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Contribution of non-exchangeable potassium forms and its accumulation in corn plants

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ABSTRACT

The state of Paraíba, Brazil, has soils from well- to poorly-developed, in which potassium (K) is found in different levels, forms and, consequently, with varying availability to plants. The objective of this study was to evaluate the contribution of non-exchangeable K forms to corn plants in 12 soils from Paraíba state, along four successive cycles. The experimental design was completely randomized block with three replicates and the 24 treatments consisted of the combination between two K levels (0 and 100 mg dm⁻³) and 12 soils. Before and after each cycle, subsamples of 0.2 dm³ were collected in each pot for the determination of non-exchangeable K (K_{ne}), exchangeable K (K_e) and soluble K (K_s). For each cycle, dry matter production, dry matter K content and plant K content (absorbed K) were determined. In the studied soils, the amounts of absorbed K after successive cycles were higher than the amounts of exchangeable K released, which shows the contribution of non-exchangeable K forms to corn nutrition.

Palavras-chave:

solos do Nordeste
mineralogia
formas de K
disponibilidade de K

Contribuição de formas não-trocáveis de potássio para seu acúmulo em plantas de milho

RESUMO

No estado da Paraíba ocorrem desde solos bem desenvolvidos até solos pouco desenvolvidos em que o potássio (K) é encontrado em diferentes teores, formas e, conseqüentemente, com disponibilidade variada para as plantas. Neste sentido se objetivou, com este trabalho, avaliar a contribuição das formas não trocáveis de K para plantas de milho em 12 solos do estado da Paraíba por meio de quatro cultivos sucessivos. O delineamento experimental utilizado foi o de blocos casualizados com três repetições e os 24 tratamentos consistiram da combinação de duas doses de K (0 e 100 mg dm⁻³) e 12 solos. Antes e após cada cultivo de milho foram retiradas, de cada vaso, subamostras de 0,2 dm³ para determinação dos teores de K não-trocável (K_{nt}), K trocável (K_t) e K solúvel (K_s). Para cada cultivo foram determinados a produção de matéria seca, o teor de K na matéria seca e o conteúdo de K na planta (K absorvido). Nos solos estudados as quantidades de K absorvido após os cultivos sucessivos foram maiores que as quantidades de K trocável liberadas o que evidencia contribuição de formas não trocáveis de K para a nutrição do milho.



INTRODUCTION

Potassium (K) is the second most required element by the majority of the cultivated plants; its absorption by plants triggers a continuous process of depletion of the different forms of K, which is more pronounced when the contents of available K are lower. The supply of K is buffered by its exchangeable and non-exchangeable forms, adsorbed with low and high binding energy in the exchange sites, respectively (Kaminski et al., 2007). Thus, the K of the structural forms of feldspars and micas and the K retained in the interlayers of some expandable 2:1 clay minerals are considered as non-exchangeable K forms that can act as a source of K to plants (Fraga et al., 2009).

In well-developed soils, the exchangeable K is the most important reserve of available K to plants, which justifies the determination of only this chemical form to evaluate its availability in these soils. Currently, it is estimated that there are more than 30 chemical extractors to evaluate the available K in the soil, and 1 mol L⁻¹ NH₄OAc at pH 7.0 is the standard extractor to evaluate the exchangeable K in the soil (Helmke & Sparks, 1996).

Extractors such as Mehlich-1 and mixed ion exchange resin only estimate the available K in the soil and are the most used in Brazil (Rajj et al., 2001); in the state of Paraíba, Mehlich-1 is the only K extractor used in routine analysis. However, all soils, to a greater or lesser degree, have K in forms that are non-exchangeable or not conventionally extracted to evaluate K availability, which contribute to the K nutrition of the cultivated plants (Werle et al., 2008).

Since the state of Paraíba has soils from well- to poorly-developed, with great variations in their chemical, physical and mineralogical characteristics (Brasil, 1972), it is essential to evaluate their capacity to supply K to plants, through its non-exchangeable forms. Therefore, this study aimed to evaluate the contribution of non-exchangeable K forms to corn plants in 12 soils of the state of Paraíba, Brazil, along four successive cycles.

MATERIAL AND METHODS

Samples from the layer of 0-30 cm of twelve soils from the state of Paraíba, Brazil, were used. The soils were classified

by Brasil (1972) and fit in the new classification proposed by EMBRAPA (2006) as Yellow Argisol (PA); Gray Argisol (PAC); Eutrophic Red Argisol (PVe); Red Yellow Argisol (PVA); Yellow Latosol (LA); Distrophic Red Argisol (PVd); Regolithic Neosol (RR); Litholic Neosol (RL); Haplic Luvisol (TX); Haplic Planosol (SX); Fluvic Neosol (RY); and Haplic Vertisol (VX). The samples were subjected to chemical, physical and mineralogical analysis (Tables 1 and 2) in the Laboratory of Soil and Rural Engineering, at the Center of Agricultural Sciences of the Federal University of Paraíba, according to the methodology described in Donagema et al. (2011).

The liming requirement of the soils was calculated through the methods of Al³⁺ neutralization and increase in the contents of Ca²⁺ and Mg²⁺, and through the base saturation method (Alvarez V. & Ribeiro, 1999), according to Farias et al. (2009a).

After correcting the acidity of all the soils, two doses of K were applied (0 and 100 mg dm⁻³) in the form of KCl (A.R. grade) in solution and the soils were incubated for 21 days. These two incubation periods were performed with soil samples (3.2 dm³) inside plastic pots in a greenhouse. After each incubation period, the samples of all the soils were air-dried, pounded to break up clods, sieved through a 4-mm screen and placed back into the pots.

Immediately after the incubation period of K doses with the soils and before corn planting, a soil sample of 0.2 dm³ was collected in each pot for the determination of the contents of exchangeable K; soluble K, extracted with distilled water and non-exchangeable K, which was estimated by subtracting the content of exchangeable K, extracted with 1 mol L⁻¹ NH₄OAc at pH 7.0, from the content of K in the soil, extracted with boiling 1 mol L⁻¹ HNO₃ (Helmke & Sparks, 1996). For each soil and all extractors, the soil K contents in mg kg⁻¹ were multiplied by soil density in order to obtain the results in mg dm⁻³.

The remaining volume of soil (3.0 dm³) received a fertilization with macro and micronutrients, except K, according to Farias et al. (2009b). After fertilization, the soil samples were placed back into the pots and moistened with an amount of distilled water corresponding to 50% of soil total porosity.

Immediately after the fertilization with macro and micronutrients, the 2C577 hybrid corn cultivar was planted.

Table 1. Chemical characteristics of 12 soils representative of the state of Paraíba, Brazil⁽¹⁾

Soil ⁽²⁾	pH (H ₂ O)	OC dag kg ⁻¹	P mg dm ⁻³	P-rem ⁽⁵⁾ mg L ⁻¹	K ⁺ exch. ⁽³⁾	K ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	Al ³⁺	(H+Al)	CEC pH 7.0
More-developed Soils ⁽⁴⁾												
PA	5.9	0.35	1.52	45	0.064	0.04	0.60	0.40	0.02	0.11	1.68	2.74
PAC	4.4	1.07	3.59	47	0.109	0.10	0.80	0.60	0.05	0.96	5.67	7.20
PVe	6.3	0.90	6.80	35	0.609	0.39	5.40	1.80	0.04	0.00	2.75	10.38
PVA	5.5	1.07	2.63	28	0.280	0.24	1.10	1.30	0.04	0.32	5.50	8.18
LA	5.9	0.59	11.42	44	0.236	0.18	1.60	1.15	0.11	0.00	2.14	5.18
PVd	5.0	0.80	2.32	28	0.245	0.19	1.90	0.80	0.04	0.32	4.28	7.20
Less-developed Soils ⁽⁴⁾												
RR	7.0	0.34	24.10	54	0.214	0.18	1.80	0.90	0.02	0.00	1.07	3.97
RL	6.2	0.38	4.31	45	0.286	0.19	2.00	1.10	0.25	0.05	2.29	5.83
TX	6.2	0.76	4.35	41	1.045	0.64	6.10	4.00	0.10	0.00	2.90	13.74
SX	7.2	0.43	21.58	37	0.257	0.21	12.20	5.60	0.30	0.00	1.53	19.84
RY	7.3	0.89	144.30	44	0.779	0.60	11.00	4.00	0.09	0.00	1.22	16.91
VX	8.4	0.37	19.77	25	1.683	0.69	29.10	10.40	2.19	0.00	0.76	43.13

⁽¹⁾Analysis performed according to the methodologies described in Donagema et al. (2011); ⁽²⁾ EMBRAPA (2006): PA - Yellow Argisol; PAC - Gray Argisol; PVe - Eutrophic Red Argisol; PVA - Red Yellow Argisol; LA - Yellow Latosol; PVd - Distrophic Red Argisol; RR - Regolithic Neosol; RL - Litholic Neosol; TX - Haplic Luvisol; SX - Haplic Planosol; RY - Fluvic Neosol; VX - Haplic Vertisol; OC - Organic carbon. ⁽³⁾Medeiros et al. (2014); ⁽⁴⁾More-developed soils: Ki ≤ 2.46; Less-developed soils: Ki ≥ 2.46; ⁽⁵⁾Alvarez V. et al. (2000)

Table 2. Soil class, geological formation and lithology⁽²⁾, textural analysis⁽³⁾ and sampling location of soils representative of the state of Paraíba, Brazil

Soil ⁽¹⁾	Sampling municipality	Geological formation and lithology ⁽²⁾	Rainfall mm	Soil density kg dm ⁻³	Texture			Minerals ⁽⁴⁾	Ki ⁽²⁾
					Sand	Silt	Clay		
More-developed soils ⁽⁵⁾									
PA	Jacumã	Tertiary/ Sediments from the Barreiras Group.	1500	1.47	88	3	9	Kt, Gb, Gt	1.72
PAC	Mamanguape	Tertiary/ Sediments from the Barreiras Group.	1600	1.48	84	4	12	Kt, Gt	1.92
PVe	Marizópolis	Metasomatic granite	600	1.44	58	24	18	Kt, Gt, Mi, (2:1)	2.11
PVA	Areia	Precambrian (CD)/ Biotite-gneiss.	900	1.36	66	11	23	Kt, Gt	2.46
LA	Cuité	Tertiary/ Sediments from the Serra do Martins Series.	600	1.35	65	6	29	Kt, Gt	2.16
PVd	Alagoa Grande	Precambrian (CD)/ Hornblende-biotite-gneiss.	1200	1.28	49	13	38	Kt, Gt, Mi, Hm	2.25
Less-developed soils ⁽⁵⁾									
RR	Esperança	Migmatite ("embrechito facoidal").	800	1.67	89	8	3	Kt, Mi, Qz, (2:1)	2.17
RL	Pocinhos	Precambrian (CD)/ Gneiss.	650	1.54	81	11	8	Mi, Kt, (2:1)	2.93
TX	São Miguel de Taipu	Precambrian (CD)/ Hornblende-gneiss.	700	1.42	67	19	14	Kt, Mi, (2:1), Fp	3.42
SX	Cuité	Precambrian (CD)/ Gneiss with Biotite and Hornblende.	600	1.43	64	17	19	(2:1), Mi, Kt, Gt	4.21
RY	Sousa	Precambrian / Sandstone and shale.	700	1.34	45	35	20	Mi, Kt, (2:1)	3.20
VX	Sousa	Cretaceous/ Sediments from Rio do Peixe Series.	700	1.29	22	35	43	(2:1), Qz, Mi	4.52

⁽¹⁾PA - Yellow Argisol; PAC - Gray Argisol; PVE - Eutrophic Red Argisol; PVA - Red Yellow Argisol; LA - Yellow Latosol; PVd - Dystrophic Red Argisol; RR - Regolithic Neosol; RL - Litholic Neosol; TX - Haplic Luvisol; SX - Haplic Planosol; RY - Fluvic Neosol; VX - Haplic Vertisol. ⁽²⁾Brasil (1972); ⁽³⁾Donagema et al. (2011); ⁽⁴⁾Kt - kaolinite; Gb - Gibbsite; Gt - Goethite; Mi - Mica; (2:1): 2:1 mineral; Hm: hematite; Qz: quartz; Fp: feldspar; Minerals are shown in the order of predominance in the soil; ⁽⁵⁾ More-developed soils: Ki ≤ 2.46 (Except RR); Less-developed soils: Ki ≥ 2.46.

Thirty days after sowing, the shoots of the plants in each pot were cut at a height of 1 cm from the soil and then subjected to a pre-drying in a greenhouse. The roots were removed from the pots and the soil adhered to them was initially separated with tap running water and then using distilled water through a quick wash.

After plant harvest at the end of the first cycle, a soil subsample of 0.1 dm³ was collected from each one of the 72 pots for the determination of the contents of soluble K, exchangeable K and non-exchangeable K. The remaining volume of soil was placed back into the pot for the next three cycles, as done for the first cycle, from sowing to harvest and not allowing the occurrence of deficiency of other nutrients to plants.

After pre-drying, the material was placed in perforated paper bags and dried in a forced-air oven at 70 °C, until constant weight. Shoot and root dry matters were mixed, ground in a Wiley-type mill and mineralized through sulfuric digestion, and K was determined in the extracts through flame photometry (Tedesco et al., 1995).

From the values of dry matter production, obtained through the weighing of the plants in each pot, and K contents in the dry matter, the total contents of K in the dry matter were calculated. The amounts of K extracted from the soil by plants were calculated by dividing the total contents of K in the dry matter by the soil volume of each pot and were expressed in the same unity (mg dm⁻³) used for the extractors.

The amounts of K_{ne} and K_e released after four successive cycles were obtained by the difference between the initial value of these K forms and the value obtained after the last cycle. Both forms were added and the percentages in relation to the K absorbed by plants were calculated.

Soil fertilization for the other cycles was performed according to Farias et al. (2009b) and consisted of two applications of N in the form of commercial urea (60 and 70 mg dm⁻³). Along with this last N application, 32.98 mg dm⁻³ of S [(NH₄)₂SO₄], 40 mg dm⁻³ of Ca (CaCl₂·2H₂O), 72.5 mg dm⁻³ of Mg (MgSO₄·7H₂O) and 50 mg dm⁻³ of P (NH₄H₂PO₄) were applied.

In the third cycle, 87.5 mg dm⁻³ of P were applied in the soils PA, LA, PVE, TX, RY, RL and SX, 75 mg dm⁻³ of P were applied in PAC and RL, and 102.5 mg dm⁻³ of P were applied in PVd, PVA and VX. In addition, all soils received 30 mg dm⁻³ of S [(NH₄)₂SO₄] and 0.2 mg dm⁻³ of B(H₃BO₃), 2 mg dm⁻³ of Fe (FeCl₃·6H₂O), 1 mg dm⁻³ of Cu (CuSO₄·5H₂O), 2 mg dm⁻³ of Mn (MnCl₂·4H₂O) and 2 mg dm⁻³ of Zn (ZnSO₄·7H₂O). This fertilization was performed only once, at sowing.

In the fourth planting, three N doses (commercial urea) were applied from the 7th day after planting on, consisting of one application of 60 mg dm⁻³ and the others of 50 mg dm⁻³ each. Along with the first N application, 50 mg dm⁻³ of P (NH₄H₂PO₄), 60 mg dm⁻³ of Ca (CaCl₂·2H₂O), 20 mg dm⁻³ of Mg and 28 mg dm⁻³ of S (MgSO₄·7H₂O) were also applied.

These fertilizations were used based on expertise and the identification of possible symptoms of nutritional deficiency. After each cycle, the procedures of harvest and preparation of the material for the analysis of plant K contents were repeated.

The statistical analysis consisted of analysis of variance, regression and correlation.

RESULTS AND DISCUSSION

Mean values of dry matter, plant K content and absorbed K decreased along the successive cycles (Table 3). Dry matter

Table 3. Dry matter production[#], plant K content and absorbed K in the four successive corn cycles, as a function of the K doses added to more- and less-developed soils of the state of Paraíba, Brazil

Soil ⁽¹⁾	Dose	Dry matter (g pot ⁻¹)					Plant K content (g kg ⁻¹)					Mean	Absorbed K (mg dm ⁻³)				
		Cycles				Total	Cycles				Total		Cycles				Total
		1 ^o	2 ^o	3 ^o	4 ^o		1 ^o	2 ^o	3 ^o	4 ^o			1 ^o	2 ^o	3 ^o	4 ^o	
More-developed soils																	
PA	0	4.6 b	2.2	0.7	-(²)	7.3	6.7 b	6.0	3.4	-(³)	4.0	10.2 b	4.7	0.8	-(³)	15.7	
	100	25.4 a	3.6	0.9	-	30.0	11.4 a	8.0	3.1	-	5.6	96.5 a	10.0	1.0	-	107.5	
PAC	0	9.5 b	1.4	0.6	-	11.8	9.7 b	7.1	4.1	-	5.2	30.7 b	3.5	0.9	-	35.1	
	100	17.6 a	3.2	1.0	-	22.3	19.9 a	9.1	4.1	-	8.3	112.7 a	10.3	1.5	-	124.5	
PVe	0	32.4 a	17.3	5.8	5.7	70.3	12.5 b	4.4	7.3	4.4	7.2	134.3 b	26.2	14.9	9.3	184.7	
	100	28.9 a	22.0	7.4	6.3	76.7	20.6 a	6.3	7.4	3.8	9.5	198.5 a	47.3	19.5	8.6	273.8	
PVA	0	27.4 a	3.3	1.2	0.5	33.9	8.4 b	7.7	6.5	-	5.6	76.7 b	8.7	2.7	-	88.0	
	100	28.8 a	7.7	1.2	0.7	39.8	15.2 a	5.6	5.7	-	6.6	145.1 a	14.7	2.6	-	162.3	
LA	0	25.3 a	4.8	1.3	0.9	33.2	8.0 b	6.0	4.9	-	4.7	66.5 b	9.7	2.2	-	78.4	
	100	28.6 a	9.4	2.6	1.5	45.8	14.3 a	5.1	6.9	-	6.6	136.4 a	15.9	6.3	-	158.5	
PVd	0	24.5 b	5.5	0.7	0.8	32.3	7.3 b	7.4	6.2	-	5.2	59.5 b	14.1	1.5	-	75.2	
	100	30.5 a	8.1	1.5	1.3	42.9	13.4 a	7.3	5.8	-	6.6	135.3 a	20.4	3.0	-	158.7	
Less-developed soils																	
RR	0	17.1 b	10.3	2.2	1.4	31.0	9.5 b	4.7	6.2	4.5	6.2	54.2 b	16.5	4.9	2.3	77.8	
	100	28.5 a	11.8	3.1	1.9	45.3	15.5 a	4.6	5.2	6.8	8.0	146.8 a	18.5	5.7	4.6	175.6	
RL	0	28.2 a	17.5	6.1	3.3	55.1	7.9 b	4.8	6.5	6.3	6.4	74.5 b	29.1	14.3	7.5	125.4	
	100	31.2 a	17.5	6.1	3.3	58.1	13.9 a	6.0	7.0	6.1	8.2	144.6 a	35.9	15.2	7.3	203.0	
TX	0	28.8 a	22.6	14.3	7.9	73.6	24.3 b	9.5	7.4	5.0	11.5	230.4 b	73.2	37.9	14.6	356.2	
	100	29.3 a	23.5	15.4	9.6	77.8	29.3 a	11.0	7.0	5.2	13.1	284.8 a	89.3	38.5	18.5	431.1	
SX	0	18.8 a	17.4	12.3	11.9	60.4	9.7 a	7.2	6.7	4.4	7.0	60.9 a	43.3	29.3	19.5	153.0	
	100	20.8 a	17.9	14.1	15.3	68.1	9.7 a	8.5	7.5	4.7	7.6	66.9 a	52.3	37.9	26.6	183.7	
RY	0	29.2 a	23.5	18.3	30.4	101.4	28.8 b	21.6	14.6	12.1	19.3	280.3 b	174.4	95.7	134.1	684.4	
	100	29.2 a	23.0	18.3	30.5	101.0	33.1 a	24.1	20.3	14.0	22.9	321.5 a	189.4	132.4	158.1	801.3	
VX	0	19.4 a	11.9	14.6	24.1	70.0	33.7 b	29.8	23.2	14.0	25.2	217.9 a	123.0	121.4	127.0	589.3	
	100	19.0 a	13.5	15.1	23.7	71.3	36.6 a	30.3	25.2	12.6	26.2	232.1 a	140.7	135.9	111.3	619.9	

⁽¹⁾ PA - Yellow Argisol; PAC - Gray Argisol; PVe - Eutrophic Red Argisol; PVA - Red Yellow Argisol; LA - Yellow Latosol; PVd - Dystrophic Red Argisol; RR - Regolithic Neosol; RL - Litholic Neosol; TX - Haplic Luvisol; SX - Haplic Planosol; RY - Fluvic Neosol; VX - Haplic Vertisol. ⁽²⁾ Dry matter was not evaluated because plants died a few days after germination. ⁽³⁾ Parameters not determined due to the lack of little amount of dry matter for the chemical analysis.

[#] Means followed by the same letter do not differ at 0.05 probability level by F test

production in the first cycle was similar between the two soil groups, with mean of 23.6 g pot⁻¹ for the more-developed soils and 24.9 g pot⁻¹ for the less-developed soils.

From the second cycle on, the difference between the two soil groups became more evident and the dry matter production in less-developed soils (17.5 g pot⁻¹) was 2.4 times higher than that observed in more-developed soils (7.4 g pot⁻¹). In the third cycle, in which corn cultivation was still possible in all the soils, the dry matter production in less-developed soils was, on average, 5.6 times higher than in more-developed soils (Table 3).

In the fourth cycle, plants cultivated in the soils PA and PAC died a few days after emergence and, in PVA, LA, PVd, RR and RL, plants showed very limited growth (Table 3) and severe symptoms of K deficiency in the leaves. The soils SX, RY and VX, which have the highest contents of clay and K-source minerals (Tables 1 and 2), were the ones with not much variation in dry matter production along the corn cycles and with the highest dry matter productions in the fourth cycle (Table 3). This shows that less-developed soils with higher proportion of mica and 2:1 silicate clays, especially the most clayey ones, are the soils with the highest capacity to supply K to plants in medium and long term. Data of Santos et al. (2013) indicate that these soils show higher K buffering capacity (KBC), which favors the maintenance of K more or less constant in the soil solution for long periods. In addition, the silt fraction in the soil can also be a great source of non-exchangeable K (Silva et al., 2008).

K fertilization increased plant K contents during the first cycle, especially in more-developed soils and in the

less-developed ones with higher sand contents (RR and RL). However, this effect only reflected in a considerable increase of corn dry matter production in the soils PA, PAC and RR (Table 3), which are the ones with the highest sand contents and the lowest Ke contents (Table 1). This beneficial effect of the K dose on plant growth was virtually limited to the first cycle (Table 3), evidencing the need to replenish the K exported by the harvests after each cycle in these soils. Soils with low KBC, such as PA, PAC, RR and RL, require split and frequent K fertilizations to maintain soil fertility (Santos et al., 2013).

The dry matter production of plants cultivated in more-developed soils did not correlate (second, third and fourth cycles) or showed low correlation (first cycle) with Ks contents (Table 4), but showed good correlation with Kne contents and especially with Ke contents.

In the more-developed soils, the correlation between Kne content and dry matter production was low in the first cycle, but it was high in the subsequent ones, possibly due to the contribution of Kne to plant nutrition and growth, which is directly proportional to the depletion of soil Ke. Therefore, the non-exchangeable K constituted a reserve of K supplied to plants, thus guaranteeing their nutrition especially in more-developed soils, as observed by Alves et al. (2013) and Rosolem et al. (2012). Similar behavior was observed in the absorbed K. It should be pointed out that the contribution of soluble K, from the second cycle on, was not significant in more-developed soils, but was significant until the third cycle in the less-developed ones.

The amounts of Kne and Ke released and absorbed by corn plants after four successive cycles are shown in Table 5. In

Table 4. Coefficients of single linear correlation between the variables non-exchangeable K content (Kne), exchangeable K content (Ke) soluble K content (Ks), dry matter and absorbed K content

Variable	Dry matter			Absorbed K		
	MDS ⁽¹⁾	LDS ⁽²⁾	ALL ⁽³⁾	MDS ⁽¹⁾	LDS ⁽²⁾	ALL ⁽³⁾
First cycle						
Kne	0.59*	-0.16 ^{ns}	0.08 ^{ns}	0.67**	0.24 ^{ns}	0.49**
Ke	0.74**	-0.08 ^{ns}	0.26 ^{ns}	0.98**	0.71**	0.81**
Ks	0.60*	0.63**	0.58**	0.92**	0.62**	0.57**
Second cycle						
Kne	0.88**	0.50*	0.69**	0.84**	0.64**	0.79**
Ke	0.99**	-0.21 ^{ns}	0.32 ^{ns}	0.97**	0.59*	0.71**
Ks	0.03 ^{ns}	0.72**	0.31 ^{ns}	0.05 ^{ns}	0.58*	0.42*
Third cycle						
Kne	0.85**	0.77*	0.88**	0.87**	0.57*	0.74**
Ke	0.92**	0.48*	0.64**	0.92**	0.82**	0.87**
Ks	-0.33 ^{ns}	0.53*	0.47**	-0.33 ^{ns}	0.35 ^{ns}	0.40*
Fourth cycle						
Kne	0.90**	0.81**	0.89**	0.89**	0.64**	0.76**
Ke	0.93**	0.60*	0.70 ^{ns}	0.91**	0.66**	0.74**
Ks	-0.60 ^{ns}	-0.01 ^{ns}	-0.16 ^{ns}	-0.49 ^{ns}	0.16 ^{ns}	0.01 ^{ns}
All the cycles						
Kne	0.41**	0.43**	0.49**	0.37**	0.38**	0.52**
Ke	0.90**	0.39**	0.58**	0.98**	0.74**	0.82**
Ks	0.80**	0.56**	0.62**	0.95**	0.70**	0.68**

⁽¹⁾MDS - More-developed soils (n = 12 for each cycle individually and n = 48 for all the cycles); ⁽²⁾LDS - Less-developed soils (n = 12 for each cycle individually and n = 48 for all the cycles); ⁽³⁾ALL - All the soils (n = 24 for each cycle individually and n = 96 for all the cycles); *,**Significant at 0.05 and 0.01 probability level, respectively; ^{ns}Not significant

more-developed soils with higher clay contents (PVe, PVA, LA and PVd), the amounts of Ke released after four successive corn cycles were similar to the amounts of K absorbed by plants in the absence of K fertilization, while in more-developed soils with lower clay contents (PA and PAC) this only occurred after the application of the K dose of 100 mg dm⁻³ (Table 5). In the soils PA and PAC, in the absence of K fertilization, the amount of Kne + Ke released after the cycles was lower than the K absorbed by plants, indicating that other forms of Kne, not extracted with boiling 1 mol L⁻¹ HNO₃, may have been released and absorbed by plants.

When K was not added to less-developed soils, the released Ke represented 20 (RY) to 74% (TX) of the K absorbed by plants. These values vary from 21 (SX) to 84% (RR) when a K dose of 100 mg dm⁻³ was added (Table 5). The less-developed soils with higher clay contents and predominance of mica and 2:1 minerals in the clay fraction (SX, RY and VX) (Table 1) were the soils in which the released Ke represented only a small fraction of the amount of K absorbed by plants (Table 5).

In the soil SX, the released amounts of Kne + Ke were higher than the amounts of K absorbed by plants, especially for the K dose of 100 mg dm⁻³ (Table 5), evidencing that the non-exchangeable forms of K released and absorbed by plants were efficiently estimated by boiling 1 mol L⁻¹ HNO₃. The same did not occur in the soils RY and VX, in which the released Ke represented only 20 to 40% of the great amount (589 to 801 mg dm⁻³, respectively) of K absorbed by plants in these soils (Table 5).

According to Meurer et al. (1996), the K extractable with boiling 1 mol L⁻¹ HNO₃, which is considered as a reserve available in the medium term, can be an unreliable approximation of the soil capacity for K supply, but it is not

Table 5. Amounts of non-exchangeable K (Kne) and exchangeable K (Ke) released and K absorbed by corn plants after four successive cycles, as a function of K doses added to more- and less-developed soils of the state of Paraíba, Brazil

Soil ⁽¹⁾	Dose	K released after four cycles			Absorbed K
		Kne	Ke	Σ (Kne + Ke)	
mg dm ⁻³					
More-developed soils					
PA	0	6.7 (43) ⁽²⁾	1.3 (08)	8.0 (51)	15.7
	100	9.9 (09)	93.1 (87)	103.0 (96)	107.5
PAC	0	7.4 (21)	19.8 (56)	27.2 (77)	35.1
	100	16.7 (13)	113.1 (91)	129.8 (104)	124.5
PVe	0	55.8 (30)	169.7 (92)	225.5 (122)	184.7
	100	109.9 (40)	278.9 (102)	388.8 (142)	273.8
PVA	0	3.8 (04)	84.3 (96)	88.1 (100)	88.0
	100	40.6 (25)	167.8 (103)	208.4 (128)	162.3
LA	0	0.3 (00)	69.1 (88)	69.4 (89)	78.4
	100	19.7 (12)	166.5 (105)	186.2 (117)	158.5
PVd	0	38.1 (51)	67.9 (90)	106.0 (141)	75.2
	100	51.6 (53)	152.6 (96)	204.2 (129)	158.7
Less-developed soils					
RR	0	41.6 (53)	56.7 (73)	98.3 (126)	77.8
	100	43.0 (24)	148.3 (84)	191.3 (109)	175.6
RL	0	194.0 (155)	70.3 (56)	264.3 (211)	125.4
	100	211.4 (104)	131.8 (65)	343.2 (169)	203.0
TX	0	48.3 (14)	262.9 (74)	311.2 (87)	356.2
	100	48.6 (11)	357.9 (83)	406.5 (94)	431.1
SX	0	124.7 (82)	41.8 (27)	166.5 (109)	153.0
	100	230.7 (126)	39.4 (21)	270.1 (147)	183.7
RY	0	-277.6 ⁽³⁾	138.3 (20)	138.3 (20)	684.4
	100	-124.0	172.5 (22)	172.5 (22)	801.3
VX	0	80.0 (14)	221.4 (38)	301.4 (51)	589.3
	100	75.4 (12)	249.6 (40)	325.0 (52)	619.9

⁽¹⁾ PA - Yellow Argisol; PAC - Gray Argisol; PVe - Eutrophic Red Argisol; PVA - Red Yellow Argisol; LA - Yellow Latosol; PVd - Dystrrophic Red Argisol; RR - Regolithic Neosol; RL - Litholic Neosol; TX - Haplic Luvisol; SX - Haplic Planosol; RY - Fluvic Neosol; VX - Haplic Vertisol. ⁽²⁾Values in parentheses are percentages calculated in relation to the absorbed K; ⁽³⁾ Final values of non-exchangeable K were higher than the initial value

necessarily related to the dynamics of K release in the soils. Furthermore, it should be considered the potential capacity of the acid treatment in the dissolution of structural K, similar to other strong acids, which can lead to an overestimation in the quantification of Kne contents in the soil. The methodology employed in the present study uses a time of 15 minutes for soil boiling with 1 mol L⁻¹ HNO₃, which is longer than the time used in most studies found (10 minutes).

In less-developed soils originated from granite, Nachtigall & Vahl (1991) observed high contents of K extracted by boiling 1 mol L⁻¹ HNO₃, which was not released to plants. Similar results were observed by Mielniczuk & Selbach (1978) in soils of the state of Rio Grande do Sul. In other cases, boiling 1 mol L⁻¹ HNO₃ can underestimate Kne, indicating a participation of non-exchangeable forms used by plants that are not extracted through this methodology (Nachtigall & Vahl, 1991; Silva et al., 2000; Cabbau et al., 2004; Villa et al., 2004). These results, as the ones observed in the present study, compromise the generalization of the use of boiling 1 mol L⁻¹ HNO₃ as an index of Kne supply to plants.

With the data from Table 5, multiple and single linear regression equations were adjusted to the accumulated K in the plants as a variable of Kne and/or Ke (Table 6). In more-developed soils, variations in the K absorbed by plants are very well explained (R² = 0.99) by the variations in the Ke released,

but little explained ($R^2 = 0.43$) by the variations in the Kne contents released. According to the multiple regression model, the variable Kne did not contribute to the increase in R^2 and the coefficient of the model associated with this variable was not significant. Thus, it can be concluded that, in more-developed soils, the variations in the amounts of K absorbed by plants are exclusively explained by the variations in the amounts of Ke released after the cycles.

In less-developed soils, variations in the K absorbed by plants were partially explained ($R^2 = 0.61$) by the variations in the Ke released, but were not explained ($R^2 = 0.13$ and not significant effect for Kne) by the variations in the contents of Kne released (Table 6). Considering the variables Kne and Ke together in the multiple regression model, the value of R^2 increased to 0.72. This R^2 value is still lower than 0.99, evidencing once more that in less-developed soils, not all the non-exchangeable forms of K susceptible to absorption by plants were extracted from the soil with boiling $1 \text{ mol L}^{-1} \text{ HNO}_3$, as previously mentioned. When these regression equations were adjusted considering the twelve soils together, the R^2 values were much lower (Table 6), evidencing that the separation of the soils into two groups according to the degree of development was important to better understand the studied phenomenon.

Table 6. Multiple and single linear regression equations for the estimation of K absorbed by corn plants along four successive cycles (Y, in mg dm^{-3}) as a function of the contents (mg dm^{-3}) of exchangeable K (Ke) and non-exchangeable K (Kne) released, in more- and less-developed soils of the state of Paraíba, Brazil

Regression equations	R^2
All the soils	
$Y = 16.03 + 1.3604^{**}K_e$	0.59
$Y = 179.84 + 0.3899^{ns}K_{ne}$	0.03
$Y = -23.16 + 1.3859^{**}K_e + 0.5155^{*}K_{ne}$	0.64
More-developed soils	
$Y = 14.63 + 0.9281^{**}K_e$	0.99
$Y = 71.49 + 1.8148^{**}K_{ne}$	0.43
$Y = 16.18 + 0.8861^{**}K_e + 0.1144^{ns}K_{ne}$	0.99
Less-developed soils	
$Y = 72.22 + 1.3876^{**}K_e$	0,61
$Y = 395.88 - 0.9508^{ns}K_{ne}$	0,13
$Y = -223.27 + 1.5093^{**}K_e + 5.7201^{*}K_{ne} - 0.0205^{*}(K_{ne})^2$	0,72

*, **, and ^{ns}Significant at 0.01, 0.05 and 0.10 probability level, respectively; ^{ns}Not significant

CONCLUSIONS

1. In all the studied soils, especially in the less-developed ones with higher contents of clay and 2:1 minerals, the amounts of K absorbed after successive cycles were higher than the released contents of exchangeable K, evidencing the contribution of non-exchangeable K forms to corn nutrition.

2. The extractor $1 \text{ mol L}^{-1} \text{ HNO}_3$ in boiling water was not efficient to extract all the non-exchangeable K forms susceptible to absorption by corn plants.

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