₄; pH 1.2) as described by Tedesco et al. (1995). Solution K was obtained after equilibration with 1.0 mmol L⁻¹ SrCl₂ solution in a soil:solution ratio of 1:10 for 30 minutes as described by Mielniczuk (1978). In all

extracts, K concentration was measured by a flame photometer.

Data were subjected to analysis of variance (F-test, $p < 0.05$), and the effects of soil type and successive cropping were unfolded for the addition or not of potash fertilizer, and the means compared by Scott-Knott test at the 0.05 level of confidence. All analyses were performed using Sisvar 5.3 software for Windows (Statistical Analysis Software, UFLA, Lavras, MG, BRA).

Results and Discussion

Soil properties

The pH value of the soils after liming varied from 5.6 to 6.4, and soil base saturation varied from 55 to 74% (data not shown). Organic matter (OM) content was higher than 15 g kg⁻¹ for the majority of soils, except for the Arenic Hapludult (Ult1). The Typic Hapludalf (Alf1) had the highest contents of OM (32.7 g kg⁻¹). Most soils had high levels of readily available K (available K ≥ 0.15 cmol_c dm⁻³), except for the Typic Endoaquert (Ert) (Table 2). This explains the slight or no response to K fertilizer observed in most soils in the first soybean cultivation (data not shown). Rhodic Acrudox (Ox1), Rhodic Hapludox (Ox2), Typic Hapludalf (Alf1), Typic Hapludalf (Alf2), Typic Plinthaqualf (Alf3), Arenic Hapludult (Ult 2) and Typic Usthorthent (Ent) were clay texture (> 400 g kg⁻¹ of clay), while Typic Endoaquert (Ert) was silty clay (> 400 g kg⁻¹ of clay and > 400 kg⁻¹ of silt). On the other hand, the Typic Hapludox (Ox3), Typic Hapludox (Ox4) and Typic Fragiudept (Ept) were sandy clay loam (200-350 g kg⁻¹ of clay), and Arenic Hapludult (Ult1) was sandy (< 100 g kg⁻¹ of clay) (Table 2).

The potential buffer capacity of K (PBC^K), which measures the ability of the soil to maintain the intensity of K in the soil solution, varied from 1.3 to 12.8 (mmol_c kg⁻¹)/(mmol L⁻¹)^{1/2} (Table 2). High PBC^K values were observed in the Arenic

Hapludult (Ult2), Typic Usthorthent (Ent) and Typic Hapludalf (Alf1), while Arenic Hapludult (Ult1), Typic Plinthaqualf (Alf3) and Typic Fragiudept (Ept) were low (Table 2). A soil with a large PBC^K will have a greater capacity to maintain the activity of K in the soil solution. This indicated that soils of high PBC^K have enough K in reserve to replenish used K by crops while those of low PBC^K will only replace used K slowly. Thus, the release of K will be rapid and slow accordingly. It then implies that soils with high PBC^K will be able to maintain solution K intensity against plant depletion for longer periods of time while those of low values will have low capacity to maintain the activity of K in the solution and hence frequent fertilization.

Soil K pools

The soil potassium pools and the contribution of each pool for the total K varied with soil type and soil parent material (Table 3). Potassium supplying capacity to plants in the short and medium term had great variation between soils. The K supplying capacity is conceived to include K supplied from soil solution K, exchangeable K and non-exchangeable K pools. The order of abundance of the K pools in the soils is structural K > non-exchangeable K > exchangeable K > solution K (Table 3). Soil total K concentrations varied from 547 mg kg⁻¹ in the Arenic Hapludult (Ult1) to 15,563 mg kg⁻¹ in the Typic Hapludalf (Alf2) with mean value of 4,714 mg kg⁻¹. These total K concentrations are similar to those normally reported for Brazilian soils (SILVA et al., 1995; MELO et al., 2005; KAMINSKI et al., 2007). The soil structural K constitutes in mean 84.0% of the total K (66.4 to 96.9%), and varied from 368 to 15,083 mg kg⁻¹ (Table 3). The K containing mineral vary with the source of parent material and the degree of weathering (SIMONSSON et al., 2007). The soil exchangeable K varied slightly with mean value of 96 mg kg⁻¹ (49 to 151 mg kg⁻¹), it constitutes 4.6% of the total K (0.7 to 13.1%). These values were lower than the values for the non-

exchangeable K, which constitutes about 11.3% of the total K (2.4 to 24.5%), and varied from 134 to 539 mg kg⁻¹ (Table 3). These data indicate that short-term supply of K in some soils depends of the release of K from non-exchangeable sources. In soils of Minas Gerais, Cabbau et al. (2004) found that the exchangeable K and solution K were the pools that most contributed to the total K. This higher contribution of non-exchangeable pool to the total K observed in this study was due to no history of K fertilization of soils studied.

Soil total K

Soil total K concentration before and after the successive cropping of plants fertilized (+K) and not fertilized (-K) with K fertilizer are shown in Table 4. There was wide variation in the total K concentration of the soils, mainly due to the parent material and the degree of weathering. The lowest concentration of the total K in Rhodic Acrudox (Ox1) may be due to the high degree of weathering of this soil (weathering index (Ki) of 1.79) and the predominance of kaolinite and Fe and Al oxides as dominant clay minerals (Table 2). These clay minerals have small amounts of primary and secondary minerals containing K in its structure. Silva et al. (2000) also found lower total K concentration in soil with high degree of weathering and/or derived from basic rocks (basalt), which are poor in K feldspars and phyllosilicates. In a tropical soil of the Ceará State, Diniz et al. (2007) found that 95% of the clay fraction is constituted of kaolinite.

Soils have been referred to as young, mature, and old, depending on the degree of weathering. The young soils, even derived from basalt (in this case, Alf1 and Ent), may have high levels of total K (Table 4). Soil youth have higher mineral reserves of K due to the presence of significant amounts of mica and feldspar in the coarse soil fraction, which are important sources of K (SPARKS, 2000). According to these authors, the total K concentration in the basic rocks (basalt) can reach 7,000 mg kg⁻¹.

Table 3. Concentration of the soil potassium pools and contribution of different pools to the total K in the soils of Paraná State.

Soil	Total K	Structural K	mg kg ⁻¹			Solution K mg L ⁻¹
			Non-exchangeable K	Exchangeable K		
Ox1	1,153±65	771±51 (66.9) [†]	231±15 (20.0)	151±13 (13.1)	8.5±2	
Ox2	8,562±132	8,042±116 (93.9)	450±23 (5.2)	70±8 (0.8)	4.4±1	
Ox3	1,003±43	740±32 (73.8)	192±12 (19.1)	74±9 (7.4)	3.9±1	
Ox4	1,649±58	1,355±45 (82.2)	207±16 (12.6)	87±10 (5.3)	12.3±2	
Alf1	5,362±172	4,698±130 (87.6)	539±28 (10.0)	125±14 (2.3)	8.1±2	
Alf2	15,563±428	15,083±398 (96.9)	374±17 (2.4)	106±13 (0.7)	9.3±2	
Alf3	7,706±176	7,373±150 (95.7)	263±18 (3.6)	70±8 (0.9)	2.8±1	
Ult1	547±32	363±21 (66.4)	134±10 (24.5)	49±6 (8.9)	4.6±1	
Ult2	1,913±58	1,560±38 (81.5)	208±16 (10.9)	145±17 (7.6)	8.7±1	
Ent	6,982±212	6,272±182 (89.8)	567±26 (8.1)	147±14 (2.1)	10.8±2	
Ert	4,074±148	3,635±120 (89.2)	384±21 (9.4)	55±7 (1.4)	4.6±1	
Ept	2,050±87	1,730±64 (84.4)	211±12 (10.3)	109±12 (5.3)	9.4±2	

[†] Value between parentheses is the percentage contribution of each pool for soil total K.

The lowest concentration of soil total K (547 mg kg⁻¹) in Arenic Hapludult (Ult2) may be due to the sandy texture of the soil (Table 2). Melo et al. (2004) found that the coarse sand fraction has mineralogy composed mainly of quartz. Although some studies have shown the importance of the sand fraction as a reserve of this nutrient (DINIZ et al., 2007), the greater majority of soil K minerals are found in the clay fraction (MELO et al., 2005).

Higher total K concentration (Table 4) was observed in the soils (Ox2, Alf2 and Alf3) derived from the Ponta Grossa Formation sediments composed of very micaceous shale's (Table 1). The pellicic sedimentary rocks (shales) can contain up to 30,000 mg kg⁻¹ of K (SPARKS, 2000). These results are associated with the presence of mica as natural source of K in its structure. The mineral K reserves of the soil are found in the primary minerals such as mica and feldspar, and secondary minerals such as illite, vermiculite and interstratified clay minerals (SPARKS; HUANG,

1985). Silva et al. (2000) also found the highest values of total K in soils derived from pellicic rocks, which according to Melo et al. (2004) are materials relatively rich in K minerals.

In general, the soil total K concentration was little affected by successive cropping, regardless of the addition of K fertilizer (Table 4). This indicates that the structural K was not easily released to the plants during the six cropping of plants, confirming the results reported by Kaminski et al. (2007) in soils of southern Brazil. However, when the Rhodic Hapludox (Ox2) was not fertilized with K, the total K concentration of this soil at the end of the sixth cropping was reduced in 14% (Table 5). These data indicate that besides the non-exchangeable K, the structural K also contributed to supply of the nutrient to plants. In a clay tropical soil of Jaboticabal, São Paulo, Chiba et al. (2008) found that the addition of potassium fertilizer increased the total content of K in the soil profile after the second cycle of banana crop.

Table 4. Total K concentration in the soils of Paraná State before and after the successive cropping of plants fertilized (+K) and no-fertilized (-K) with K fertilizer.

Potassic fertilization	Soil	Initial	Successive cropping †						CV (%)
			1 st	2 nd	3 rd	4 th	5 th	6 th	
			----- mg kg ⁻¹ -----						
+K	Ox1	1,153 hA	–	1,155 hA	–	1,158 hA	–	1,164 hA	8.6
	Ox2	8,562 bA	–	8,592 bA	–	8,623 bA	–	8,685 bA	
	Ox3	1,003 hA	–	1,013 hA	–	1,023 hA	–	1,043 hA	
	Ox4	1,649 gA	–	1,649 gA	–	1,648 gA	–	1,648 gA	
	Alf1	5,362 eA	–	5,363 eA	–	5,365 eA	–	5,368 eA	
	Alf2	15,563 aA	–	15,621 aA	–	15,680 aA	–	15,797 aA	
	Alf3	7,706 cA	–	7,756 cA	–	7,806 cA	–	7,907 cA	
	Ult1	547 iA	–	554 iA	–	562 iA	–	577 iA	
	Ult2	1,913 gA	–	1,903 gA	–	1,893 gA	–	1,919 gA	
	Ent	6,982 dA	–	7,023 dA	–	7,063 dA	–	7,145 dA	
	Ert	4,074 fA	–	4,101 fA	–	4,127 fA	–	4,181 fA	
	Ept	2,050 gA	–	2,072 gA	–	2,094 gA	–	2,138 gA	
	Mean	4,714		4,734		4,754		4,798	
	-K	Ox1	1,153 hA	–	1,191 hA	–	1,129 hA	–	
Ox2		8,562 bA	–	8,006 bA	–	7,452 bB	–	7,341 bB	
Ox3		1,003 hA	–	973 hA	–	943 hA	–	922 hA	
Ox4		1,649 gA	–	1,584 gA	–	1,518 gA	–	1,386 eA	
Alf1		5,362 eA	–	5,171 eA	–	4,980 eA	–	4,898 eA	
Alf2		15,563 aA	–	15,147 aA	–	14,731 aA	–	14,599 aA	
Alf3		7,706 cA	–	7,639 cA	–	7,572 cA	–	7,437 bA	
Ult1		547 iA	–	520 iA	–	494 iA	–	441 iA	
Ult2		1,913 gA	–	1,833 gA	–	1,752 gA	–	1,692 gA	
Ent		6,982 dA	–	6,833 dA	–	6,684 dA	–	6,584 dA	
Ert		4,074 fA	–	4,056 fA	–	4,038 fA	–	4,003 fA	
Ept		2,050 gA	–	2,041 gA	–	2,032 gA	–	2,015 gA	
Mean		4,714		4,583		4,444		4,369	

† 1st: soybean, 2nd: pearl millet, 3rd: wheat, 4th: common bean, 5th: soybean and 6th: maize. Values represented by the different lower case letters in the column and upper case letters in the lines, show significant differences (Scott-Knott test, P < 0.05). (–) not determined.

Soil non-exchangeable K

Non-exchangeable K concentration in the soils were affected by successive cropping and potash fertilizer application (Table 5). The higher non-exchangeable K concentration in Typic Hapludalf (Alf1) and Typic Usthorthent (Ent) was due to higher levels of silt (Table 2) and total K (Table 3) of these soils. Soil young and with high levels of silt have also highest concentrations of non-exchangeable K,

and total K (VILLA et al., 2004). Diniz et al. (2007) verified that around 58-67% of non-exchangeable K of tropical soils were found in the silt fraction. Confirming the importance of silt fraction for the reserve of non-exchangeable K in agricultural soils.

When the soils were fertilized with K (+K), there was an increase in the non-exchangeable K concentrations in most soils with successive cropping (Table 5). The increase in the non-

exchangeable K concentration may be because the frequent application of potash fertilizers results in changes in soil K minerals (PERNES-DEBUYSER et al., 2003; BORTOLUZZI et al., 2005).

Table 5. Non-exchangeable K concentration in the soils of Paraná State before and after the successive cropping of plants fertilized (+K) and no-fertilized (-K) with K fertilizer.

Potassic fertilization	Soil	Initial	Successive cropping †						CV (%)
			1 st	2 nd	3 rd	4 th	5 th	6 th	
			----- mg kg ⁻¹ -----						
+K	Ox1	231 dB	–	274 dA	–	233 dB	–	301 dA	11.3
	Ox2	450 bA	–	425 cA	–	392 cB	–	360 dB	
	Ox3	192 dB	–	255 dA	–	250 dA	–	231 eA	
	Ox4	207 dB	–	284 dA	–	198 eB	–	214 eB	
	Alf1	539 aA	–	530 bA	–	507 bA	–	520 bA	
	Alf2	374 cB	–	639 aA	–	665 aA	–	640 aA	
	Alf3	263 dA	–	251 dA	–	208 dB	–	244 eA	
	Ult1	134 eA	–	145 eA	–	150 fA	–	168 fA	
	Ult2	208 dB	–	472 cA	–	482 bA	–	473 cA	
	Ent	567 aA	–	531 bA	–	536 bA	–	556 bA	
	Ert	384 cB	–	429 cB	–	499 bA	–	505 cA	
	Ept	211 dB	–	314 dA	–	313 cA	–	316 dA	
	Mean	314		379		370		377	
-K	Ox1	231 dA	–	188 cB	–	139 cC	–	92 cD	13.6
	Ox2	450 bA	–	280 bB	–	136 cC	–	96 cD	
	Ox3	192 dA	–	108 eB	–	106 dB	–	93 cB	
	Ox4	207 dA	–	148 dB	–	121 cC	–	101 cC	
	Alf1	539 aA	–	334 aB	–	261 aC	–	179 aD	
	Alf2	374 cA	–	264 bB	–	200 bC	–	136 bD	
	Alf3	263 dA	–	141 dA	–	97 dB	–	59 dC	
	Ult1	134 eA	–	98 eB	–	82 dB	–	50 dC	
	Ult2	208 dA	–	163 cB	–	135 cC	–	97 cD	
	Ent	567 aA	–	338 aB	–	192 bC	–	137 bD	
	Ert	384 cA	–	265 dB	–	126 cC	–	72 dD	
	Ept	211 dA	–	132 dB	–	113 dB	–	60 dC	
	Mean	314		205		142		98	

† 1st: soybean, 2nd: pearl millet, 3rd: wheat, 4th: common bean, 5th: soybean and 6th: maize. Values represented by the different lower case letters in the column and upper case letters in the lines, show significant differences (Scott-Knott test, $P < 0.05$). (–) not determined.

In a clay soil of the Jaboticabal, São Paulo, Chiba et al. (2008) found that the application of 900 kg ha⁻¹ yr⁻¹ of K₂O resulted in increased of the non-exchangeable K concentration of 40%. In a study conducted for 11 years in an Arenic

Hapludult of Santa Maria (RS), Bortoluzzi et al. (2005) found increased of non-exchangeable K with the addition of potassium fertilizers, reflecting in the increased of micaceous minerals (i.e., illite and illite-smectite interstratified clay), compared

to the soil without K fertilization.

Velde and Peck (2002) in experiment conducted in silt clay soil for 86 years in Illinois–USA found that crop rotation resulted in changes in soil mineralogy when compared to maize grown in succession. These authors observed changes in the proportion of illite layers in relation to the smectite interstratified mineral. The interstratified illite-smectite clay minerals showed up as a source when the soil solution was poor in K and as drain when the K availability was high. According to Pernes-Debuyser et al. (2003), the change of potassium minerals due to weathering process can be minimized with the addition of K fertilizers.

The intense cropping and/or potash fertilizer application may affect the soil K dynamic, leading to changes in clay mineral composition (VELDE; PECK, 2002; PERNES-DEBUYSER et al., 2003; BORTOLUZZI et al., 2005; ROSOLEM et al., 2012). Hinsinger and Jaillard (1993) observed the formation of vermiculite, in detriment of illite, in the rhizosphere soil of rye grass plants in only 32 days of grown. Under these conditions, the release of K from the illite layers, induced by the action of plant roots, was almost complete. Rosolem et al. (2012) showed that the K depletion in soil under intense cropping can occur in both exchangeable and non-exchangeable pools, even when frequent additions of K fertilizers are performed. In this study, similar results were observed only in the Ox2, where the non-exchangeable K concentration decreased from 450 mg kg⁻¹ (before cropping) to 360 mg kg⁻¹ (at the end of the sixth cropping), representing mean reduction of 20% (Table 5).

When the soils were not fertilized with K (–K), the non-exchangeable K concentration decreases in all the soils (Table 5), indicating that these non-exchangeable sources contributed to the supply of K to plants. Initial non-exchangeable K concentrations ranged from 134 to 567 mg kg⁻¹ (314 mg kg⁻¹, on average), and after the second cropping this concentrations decreased from 98 to 338 mg kg⁻¹

(205 mg kg⁻¹, on average), indicating mean reduction of 35%. After the fourth and sixth cropping, the non-exchangeable K ranged from 82 to 261 mg kg⁻¹ (142 mg kg⁻¹, on average) and from 50 to 179 mg kg⁻¹ (98 mg kg⁻¹, on average), representing a decrease from the initial mean of 55 and 69%, respectively. The depletion of soil non-exchangeable K pools with successive cropping, confirms the results reported by Kaminski et al. (2007), who found that the non-exchangeable K concentration at the end of the 5th cropping was reduced in up to 80% in the treatment without K fertilizer.

Fraga et al. (2009) showed that the K supply in the short term (1st cropping) was conditioned by the soil exchangeable K concentration, while in the course of successive cropping (2nd and 3rd cropping) this supply was obtained by the release of K from non-exchangeable sources. In fact, when solution K and exchangeable K are reduced to low levels by plant uptake, non-exchangeable K can be released from clay interlayers (BORTOLUZZI et al., 2005). Non-exchangeable K can be a source available to plants in the medium term. However, the release rate of K from non-exchangeable pool is influenced by particle size and chemical and mineralogical composition of the soil (MELO et al., 2005).

Soil exchangeable K

Soil exchangeable K concentration was affected by successive cropping and K fertilizer application (Table 6). As expected, the K application significantly increased exchangeable K concentration in most soils (Table 6). These increases, however, were dependents of soil type and initial exchangeable K concentration.

Initial exchangeable K concentrations ranged from 49 to 147 mg kg⁻¹ (96 mg kg⁻¹, on average), and after the second cropping these concentrations increased from 106 to 182 mg kg⁻¹ (136 mg kg⁻¹, on average), indicating mean increase of 42%. After the fourth and sixth cropping, the exchangeable K

concentration was constant, ranging from 102 to 168 mg kg⁻¹ (144 mg kg⁻¹, on average) and from 102 to 185 mg kg⁻¹ (143 mg kg⁻¹, on average), representing an increase from the initial mean of 50 and 49%, respectively. After the second cropping, the exchangeable K concentrations were stabilized around 140 mg kg⁻¹. Assuming that there is an equilibrium with non-exchangeable K, in this case,

may occur the specific adsorption process of K ion in the soil mineral phase, as reported by Velde and Peck (2002). This process, however, is limited to clay minerals that have the ability to receive K in its structure. These exchangeable K levels is determined by the ability of exchange sites in adsorb K ion, where its increase is only possible by the increase in the number of such sites.

Table 6. Exchangeable K concentration in the soils of Paraná State before and after the successive cropping of plants fertilized (+K) and no-fertilized (-K) with K fertilizer.

Potassic fertilization	Soil	Initial	Successive cropping [†]						CV
			1 st	2 nd	3 rd	4 th	5 th	6 th	
			----- mg kg ⁻¹ -----						(%)
+K	Ox1	111 cB	–	145 bA	–	147 bA	–	165 aA	9.7
	Ox2	70 dB	–	182 aA	–	168 aA	–	162 aA	
	Ox3	74 dB	–	106 cA	–	117 cA	–	131 bA	
	Ox4	87 dB	–	132 bA	–	102 cA	–	120 cA	
	Alf1	125 bB	–	123 cB	–	167 aA	–	179 aA	
	Alf2	106 cB	–	113 cB	–	145 bA	–	102 cB	
	Alf3	70 dB	–	163 aA	–	159 aA	–	155 bA	
	Ult1	49 eB	–	115 cA	–	125 cA	–	118 cA	
	Ult2	145 aB	–	161 aA	–	145 bB	–	137 bB	
	Ent	147 aB	–	141 bB	–	160 aA	–	145 bB	
	Ert	55 eC	–	135 bB	–	164 aA	–	185 aA	
	Ept	109 cB	–	116 cB	–	134 bA	–	121 cB	
	Mean	96			136		144		
-K	Ox1	111 cA	–	41 dB	–	34 cC	–	33 bC	9.0
	Ox2	70 dA	–	50 cB	–	32 cC	–	31 bC	
	Ox3	74 dA	–	38 dB	–	24 dC	–	26 cC	
	Ox4	87 dA	–	39 dB	–	27 cB	–	27 cB	
	Alf1	125 bA	–	86 aB	–	55 aC	–	52 aC	
	Alf2	106 cA	–	41 dB	–	33 cC	–	28 cC	
	Alf3	70 dA	–	24 fB	–	24 dB	–	20 dC	
	Ult1	49 eA	–	24 fB	–	18 dB	–	16 dB	
	Ult2	145 aA	–	66 bB	–	44 bC	–	48 aC	
	Ent	147 aA	–	87 aB	–	35 cC	–	34 bC	
	Ert	55 eA	–	37 dB	–	21 dC	–	20 dC	
	Ept	109 cA	–	31 eB	–	32 cB	–	26 cB	
	Mean	96			47		32		

[†] 1st: soybean, 2nd: pearl millet, 3rd: wheat, 4th: common bean, 5th: soybean and 6th: maize. Values represented by the different lower case letters in the column and upper case letters in the lines, show significant differences (Scott-Knott test, P < 0.05). (–) not determined.

When the soils were not fertilized with K (-K), the exchangeable K concentration decreases in all the soils (Table 6). Before of the cropping, the exchangeable K concentrations ranged from 49 to 147 mg kg⁻¹ (96 mg kg⁻¹, on average), and after the second cropping these concentrations decreased from 24 to 87 mg kg⁻¹ (47 mg kg⁻¹, on average), indicating mean reduction of 51%. After fourth and sixth cropping, the exchangeable K concentration was constant, ranging from 18 to 55 mg kg⁻¹ (32 mg kg⁻¹, on average) and from 16 to 52 mg kg⁻¹ (30 mg kg⁻¹, on average), representing a decrease from the initial mean of 67 and 69%, respectively (Table 6). The exchangeable K was stabilized with values around 30 mg kg⁻¹, indicating that it has reached a balance between pools of exchangeable K and non-exchangeable K with a minimum of K⁺ in the soil-plant system.

Bortoluzzi et al. (2005) reported similar results in an experiment conducted for 11 years in an Arenic Hapludult. These authors found that when the soil was not fertilized with K, the soil available reduced from 50 mg kg⁻¹ in the beginning of experiment to 38 mg kg⁻¹ in the first year, and 30 mg kg⁻¹ at the end of second year. On the other hand, when the soil was fertilized with K, the soil available K concentrations increased from 50 mg kg⁻¹ to 80 and 85 mg kg⁻¹, at the end of first and second year, respectively. After this period, the available K levels in both treatments remained constant around 30 and 90 mg kg⁻¹, respectively, with and without K fertilization. According to these authors, the maintenance of these levels for nearly a decade with intense cropping of K-demanding crops was only ensured by the release of K from weathering of K feldspars and phyllosilicates.

The highest exchangeable K concentrations observed in Typic Hapludalf (Alf1) (52 mg kg⁻¹) and Arenic Hapludult (Ult2) (48 mg kg⁻¹), especially without the addition of K fertilizer may be due to higher PBC^K and CEC of these soils (Table 2). A soil with a high PBC^K will have a greater capacity to maintain the activity of K in the soil solution. In

turn, the lower exchangeable K concentration (16 mg kg⁻¹) observed in Arenic Hapludult (Ult1) is due the lowest PBC^K and CEC of these soil.

In general, the exchangeable K concentration of 30 and 140 mg kg⁻¹ may be considered the upper and lower limits for the soil K balance in case of exhaustion and excess of K, respectively. According to Velde and Peck (2002), these limits are determined mainly by the mineralogy of soils. The results presented here for the exchangeable K and non-exchangeable K in the soil obtained without K fertilization (Tables 5 and 6) confirm the results reported by Rosolem et al. (1988), Bortoluzzi et al. (2005), Brunetto et al. (2005), Kaminski et al. (2007) and Rosolem et al. (2012). These authors showed that the non-exchangeable K pool can maintain or even enhance soil exchangeable K reserves in the long term. However, maintaining such a situation in the long term may decrease soil K reserves, compromising the movement of the nutrient into the soil solution and thus also the successful establishment and growth of crops. In long-term experiments conducted by Borkert et al. (1997) also observed a decrease in exchangeable K concentration in different soil types during successive years of soybean crop, and found that it would be necessary to apply at least 80 kg ha⁻¹ yr⁻¹ of K₂O to maintain soil exchangeable K concentrations and avoid depletion of the soil K reserves.

Soil solution K

As expected, the soil solution K concentration was affected by successive cropping and K fertilizer application (Table 7). The addition of K fertilizer (+ K) resulted in significant increases in solution K concentration for most soils (Table 7). These results were expected due to the balance of this pool with soil exchangeable K. Initial solution K concentration ranged from 2.8 to 12.3 mg L⁻¹ (7.3 mg L⁻¹, on average), and at the end of the second cropping these concentrations increased from 7.3 to 14.5 mg L⁻¹ (9.4 mg L⁻¹, on average), indicating

mean increase of 29%. After the fourth and sixth cropping, the K concentration was constant, ranging from 6.4 to 12.8 mg L⁻¹ (9.8 mg L⁻¹, on average) and from 6.6 to 11.7 mg L⁻¹ (9.6 mg L⁻¹, on average), representing an increase from the initial mean of 34 and 32%, respectively.

Table 7. Solution K concentration in the soils of Paraná State before and after the successive cropping of plants fertilized (+K) and no-fertilized (-K) with K fertilizer.

Potassic fertilization	Soil	Initial	Successive cropping †						CV
			1 st	2 nd	3 rd	4 th	5 th	6 th	
			----- mg L ⁻¹ -----						
+K	Ox1	8.5 cB	–	9.4 cA	–	9.7 bA	–	10.2 bA	15.5
	Ox2	4.4 dC	–	14.5 aA	–	12.2 aB	–	11.3 aB	
	Ox3	3.9 dB	–	9.8 cA	–	6.4 cB	–	6.6 dB	
	Ox4	12.3 aA	–	6.9 dB	–	9.4 bB	–	8.6 cB	
	Alf1	8.1 cA	–	9.6 cA	–	10.4 bA	–	9.2 cA	
	Alf2	9.3 cA	–	9.3 cA	–	6.9 cA	–	9.8 bA	
	Alf3	2.8 eC	–	5.8 eB	–	9.5 bA	–	8.9 cA	
	Ult1	4.6 dA	–	7.3 dA	–	6.7 cA	–	6.9 dA	
	Ult2	8.7 cB	–	10.4 cA	–	12.6 aA	–	10.4 bA	
	Ent	10.8 bB	–	11.6 bA	–	12.8 aA	–	10.8 bB	
	Ert	4.6 dB	–	10.4 cA	–	12.3 aA	–	11.7 aA	
	Ept	9.4 cA	–	10.2 cA	–	10.0 bA	–	10.5 bA	
	Mean	7.3		9.4		9.8		9.6	
-K	Ox1	8.5 dA	–	3.6 bB	–	2.2 aC	–	2.0 aC	8.5
	Ox2	4.4 eA	–	2.8 cB	–	2.0 aC	–	1.8 aC	
	Ox3	3.9 eA	–	1.8 dB	–	1.6 cB	–	1.5 bB	
	Ox4	12.3 aA	–	3.1 cB	–	1.5 cC	–	1.3 cC	
	Alf1	8.1 dA	–	2.9 cB	–	2.4 aC	–	2.2 aC	
	Alf2	9.3 cA	–	1.7 dB	–	1.6 cB	–	1.5 bB	
	Alf3	2.8 fA	–	1.1 eB	–	1.3 cB	–	1.0 cB	
	Ult1	4.6 eA	–	1.6 dB	–	0.9 dC	–	1.0 cC	
	Ult2	8.7 dA	–	4.4 aB	–	2.3 aC	–	1.6 bD	
	Ent	10.8 bA	–	4.2 aB	–	2.0 bC	–	1.9 aC	
	Ert	4.6 eA	–	2.0 dB	–	1.3 cC	–	1.0 cC	
	Ept	9.4 cA	–	2.0 dB	–	1.9 bB	–	1.9 aB	
	Mean	7.3		2.6		1.8		1.6	

† 1st: soybean, 2nd: pearl millet, 3rd: wheat, 4th: common bean, 5th: soybean and 6th: maize. Values represented by the different lower case letters in the column and upper case letters in the lines, show significant differences (Scott-Knott test, P < 0.05). (–) not determined.

When the soils were not fertilized with K (-K), the initial solution K concentrations ranged from 2.8 to 12.3 mg L⁻¹ (7.3 mg L⁻¹, on average), and at the end of the second cropping these values decreased from 1.1 to 4.4 mg L⁻¹ (2.6 mg kg⁻¹, on average), indicating mean reduction of 64%. After the fourth and sixth cropping, the solution K concentration was constant, ranging from 0.9 to

2.3 mg L⁻¹ (1.8 mg L⁻¹, on average) and from 1.0 to 2.2 mg L⁻¹ (1.6 mg L⁻¹, on average), representing a decrease from the initial mean of 75 and 78%, respectively. These results indicate that has reached a balance between pools of solution K and exchangeable K with a minimum of soluble K in the soil-plant system.

Conclusions

Soils differ in the ability to supply potassium to the plants in the short to medium term, due to the wide range of parent material and the degree of soil weathering.

When the soils were not fertilized with K, the successive cropping of plants resulted in a continuous process of depletion of non-exchangeable K and exchangeable K pools; however, this depletion was less pronounced in soils with higher potential buffer capacity of K.

The concentrations of K non-exchangeable and exchangeable K were increased with the addition of potassium fertilizers, indicating the occurrence of K fixation in soil.

After the second cropping, the soil exchangeable K levels remained constant with values of 141 and 36 mg kg⁻¹, respectively, with and without the addition of K fertilizer, reflecting in establishing of a new dynamic equilibrium of K in the soil.

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