CATION SELECTIVITY COEFFICIENTS AND DIFFUSION PARAMETERS OF POTASSIUM IN SOILS OF THE STATE OF RIO GRANDE DO SUL, BRAZIL[1]

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SUMMARY

Transport of potassium (K) in the soil towards roots depends mainly on diffusion. There is a lack of routine procedures for the determination of diffusion parameters. The objectives of this study were to: 1) determine multielement selectivity coefficients of soil exchange reactions of the main soil cations; 2) estimate these coefficients through soil factors routinely determined; and 3) calculate diffusion parameters of K using selectivity coefficients, activity in the soil solution, and concentration of the exchangeable phase. Soil solution cation concentrations were determined by strontium equilibration, and exchangeable cations were determined by extraction with 1M NH_4Cl. Average values of the selectivity coefficients, using Gapon's equation, were: $k_{Ca}^{Sr} = 0.84$, $k_{Mg}^{Sr} = 1.15$, $k_{Mn}^{Sr} = 0.78$, $k_{Ca}^{Mg} = 0.71$, $k_{Ca}^{Mn} = 1.14$, $k_{K}^{Na} = 0.48$, $k_{D_{Ca}}^{M_K} = 0.34$, $k_{Al}^{M_K} = 0.14$ and $k_{D_{Ca}}^{Al} = 3.07$, in which $(M^+)_K$ represents the monovalent cation activity equivalence of K and $(D^{2+})_{Ca}$ represents the divalent cation activity equivalence of Ca. The soil factors best related to these selectivity coefficients were pH in water, pH in $CaCl_2$, pH in the SMP buffer solution, clay content, organic matter content, and the activity ratio between divalent cations and K. Regression equations between these soil parameters and the selectivity coefficients presented r^2 values greater than 0.8. Buffer power of the soil for K was calculated with a differential equation including selectivity coefficients, activity in the soil solution, and concentration on the exchange phase of Na, K, Sr, Ca, Mg, Mn, and Al. The utilized methodology allowed an easy determination of soil K diffusion factors.

Index terms: Sr equilibration, soil solution, K buffer power, availability index, oxisols.

RESUMO: *COEFICIENTES DE SELETIVIDADE E PARÂMETROS DE DIFUSÃO DE POTÁSSIO EM SOLOS DO ESTADO DO RIO GRANDE DO SUL*

O transporte de potássio (K) no solo na direção das raízes depende principalmente do processo de difusão. Há escassez de procedimentos de rotina para determinar os parâmetros de difusão. Os objetivos deste trabalho foram: (1) determinar coeficientes de seletividade multielementos de reações de troca dos principais cátions do solo; (2) estimar esses coeficientes por fatores determinados em análise de rotina de solo, e (3) calcular parâmetros de difusão de K usando coeficientes de seletividade, atividade na solução do solo e concentração na fase

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trocável. A concentração dos cátions na solução foi determinada pelo equilíbrio do solo com estrôncio e, os cátions trocáveis, pela extração com NH_4Cl 1M. Valores médios dos coeficientes de seletividade, usando a equação de Gapon, foram: k_{Ca}^{Sr} = 0,84, k_{Mg}^{Sr} = 1,15, k_{Mn}^{Sr} = 0,78, k_{Ca}^{Mg} = 0,71, k_{Ca}^{Mn} = 1,14, k_{K}^{Na} = 0,48, $k_{D_{Ca}}^{M_K}$ = 0,34, $k_{Al}^{M_K}$ = 0,14 e $k_{D_{Ca}}^{Al}$ = 3,07, na qual $(M^+)_K$ representa a atividade dos cátions monovalentes expressos em K e $(D^{2+})_{Ca}$, a atividade dos cátions divalentes expressos em Ca. Os fatores que melhor se relacionaram com esses coeficientes de seletividade foram pH em água, pH em $CaCl_2$, pH na solução tampo SMP, teores de argila e de matéria orgânica, e o quociente de atividade entre cátions divalentes e K. Equações de regressão entre esses parâmetros e os coeficientes de seletividade apresentaram valores de r^2 superiores a 0,8. O poder tampão do solo em K foi calculado por uma equação diferencial, incluindo coeficientes de seletividade, atividade dos íons na solução do solo e concentração na fase trocável de Na, K, Sr, Ca, Mg, Mn e Al. O método empregado permitiu fácil determinação dos fatores de difusão de K no solo.

Termos de indexação: equilíbrio com estrôncio, solução do solo, poder tampão de potássio, índice de disponibilidade, oxissolos.

INTRODUCTION

Plant nutrient cations undergo electrostatic exchange between the soil solution and negatively charged soil particles. The specificity or preference of a particular cation to occupy an adsorption site depends basically on three factors: the charge density of the soil particles ($mol_c\ cm^{-2}$), the hydrated ionic radii (nm) and the valence of the competing cations. These factors determine the spatial arrangement of the cations in the electric double layer (Singh & Uehara, 1990).

Although plant nutrients are absorbed from the soil solution (Lagerwerff, 1960), the amount of K in the soil solution is low in terms of plant requirements. Therefore, exchangeable K from the diffuse double layer will be the main source of available K. As K is removed from the soil solution another cation occupies its place, maintaining, in consequence, the electrical neutrality of the system. Hence, the concentration of K in the soil solution, to some extent, is related to the presence of other cations, like Ca and Mg, in spite of the fact that plants usually respond to the individual concentration of these nutrients. The ratios of these cations at the root surface, however, will not hold as absorption goes on, due to different rates of transport to the root surface and different rates of absorption by the roots.

Nutrient movement toward root surfaces is dependent on mass flow and diffusion. Diffusion is the most important process for K availability (Barber et al., 1963). It takes place in response to a concentration gradient between the initial concentration of K in the soil solution away from the root surface (C_{li}) and the concentration in the soil solution at the root surface (C_{la}). When K is removed from the soil solution by root absorption, adsorbed K will replenish it. Thus, selectivity coefficients will dictate which cations are going to exchange preferably with K. Therefore, knowing the selectivity coefficients of the exchange reactions might be useful in predicting the rate of K release to plant roots, in particular for the calculation of the buffer power of the soil for K.

Table 1. Soils of the State of Rio Grande do Sul used in the study and their classification (Brasil, 1973)

Sample[1]	Soil	Classification	Area in the State
			%
1, 2	Alto das Canas	Laterítico bruno avermelhado eutrófico - Paleudalf	1.04
3, 4	Bagé	Planossolo vértico - Argiaquoll	0.68
5, 6	Charrua	Litólico eutrófico - Hapludoll	1.41
7, 8	Ciríaco-Charrua	Brunizem avermelhado - Argiudoll	11.86
9, 10	Cruz Alta	Latossolo vermelho escuro distrófico - Haplorthox	2.95
11, 12	Durox	Latossolo húmico distrófico - Haplohumox	1.13
13, 14	Erexim	Latossolo roxo distrófico - Haplorthox	4.75
15, 16	Estação	Laterítico bruno avermelhado distrófico - Paleudult	1.22
17, 18	Júlio de Castilhos	Podzólico vermelho amarelo - Paleuhumult	0.73
19, 20	Passo Fundo	Latossolo vermelho escuro distrófico - Haplorthox	2.80
21, 22	Santo Ângelo	Latossolo roxo distrófico - Haplorthox	7.26
23, 24	São Borja	Laterítico bruno avermelhado distrófico - Paleudalf	0.77
25, 26	Tupanciret	Podzólico vermelho amarelo - Paleudult	0.29
27, 28	Vacaria	Latossolo bruno distrófico - Haplohumox	1.71
Total			38.60

[1] Odd sample numbers were collected from cultivated areas and even sample numbers were collected from uncultivated areas.

Soils of the State of Rio Grande do Sul, Brazil, are mostly Oxisols and Ultisols with medium to low K content. Originally these soils presented an adequate supply of K to plants. As a more intensive agriculture was established, many soils became K deficient, which brought about the need for a better understanding of the behavior of this element in these soils in terms of availability indices to plants.

The objectives of this study were to: a) determine selectivity coefficients of the main cations in the soil; b) indicate how these coefficients could be estimated through soil parameters commonly determined, and c) calculate diffusion parameters of K for these soils by using selectivity coefficients.

MATERIALS AND METHODS

Soils - Fourteen soils representing the main areas of the State of Rio Grande do Sul cultivated to wheat, soybean, corn, and forages were sampled from cultivated and uncultivated (undisturbed natural vegetation) areas, yielding a total of 28 samples (Table 1). The cultivated and uncultivated sites were closely located. Sites were chosen to represent the original profiles used for soil classification purposes (Brasil, 1973). Sampling depth was 0 to 20 cm. Samples were dried at 55°C, ground and sieved through an opening of 2 mm. Soils were sampled in 1987 and 1988.

According to Table 1, the most common great soil group was Oxisols, and the soils sampled represented 38.6% of the area of the State of Rio Grande do Sul. In terms of agricultural use, these soils represent about 3 million hectares of cultivated land. The average pH in water of these soils was 5 and they were P and/or K deficient (Table 2). The mean total K content of the soils used in this study is about 0.4 % (Oliveira et al., 1971).

Experimental procedures

Soil solution - The amounts of K, Na, Sr, Ca, Mg, Mn, and Al in the soil solution were determined using the strontium equilibration procedure (Goedert & Corey, 1973; Wiethölter & Corey, 1994). Samples of 10 g of soil were placed in 50-mL polypropylene oak ridge centrifuge tubes of known weights. Twenty five mL of 0.004 M $Sr(NO_3)_2$ were added to each soil. The suspension was shaken at 150 rpm during one hour with a rotary shaker, at room temperature, and then centrifuged at 2000 rpm for 5 min. The supernatant was then filtered through a Whatman number 2 filter paper and analyzed for K, Na, Sr, Ca, Mg, Mn, and Al. Potassium was determined with a flame photometer and the other elements by an atomic absorption spectrophotometer.

The 0.004 M $Sr(NO_3)_2$ solution, used at the soil to solution ratio of 1:2.5, is sufficiently concentrated to promote flocculation and to overcome differences in the soil solution salt concentration.

Exchangeable amounts - The soil and the remaining $Sr(NO_3)_2$ solution left in the centrifuge tubes were weighed to determine the amounts of K, Na, Sr, Ca, Mg, Mn, and Al in the entrained soil solution to be subtracted from the total labile pool. Then, about 90 mL (by weight) of 1M NH_4Cl was used to transfer the soil from the centrifuge tube to a 250-mL Erlenmeyer flask. The suspension was shaken with a rotary shaker at 150 rpm for one hour at room temperature and the supernatant was transferred back into the centrifuge tube, centrifuged at 2000 rpm for 5 min and filtered through a Whatman number 2 filter paper. In order to avoid precipitation of NH_4Cl in the aspirator tubes of the flame photometer and atomic absorption spectrophotometer, the remaining NH_4Cl salt was removed from the solution

Table 2. Values of pH in water, in $CaCl_2$, and in SMP buffer solution, and contents of organic matter, clay, P, and K of the soils used

Sample	pH H_2O[1]	pH salt[2]	pH SMP[3]	Organic Matter[4]	Clay[5]	P[6]	K[6]
				—— % ——		mg L^{-1} soil	
1	5.1	4.4	5.8	2.9	26	19.3	63
2	5.0	4.2	5.7	3.8	19	2.3	56
3	5.5	4.8	6.1	4.6	12	2.5	81
4	5.3	4.5	6.0	3.9	12	2.8	55
5	6.0	5.6	6.3	5.7	21	7.3	349
6	6.0	5.8	6.4	7.5	17	6.9	390
7	6.2	5.8	6.3	3.7	52	9.4	237
8	5.3	4.8	5.5	4.8	31	2.1	192
9	4.4	4.1	5.7	2.9	28	14.3	38
10	4.7	4.2	5.7	3.6	30	2.4	30
11	5.1	4.7	5.6	5.1	61	4.8	48
12	4.6	4.1	4.9	5.6	57	1.6	102
13	4.9	4.4	5.7	4.1	65	4.1	135
14	4.5	4.0	4.9	3.5	65	1.7	26
15	4.7	4.0	4.7	5.2	63	7.3	58
16	4.5	3.9	4.4	6.2	60	1.8	103
17	4.4	3.9	4.9	4.5	34	7.3	37
18	4.5	4.0	5.2	4.8	22	4.2	40
19	6.2	5.5	6.4	4.5	28	5.0	56
20	4.9	4.0	4.9	5.5	33	2.3	42
21	4.6	4.3	5.4	3.9	63	4.4	67
22	4.6	4.1	5.4	4.0	60	1.4	35
23	5.6	5.1	6.0	4.6	48	5.6	45
24	5.2	4.6	5.6	4.6	52	10.2	38
25	5.1	4.2	5.5	3.8	36	10.0	175
26	5.0	4.2	5.5	4.2	35	5.2	242
27	4.4	4.0	4.6	6.1	47	5.6	47
28	4.6	4.1	4.7	6.5	50	1.5	54
Average	5.0	4.5	5.5	4.6	40	5.5	101

[1] 1:1 soil to solution ratio. [2] 0.01 M $CaCl_2$. [3] Shoemaker, McLean and Pratt (SMP) buffer solution, according to Tedesco et al. (1985). [4] Wet digestion with sodium bicromate, according to Tedesco et al. (1985). [5] Densimeter method, according to Tedesco et al. (1985). [6] Method of Mehlich-I (Tedesco et al., 1985).

by following the procedure of Piper (1947, p.172): 25 mL of the filtrate were transferred to a 150-mL beaker, placed in a water bath under moderate heat and evaporated to dryness; when cool, 9 mL of a mixture of 3.5 parts of concentrated HNO_3 and 5 parts of deionized water was added; after the salt had dissolved, the solution was again evaporated to dryness in the water bath. The residue was dissolved in 25 mL deionized water and then analyzed for K, Na, Sr, Ca, Mg, Mn, and Al.

Values in Tables 2 to 4 are averages of three analytical determinations. Calculations were performed by using a computer program written in BASIC language (Ancines & Wiethölter, 1989).

Calculations

The exchange reactions among the cations adsorbed by the soil with those in the soil solution have been described with the use of several equations (Sposito, 1981, White & Zelazny, 1990). However, the Gapon exchange equation (Gapon, 1933) has been widely used to calculate the selectivity coefficients of these reactions and was also used in this study.

The data in Table 3 are the concentrations of K, Na, Sr, Ca, Mg, Mn, and Al in the 0.004M $Sr(NO_3)_2$ equilibrating solution and were assumed to be the initial concentrations in the soil solution (C_{li}). Table 4 presents the concentrations of the same cations in the exchangeable form extracted with 1M NH_4Cl. The values in Table 5 were calculated on the basis of the data in Table 4, in which

$$[MX] = [KX] + [NaX] \quad [1]$$

and

$$[DX_2] = [SrX_2] + [CaX_2] + [MgX_2] + [MnX_2], \quad [2]$$

where [ ] refers to concentration in cmol kg^{-1} soil (= mmol/100 g soil) and X represents one mol of anionic charge on the soil particles.

Table 3. Concentration of cations in the 0.004 M $Sr(NO_3)_2$ equilibrating solution

Sample	$[K^+]$	$[Na^+]$	$[Sr^{2+}]$	$[Ca^{2+}]$	$[Mg^{2+}]$	$[Mn^{2+}]$	$[D^{2+}]^{(1)}$	$[Al^{3+}]$
	mmol L^{-1}							
1	0.22	0.25	1.56	1.62	1.08	0.02	4.28	0.07
2	0.20	0.28	1.68	1.51	0.95	0.09	4.23	0.02
3	0.25	0.47	0.84	1.96	1.20	0.10	4.10	0.02
4	0.18	0.32	1.08	2.14	1.10	0.09	4.41	0.01
5	0.65	0.27	0.37	3.00	1.06	0.07	4.50	0.04
6	1.08	0.29	0.35	2.75	1.64	0.12	4.86	0.07
7	0.43	0.36	0.41	2.36	1.59	0.00	4.36	0.04
8	0.38	0.28	0.38	2.88	1.06	0.07	4.39	0.01
9	0.21	0.26	1.93	1.79	1.02	0.13	4.87	0.05
10	0.14	0.26	1.76	1.19	1.29	0.12	4.36	0.02
11	0.15	0.28	0.85	1.77	1.54	0.18	4.34	0.03
12	0.41	0.30	1.32	1.07	1.18	0.23	3.80	0.09
13	0.49	0.24	0.88	1.76	1.31	0.24	4.19	0.03
14	0.11	0.31	1.31	1.11	0.79	0.40	3.61	0.09
15	0.20	0.25	1.44	1.80	0.72	0.12	4.08	0.10
16	0.44	0.25	1.61	1.37	0.73	0.14	3.85	0.18
17	0.17	0.22	1.66	1.60	0.81	0.05	4.12	0.16
18	0.18	0.22	1.96	1.20	0.91	0.06	4.13	0.06
19	0.13	0.27	0.71	1.84	1.92	0.00	4.47	0.01
20	0.17	0.25	2.01	0.96	0.89	0.06	3.92	0.14
21	0.26	0.27	1.20	1.62	1.09	0.32	4.23	0.04
22	0.14	0.26	1.23	1.55	0.99	0.34	4.11	0.08
23	0.08	0.25	0.74	2.47	1.40	0.02	4.63	0.05
24	0.09	0.26	0.87	2.39	1.00	0.10	4.36	0.05
25	0.82	0.26	1.58	1.53	0.93	0.09	4.14	0.05
26	1.28	0.26	1.58	1.20	1.12	0.08	3.98	0.03
27	0.17	0.28	1.19	1.70	0.99	0.24	4.12	0.08
28	0.23	0.28	1.36	1.53	1.06	0.17	4.12	0.08
Average	0.33	0.28	1.21	1.77	1.12	0.13	4.23	0.06
Average, mg L^{-1}	13	6	106	71	27	7	-	2

(1) Summation of the divalent cations.

The values of $[M^+]$ and $[D^{2+}]$ in Table 6 refer to the summation of the concentrations of the monovalent (K and Na) and divalent (Sr, Ca, Mg, and Mn) cations in the soil solution, respectively. The ionic strength (I, mol L^{-1}) was calculated using Lewis' equation, assuming that all cations were associated to monovalent anions, yielding the following equation,

$$I = 0.001([M^+] + 3[D^{2+}] + 6[Al^{3+}]), \quad [3]$$

where [ ] represents concentration in mmol L^{-1}.

The values of γ^+, γ^{2+} and γ^{3+} in Table 6 are, respectively, the activity coefficients of the monovalent and divalent cations and of Al in the soil solution. They were calculated with the Debye-Hückel equation, modified by Davies (1962, p.41).

All selectivity coefficients in Table 7 were calculated using the Gapon equation for ion selectivity, which, for Sr and Ca, is

$$k_{Ca}^{Sr} = \frac{[SrX_2]\,(Ca^{2+})}{[CaX_2]\,(Sr^{2+})}. \quad [4]$$

The values of $(M^+)_K$ and $(D^{2+})_{Ca}$ in Table 6 represent the monovalent activity equivalence of K and the divalent activity equivalence of Ca, respectively. These values were calculated according to Eqs. [16] and [13] of Wiethölter & Corey (1994) and are

$$(M^+)_K = (K^+) + k_K^{Na}\,(Na^+) \quad [5]$$

and

$$(D^{2+})_{Ca} = (Ca^{2+}) + k_{Ca}^{Sr}\,(Sr^{2+}) + k_{Ca}^{Mg}\,(Mg^{2+}) + k_{Ca}^{Mn}\,(Mn^{2+}), \quad [6]$$

where ( ) represents activity in the soil solution (mmol L^{-1}) and k's are the selectivity coefficients of the cations, according to Eqs. [12], [2], [14] and [15] of Wiethölter & Corey (1994), respectively for k_K^{Na}, k_{Ca}^{Sr}, k_{Ca}^{Mg} and k_{Ca}^{Mn}. Based on Eqs. [5] and [6], the selectivity coefficient between the monovalent and divalent cations was calculated by the following equation:

$$k_{D_{Ca}}^{M_K} = \frac{\{MX\}\,(D^{2+})_{Ca}^{\frac{1}{2}}}{\{D_{\frac{1}{2}}X\}\,(M^+)_K} \quad [7]$$

Table 4. Concentration of the exchangeable cations extracted with 1 M NH_4Cl

Sample	[KX]	[NaX]	$[SrX_2]^{(1)}$	$[CaX_2]$	$[MgX_2]$	$[MnX_2]$	$\{Al_{\frac{1}{3}}X\}$
	mmol/100 g						$cmol_c/kg$
1	0.14	0.11	0.56	0.72	0.33	0.02	0.53
2	0.12	0.12	0.52	0.58	0.25	0.05	0.55
3	0.22	0.16	0.66	1.76	0.78	0.15	0.07
4	0.15	0.13	0.70	1.41	0.54	0.09	0.19
5	0.81	0.10	0.72	5.96	1.39	0.17	0.07
6	0.94	0.11	0.72	6.02	2.00	0.26	0.03
7	0.78	0.10	0.85	5.14	2.60	0.03	0.06
8	0.75	0.11	0.81	6.48	1.84	0.22	0.11
9	0.10	0.10	0.46	0.51	0.21	0.04	0.87
10	0.09	0.11	0.54	0.46	0.33	0.05	1.02
11	0.17	0.10	0.70	1.76	1.12	0.17	0.36
12	0.28	0.10	0.65	0.64	0.49	0.12	2.62
13	0.43	0.08	0.70	1.56	0.88	0.23	0.45
14	0.11	0.07	0.60	0.60	0.34	0.21	2.92
15	0.18	0.09	0.59	1.04	0.32	0.07	2.84
16	0.24	0.08	0.55	0.61	0.24	0.08	3.50
17	0.11	0.24	0.49	0.67	0.23	0.02	3.48
18	0.14	0.31	0.44	0.45	0.19	0.02	2.36
19	0.14	0.08	0.73	1.97	1.30	0.01	0.02
20	0.11	0.09	0.43	0.32	0.22	0.02	2.62
21	0.20	0.11	0.75	1.10	0.53	0.18	1.22
22	0.13	0.10	0.65	0.87	0.44	0.18	1.44
23	0.15	0.09	0.70	2.96	1.14	0.06	0.11
24	0.15	0.10	0.71	2.09	0.64	0.13	0.47
25	0.33	0.09	0.52	0.72	0.32	0.05	0.74
26	0.40	0.10	0.60	0.54	0.35	0.05	0.68
27	0.16	0.12	0.66	1.10	0.46	0.13	2.90
28	0.17	0.14	0.63	0.71	0.41	0.08	2.84
Average	0.28	0.12	0.63	1.74	0.71	0.10	1.25
Average, mg kg^{-1}	109	28	552	697	173	55	112

in which { } refers to $cmol_c\ kg^{-1}$ soil. The selectivity coefficient between Al and either monovalent or divalent cations was calculated with an equation similar to Eq. [7].

In Table 9, C_{li} represents the initial soil solution concentration, b the buffer power, and D the diffusion coefficient of K in the soil. The value of b was calculated using Eq. [20] of Wiethölter & Corey[4]. This equation is a differential equation in which K, Na, Sr, Ca, Mg, Mn, and Al are considered both in the exchangeable and in the solution phase and assumes that all major cations are important in establishing the buffer power of K. To facilitate the understanding of the concept involved in the derivation, the equation to calculate b is repeated here:

$$b = \frac{dC}{dC_{li}} = 10\rho \left\{ \frac{k^{Mx}_{Ca} [\{CEC\} - \{KX\}]}{[k^{Mx}_{Ca} (K^+) + k^{Na}_{K} k^{Mx}_{Ca} (Na^+) + (D^{2+})^{1/2} + k^{Al}_{Ca} (Al^{3+})^{1/3}]/\gamma^+} + 0.25 \right\} \quad [8]$$

in which C is equal to the labile pool of K (exchangeable + solution) and C_{li} represents the initial soil solution concentration (assumed to be equal to the concentration in the $Sr(NO_3)_2$ equilibrating solution). The buffer power expresses the amount (mmol) of labile K per cm^3 soil required to increase the soil solution concentration by 1 mmol per cm^3 solution. The constant 0.25 in Eq. [8] arises from the soil to solution ratio used in the $Sr(NO_3)_2$ equilibration procedure and ρ is the soil density (g soil cm^{-3} soil). As shown in Eqs. [4] and [7], whenever the values of the activity of the cations in the soil solution and the concentrations in the exchangeable form are known, the values for the selectivity coefficients (k's) can be calculated. Then, by using Eq. [8], a value for the buffer power can be obtained for any soil. Alternatively, if the values for the selectivity coefficients are known (Table 7), the activities in the

[4] WIETHÖLTER, S. & COREY, R.B. Derivation of differential buffer powers of the soil for cations. R. bras. Ci. Solo, Campinas (in press).

Table 5. Summation of monovalent exchangeable cations [MX], calculated exchangeable strontium, $[SrX_2]_c$, total strontium, $[Sr_T]$, determined exchangeable divalent cations, $[DX_2]_d$, calculated exchangeable divalent cations, $[DX_2]_c$, determined cation exchange capacity, $\{CEC\}_d$, and calculated cation exchange capacity, $\{CEC\}_c$

Sample	[MX]	$[SrX_2]_c$ [1]	$[Sr_T]_d$ [2]	$[DX_2]_d$	$[DX_2]_c$	$\{CEC\}_d$	$\{CEC\}_c$
	mmol/100 g					$cmol_c/kg$	
1	0.25	0.61	0.95	1.64	1.68	4.06	4.15
2	0.24	0.58	0.94	1.40	1.47	3.60	3.73
3	0.38	0.79	0.87	3.35	3.48	7.15	7.41
4	0.28	0.73	0.96	2.73	2.77	5.93	6.00
5	0.91	0.91	0.81	8.24	8.43	17.46	17.84
6	1.06	0.91	0.80	9.00	9.19	19.07	19.47
7	0.88	0.90	0.95	8.61	8.66	18.17	18.26
8	0.86	0.91	0.90	9.35	9.45	19.68	19.87
9	0.20	0.52	0.94	1.22	1.28	3.50	3.62
10	0.19	0.56	0.98	1.37	1.40	3.95	4.00
11	0.27	0.79	0.92	3.75	3.84	8.14	8.30
12	0.38	0.67	0.98	1.90	1.91	6.79	6.82
13	0.51	0.78	0.92	3.37	3.46	7.71	7.87
14	0.19	0.67	0.93	1.75	1.82	6.62	6.75
15	0.27	0.64	0.95	2.01	2.06	7.14	7.25
16	0.32	0.60	0.95	1.47	1.52	6.75	6.85
17	0.35	0.58	0.90	1.40	1.50	6.65	6.84
18	0.45	0.51	0.93	1.10	1.17	5.01	5.16
19	0.22	0.82	0.91	4.02	4.11	8.27	8.44
20	0.20	0.50	0.93	0.99	1.06	4.80	4.94
21	0.32	0.70	1.05	2.57	2.52	6.67	6.57
22	0.22	0.69	0.96	2.14	2.18	5.95	6.03
23	0.24	0.82	0.88	4.85	4.97	10.05	10.29
24	0.25	0.78	0.93	3.57	3.64	7.87	8.01
25	0.42	0.60	0.91	1.61	1.70	4.38	4.56
26	0.50	0.61	1.00	1.54	1.54	4.25	4.26
27	0.28	0.70	0.95	2.34	2.39	7.87	7.96
28	0.31	0.66	0.97	1.83	1.86	6.80	6.86
Average	0.39	0.70	0.93	3.18	3.25	8.01	8.15
Standard deviation	-	0.13	0.05	-	-	-	-
Average, mg kg^{-1}	-	613	815	-	-	-	-

[1] $[SrX_2]_c = 1 - 0.25[Sr^{2+}]$. Henceforth the subscript c will be used to indicate calculated exchangeable strontium. [2] $[Sr_T] = [SrX_2]_d + 0.25[Sr^{2+}]$. A total of 876.2 mg Sr/kg was added to the soil.

soil solution determined and the amount of exchangeable Sr calculated $[SrX_2]_c$, the exchangeable amounts of all cations can be calculated, as it has been outlined by Wiethölter & Corey (1994). This procedure, therefore, allows the routine calculation of diffusion parameters based on data obtained solely on one equilibration of the soil with $Sr(NO_3)_2$. Even though Eq. [8] covers the whole extension of the adsorption isotherm relating C and C_{li}, the inclusion of H^+ would probably enhance its validity, if it were used in a closed system of electrical neutrality, as proposed by Bouldin (1989). It must be considered, however, that Eq. [8] does not include specific adsorption of K, which might be an important factor of K availability in the so-called equivalent cylinder or root-hair zone (Jungk et al., 1982).

The diffusion coefficient was calculated using the equation proposed by Nye & Marriott (1969), $D = D_l\theta f_l/b$, in which D_l is the diffusion coefficient in water (1.77×10^{-5} cm^2 s^{-1} at 20°C), θ is the volumetric water content, cm^3 water cm^{-3} soil, and f_l is the pore continuity factor, in units of cm^2 soil cm^{-2} water. The value of f_l was calculated by the equation proposed by Van Rees et al. (1990), $f_l = 3.1\theta^{1.9}$.

RESULTS AND DISCUSSION

Selectivity coefficients

Tables 3 to 6 present the necessary data to calculate the multielement selectivity coefficients in Table 7. All coefficients were calculated using activity in the soil solution and concentration in the adsorbed phase, as indicated in Eqs. [4] and [7]. Selectivity coefficients were calculated using either determined or calculated exchangeable Sr (Table 5).

Table 6. Summation of monovalent $[M^+]$ and divalent $[D^{2+}]$ cations in the equilibrium solution, ionic strength (I), monovalent (γ^+), divalent (γ^{2+}), and trivalent (γ^{3+}) activity coefficients, activity of cations in the $Sr(NO_3)_2$ equilibrating solution ( ), monovalent activity equivalence of K, $(M^+)_K$, and divalent activity equivalence of Ca, $(D^{2+})_{Ca}$

Sample	$[M^+]$	$[D^{2+}]$	I	γ^+	γ^{2+}	γ^{3+}	(K^+)	(Na^+)	(Sr^{2+})	(Ca^{2+})	(Mg^{2+})	(Mn^{2+})	(Al^{3+})	$(M^+)_K$	$(D^{2+})_{Ca}$	$(D^{2+})_{Ca_c}$
	—mmol L^{-1}—		mol L^{-1}	—dimensionless—			mmol L^{-1}									
1	0.47	4.29	0.014	0.889	0.623	0.345	0.20	0.22	0.97	1.01	0.67	0.02	0.02	0.34	2.29	2.35
2	0.48	4.23	0.013	0.890	0.628	0.351	0.18	0.25	1.05	0.95	0.60	0.06	0.01	0.36	2.28	2.38
3	0.73	4.10	0.013	0.891	0.629	0.352	0.22	0.42	0.53	1.23	0.75	0.06	0.01	0.39	2.34	2.44
4	0.49	4.41	0.014	0.888	0.623	0.345	0.16	0.28	0.67	1.34	0.68	0.06	0.00	0.29	2.58	2.61
5	0.92	4.49	0.015	0.886	0.615	0.335	0.57	0.24	0.23	1.84	0.65	0.04	0.02	0.64	2.55	2.61
6	1.37	4.86	0.016	0.881	0.601	0.318	0.95	0.26	0.21	1.65	0.98	0.08	0.02	1.06	2.47	2.53
7	0.78	4.36	0.014	0.887	0.620	0.342	0.38	0.32	0.25	1.46	0.98	0.00	0.01	0.43	2.45	2.47
8	0.66	4.38	0.014	0.888	0.622	0.344	0.34	0.25	0.24	1.79	0.66	0.05	0.00	0.39	2.58	2.61
9	0.47	4.88	0.015	0.883	0.609	0.328	0.18	0.23	1.18	1.09	0.62	0.08	0.02	0.36	2.61	2.73
10	0.40	4.36	0.014	0.889	0.625	0.347	0.12	0.23	1.10	0.74	0.80	0.08	0.01	0.27	2.22	2.26
11	0.42	4.34	0.014	0.889	0.625	0.347	0.13	0.24	0.53	1.10	0.96	0.11	0.01	0.20	2.35	2.40
12	0.72	3.80	0.013	0.892	0.634	0.358	0.37	0.27	0.84	0.68	0.75	0.15	0.03	0.50	2.02	2.03
13	0.73	4.19	0.013	0.889	0.626	0.348	0.44	0.22	0.55	1.10	0.82	0.15	0.01	0.52	2.38	2.44
14	0.42	3.61	0.012	0.895	0.643	0.370	0.10	0.28	0.84	0.71	0.50	0.26	0.03	0.16	2.07	2.16
15	0.45	4.08	0.013	0.890	0.627	0.350	0.18	0.22	0.90	1.13	0.45	0.08	0.04	0.27	2.20	2.26
16	0.69	3.85	0.013	0.890	0.627	0.350	0.40	0.22	1.01	0.86	0.46	0.09	0.06	0.53	2.07	2.14
17	0.39	4.12	0.014	0.889	0.623	0.345	0.15	0.20	1.04	1.00	0.50	0.03	0.06	0.49	2.08	2.22
18	0.39	4.13	0.013	0.891	0.629	0.352	0.16	0.19	1.23	0.75	0.57	0.04	0.02	0.49	1.84	1.96
19	0.40	4.47	0.014	0.888	0.622	0.344	0.12	0.24	0.44	1.14	1.19	0.00	0.00	0.18	2.33	2.38
20	0.42	3.91	0.013	0.891	0.630	0.354	0.15	0.22	1.27	0.60	0.56	0.04	0.05	0.27	1.88	2.01
21	0.53	4.24	0.014	0.889	0.626	0.348	0.24	0.24	0.75	1.02	0.68	0.20	0.02	0.37	2.36	2.32
22	0.41	4.10	0.013	0.890	0.628	0.351	0.13	0.24	0.77	0.97	0.62	0.21	0.03	0.23	2.38	2.43
23	0.33	4.63	0.015	0.886	0.617	0.337	0.07	0.22	0.46	1.52	0.86	0.01	0.02	0.11	2.50	2.56
24	0.34	4.36	0.014	0.889	0.624	0.346	0.08	0.23	0.54	1.49	0.62	0.07	0.02	0.13	2.55	2.60
25	1.09	4.14	0.014	0.888	0.623	0.345	0.73	0.23	0.99	0.95	0.58	0.06	0.02	0.92	2.12	2.24
26	1.54	3.98	0.014	0.889	0.624	0.346	1.13	0.23	0.98	0.75	0.70	0.05	0.01	1.41	2.14	2.15
27	0.45	4.12	0.013	0.890	0.628	0.351	0.15	0.25	0.75	1.07	0.62	0.15	0.03	0.27	2.27	2.32
28	0.52	4.12	0.013	0.890	0.627	0.349	0.21	0.25	0.85	0.96	0.67	0.10	0.03	0.38	2.49	2.53
Average	0.61	4.23	0.014	0.889	0.624	0.346	0.29	0.25	0.76	1.10	0.70	0.08	0.02	0.43	2.30	2.36

The interpretation of the values of the selectivity coefficients is as follows: a value smaller than 1 indicates preference of adsorption sites for the exchangeable cation written in the denominator of Eq. [4]. For example, the average value for k_{Ca}^{Sr} was 0.84 (Table 7), which indicates that the adsorption sites preferred Ca instead of Sr. Due to a much larger ionic radii of the monovalent cations than the divalent ones, the value for $k_{D_{Ca}}^{M_K}$ has to be much smaller than 1. In fact, its value, in average, was 0.34. Since the ionic radii of Al is much smaller than the divalent cations, the mean value for $k_{D_{Ca}}^{Al}$ was 3.07, indicating that Al is held preferably than divalent cations. The coefficients using either determined or calculated (subscript c) exchangeable Sr (see footnote of Table 5) were similar (compare columns 1 to 10, 2 to 11, 3 to 12, 7 to 13, and 9 to 14 in Table 7).

Precision in determining selectivity coefficients involving Al was low, mostly due to analytical values of Al close to the detection limit of either concentration in solution or on the exchange phase. As a result, some values of k's were omitted from the regressions to obtain the equations in Table 8.

In general, the individual values of the coefficients agreed with those expected, based on the ionic radii (Cotton & Wilkinson, 1980, p.14) and on the hydrated ionic radii (Gast, 1977, p.44) of the pairs of cations or groups of cations of the same charge. For most selectivity coefficients, the standard deviation was quite low (Table 7), indicating, therefore, that selectivity coefficients are basically a function of the ionic radii of the cations.

Table 7. Selectivity coefficients among cations using Gapon's equation

Sample	k_{Ca}^{Sr}	k_{Mg}^{Sr}	k_{Mn}^{Sr}	k_{Ca}^{Mg}	k_{Ca}^{Mn}	k_{K}^{Na}	$k_{D_{Ca}}^{M_K}$ (1)	$k_{Al}^{M_K}$ (2)	$k_{D_{Ca}}^{Al}$ (3)	$k_{Ca}^{Sr_c}$	$k_{Mg}^{Sr_c}$	$k_{Mn}^{Sr_c}$	$k_{D_{Ca_c}}^{M_K}$ (1)	$k_{D_{Ca_c}}^{Al}$ (3)
	dimensionless									dimensionless				
1	0.81	1.18	0.58	0.69	1.40	0.68	0.33	0.40*	0.84*	0.88	1.27	0.63	0.32	0.83*
2	0.80	1.16	0.57	0.68	1.40	0.74	0.36	0.22	1.61	0.90	1.31	0.64	0.35	1.57
3	0.87	1.20	0.52	0.73	1.66	0.40	0.22	2.60*	0.09*	1.04	1.44	0.63	0.22	0.08*
4	0.98	1.32	0.66	0.74	1.48	0.48	0.28	0.85*	0.32*	1.03	1.39	0.69	0.28	0.32*
5	0.96	1.45*	0.74	0.66	1.30	0.29	0.14*	4.94*	0.03*	1.22	1.84	0.94	0.14*	0.03*
6	0.94	1.69*	0.98	0.56	0.96	0.44	0.09*	9.57*	0.01*	1.20	2.15	1.26	0.09*	0.01*
7	0.96	1.27	0.29	0.75	3.33*	0.16*	0.19*	8.68*	0.02*	1.01	1.34	0.30	0.19*	0.02*
8	0.95	1.23	0.71	0.77	1.34	0.20*	0.19*	2.65*	0.07*	1.07	1.38	0.80	0.19*	0.07*
9	0.83	1.17	0.74	0.71	1.12	0.76	0.37	0.16	2.28	0.94	1.32	0.84	0.36	2.23
10	0.79	1.20	0.79	0.66	1.00	0.65	0.38	0.13	2.90	0.83	1.26	0.83	0.38	2.87
11	0.83	1.14	0.91	0.73	0.91	0.29	0.27	0.76*	0.36*	0.93	1.27	1.02	0.27	0.35*
12	0.83	1.19	0.98	0.70	0.85	0.48	0.28	0.09*	3.11	0.85	1.22	1.00	0.28	3.10
13	0.89	1.18	0.82	0.76	1.09	0.37	0.23	0.50*	0.46*	1.00	1.32	0.91	0.22	0.45*
14	0.84	1.06	0.88	0.80	0.96	0.23	0.48	0.12	3.79	0.94	1.18	0.98	0.47	3.72
15	0.71	0.92	0.69	0.77	1.02	0.40	0.37	0.12	3.20	0.78	1.00	0.76	0.37	3.16
16	0.76	1.05	0.63	0.73	1.20	0.61	0.30	0.07*	4.31	0.83	1.15	0.69	0.29	4.24
17	0.70	1.05	0.90	0.67	0.78	1.71*	0.37	0.08*	4.65	0.83	1.25	1.08	0.36	4.50
18	0.59	1.08	0.66	0.55	0.90	1.70*	0.57	0.11	5.31	0.69	1.26	0.77	0.55	5.14
19	0.97	1.53*	0.43	0.63	2.24*	0.26	0.23	10.59*	0.02*	1.09	1.72	0.49	0.23	0.02*
20	0.64	0.87	0.47	0.74	1.37	0.53	0.52	0.10	4.92	0.75	1.01	0.54	0.50	4.76
21	0.92	1.28	1.10	0.72	0.84	0.55	0.26	0.18	1.46	0.86	1.20	1.02	0.26	1.48
22	0.94	1.20	1.02	0.79	0.92	0.42	0.36	0.21	1.68	1.00	1.27	1.09	0.36	1.66
23	0.79	1.15	0.37	0.68	2.14*	0.19*	0.35	4.96*	0.07*	0.92	1.35	0.43	0.34	0.07*
24	0.94	1.29	0.68	0.73	1.40	0.24	0.43	1.04*	0.42*	1.04	1.41	0.74	0.43	0.41*
25	0.69	0.96	0.55	0.72	1.26	0.81	0.21	0.15	1.33	0.81	1.12	0.64	0.20	1.30
26	0.86	1.24	0.64	0.69	1.34	1.19*	0.17*	0.12	1.43	0.86	1.25	0.64	0.17*	1.42
27	0.85	1.19	1.02	0.72	0.83	0.46	0.34	0.11	3.12	0.91	1.27	1.10	0.33	3.09
28	1.00	1.19	0.93	0.84	1.07	0.67	0.35	0.09*	3.98	1.05	1.25	0.98	0.35	3.94
Average	0.84	1.19	0.72	0.71	1.29	0.57	0.31	1.77	1.85	0.94	1.33	0.80	0.30	1.82
Std dev	0.11	0.17	0.21	0.06	0.54	0.40	0.11	3.09	1.75	0.13	0.24	0.23	0.11	1.71
Average*	-	1.15	0.78	-	1.14	0.48	0.34	0.14	3.07	-	-	-	0.34	3.01
Std.deviation*		0.11	0.17	-	0.24	0.18	0.09	0.04	1.34	-	-	-	0.09	1.29

(1) $(mmol/L)^{\frac{1}{2}}(mmol/L)^{-1}$. (2) $(mmol/L)^{\frac{1}{3}}(mmol/L)^{-1}$. (3) $(mmol/L)^{\frac{1}{2}}(mmol/L)^{-\frac{1}{3}}$.

* Due to analytical values of concentration in the soil solution and/or on the exchange phase close to the detection limits, yielding values of k's far out of the expected range, the assigned values were omitted from the regressions to obtain the equations in Table 8.

Table 8. Regression equations among selectivity coefficients and soil factors

Number	Regression equation	n	r^2	SEE[1]
1	$k_{Ca}^{Sr} = 0.566 \ln pH_{salt}$	28	0.99	0.0114
2	$k_{Mg}^{Sr} = 0.685 \ln pH_{SMP}$	25	0.99	0.0115
3	$k_{Mn}^{Sr} = 0.462 \log clay$	28	0.93	0.0248
4	$k_{Ca}^{Mg} = 0.439 \ln pH_{water}$	28	0.99	0.0103
5	$k_{Ca}^{Mn} = 0.232\ pH_{water}$	25	0.97	0.0084
6	$k_{K}^{Na} = 0.659 \log pH_{SMP}$	22	0.88	0.0534
7	$k_{D_{Ca}}^{M_K} = 0.155 \ln \frac{(D^{2+})_{Ca}^{\frac{1}{2}}}{(K^+)}$	23	0.93	0.0090
8	$k_{Al}^{M_K} = 0.005\ (pH_{SMP})^2$	12	0.96	0.0003
9	$k_{D_{Ca}}^{Al} = 0.662$ (Organic Matter)	16	0.89	0.0595
10	$k_{Ca}^{Sr_c} = 0.630 \ln pH_{salt}$	28	0.99	0.0111
11	$k_{Mg}^{Sr_c} = 0.297\ pH_{salt}$	28	0.99	0.0059
12	$k_{Mn}^{Sr_c} = 0.526 \ln$ (Organic Matter)	28	0.93	0.0270
13	$k_{D_{Ca_c}}^{M_K} = 0.152 \ln \frac{(D^{2+})_{Ca_c}^{\frac{1}{2}}}{(K^+)}$	23	0.94	0.0084
14	$k_{D_{Ca_c}}^{Al} = 0.650$ (Organic Matter)	16	0.90	0.0569

[1] Standard error of estimate.
All equations presented $P \leq 0.0001$.
SAS Stepwise Noint procedure (SAS Institute, 1985).
Data of soil factors from Tables 2, 6, and 7.

Estimation of the selectivity coefficients

In order to develop a simple procedure for calculating the buffer power of K (Eq. [8]), it is necessary to estimate the values of the selectivity coefficients (Table 7). This was done by using soil factors routinely determined: pH in water, pH in 0.01 M $CaCl_2$, pH in the SMP buffer solution, organic matter content, clay content (Table 2), and activity ratios in the equilibrium solution (Table 6). Within the possible regressions, Table 8 contains the equations with the best values of r^2. All values of r^2 were greater than 0.8 and significant at 1 % level. Six of the first 9 selectivity coefficients in Table 8 were related to pH (equations 1, 2, 4, 5, 6, and 8). This implies that as an increase in pH occurs and, as a consequence, a larger charge density established, the negatively charged sites have increased their energy of adsorption for the cation (or group of cations) that was initially less preferred. This was verified for the following pairs: Sr-Ca, Sr-Mg, Mg-Ca, Mn-Ca, Na-K, and M-Al. Keren & O'Connor (1983) demonstrated that for the Sr-Ca pair, in a system of ionic strength similar to the average value obtained in this study (0.014 mol L^{-1}, Table 6), the adsorption of Sr was enhanced as a consequence of an increase in pH. In the present study an average value of 0.84 was determined and only at a pH of 5.9 the estimated value of k_{Ca}^{Sr} would be equal to 1. An increase in clay and organic matter content was also positively related to an increase in specificity for the less preferred cations (eqs. 3 and 9, Table 8). This was also expected, since an increase in both clay and organic matter should increase the charge density of the soil. Values of k_{Ca}^{Sr} varied from 0.59 to 1.00, whereas Khasawneh et al. (1968) determined values ranging from 0.61 to 1.51 for soils of the State of Indiana, USA.

The multielement selectivity coefficient between the monovalent and divalent cations, $k_{D_{Ca}}^{M_K}$, was best related with the activity ratio of the divalent activity equivalence of Ca, $(D^{2+})_{Ca}$, and the activity of K in the equilibrating solution (Table 8, eqs. 7 and 13). Since $k_{D_{Ca}}^{M_K}$ is the most important selectivity coefficient to calculate the buffer power of K (see Eq. [8]), knowing simply the activity ratio in the soil solution of $(D^{2+})_{Ca}$ and (K^+) allows to determine most of the factors necessary to calculate the buffer power of the soil for K.

Diffusion parameters

For more than 20 years diffusion of nutrients in the soil and their absorption by plant roots has been modelled mostly for plants grown under controlled conditions. However, little of this experience has actually been transferred to increase the precision of nutrient availability estimation for practical purposes. Apparently no fertilizer recommendation system based on the enormous scientific knowledge accumulated on diffusion and nutrient uptake modelling has been developed. One of the main limitations to model diffusion in the soil and absorption of nutrients by plant roots under field conditions, on a routine basis, is the lack of a simple method to determine diffusion parameters. The use of the $Sr(NO_3)_2$ equilibration procedure and the approach used in Eq. [8] to calculate the buffer power of the soil for K might contribute, to some extent, to overcome this problem, since the analytical procedure is simple and the buffer power can be easily calculated when the selectivity coefficients (Table 7) are known. Therefore, once the diffusion parameters have been determined, total inflow to the root during a given time (mol cm^{-1} root) could be modelled and used as an availability index instead of the presently use of a concentration. Average values of the three main diffusion parameters are given in Table 9, $C_{li} = 3.31 \times 10^{-4}$ mmol cm^{-3} solution, b = 14.06(mmol cm^{-3} soil)/(mmol cm^{-3} solution), and $D = 2.21 \times 10^{-7}$ cm^2 soil $second^{-1}$.

Strontium equilibration and the natural soil solution

Natural strontium concentration in the soils (data not shown) was within the detection limit. As indicated, 1 mmol Sr/100 g was added to the soil

Table 9. Volumetric soil water content (θ), soil density (ρ), initial soil solution concentration (C_{li}), K soil buffer power (b) and diffusion coefficient of K in the soil (D), using data from Tables 2 to 7

Sample	θ[1]	ρ[2]	$C_{li} \times 10^4$[3]	b[4]	$D \times 10^7$[5]
1	0.25	1.15	2.19	9.97	0.99
2	0.25	1.15	2.00	9.49	1.04
3	0.20	1.20	2.52	13.11	0.39
4	0.20	1.20	1.77	12.78	0.40
5	0.27	1.14	6.48	16.50	0.75
6	0.36	1.21	10.80	13.06	2.17
7	0.45	1.20	4.26	24.08	2.25
8	0.35	1.20	3.83	25.52	1.02
9	0.30	1.41	2.08	10.24	1.63
10	0.27	1.36	1.38	12.69	0.97
11	0.42	1.28	1.47	18.03	2.46
12	0.44	1.23	4.13	10.99	4.62
13	0.42	1.27	4.91	13.75	3.22
14	0.41	1.17	1.10	14.84	2.79
15	0.45	1.20	2.00	13.53	4.00
16	0.45	1.20	4.44	9.21	5.88
17	0.30	1.20	1.71	10.59	1.58
18	0.30	1.20	1.76	12.60	1.33
19	0.30	1.20	1.29	15.80	1.06
20	0.30	1.20	1.72	10.76	1.55
21	0.40	1.26	2.65	12.55	3.07
22	0.41	1.26	1.42	14.09	2.93
23	0.40	1.20	0.80	25.31	1.52
24	0.40	1.20	0.87	23.16	1.66
25	0.30	1.30	8.25	8.11	2.06
26	0.30	1.30	12.76	6.98	2.39
27	0.38	1.21	1.67	14.03	2.36
28	0.49	1.24	2.32	11.86	5.85
Average	0.35	1.23	3.31	14.06	2.21

[1] cm^3 water cm^{-3} soil. [2] g soil cm^{-3} soil (used in Eq. [8]). [3] mmol cm^{-3} solution, equal to the concentration of K in the $Sr(NO_3)_2$ equilibrating solution. [4] (mmol cm^{-3} soil)/(mmol cm^{-3} solution), according to Eq. [20] of Wiethölter & Corey[4]. [5] cm^2 soil $second^{-1}$, according to Eq. [9] of Nye & Marriott (1969).

[10 g soil + 25 mL 0.004 M $Sr(NO_3)_2$]. After the equilibration, in average, 0.30 mmol Sr/100 g remained in solution (Table 3) and 0.63 mmol Sr/100 g was retained by the solid phase (Table 4), yielding a total labile Sr, [Sr_T], of 0.93 mmol/100 g (Table 5). Therefore, only 0.07 mmol Sr/100 g was not recovered with 1 M NH_4Cl, and could be considered to have been specifically adsorbed. Values of Sr lower than 0.9 mmol/100 g were observed in soils with higher pH and high cation exchange capacity (Tables 2 and 5), which agrees with equations 1 and 2 of Table 8, i.e. adsorption of Sr increased with an increase in pH.

[4] WIETHÖLTER, S. & COREY, R.B. Derivation of differential buffer powers of the soil for cations. R. bras. Ci. Solo, Campinas (in press).

According to Table 3, the summation of the divalent cation concentration in the equilibrium solution, [D^{2+}], in average, was 4.23 mmol L^{-1}, with a standard deviation (not shown) of 0.29 mmol L^{-1}. Since a solution containing 4 mmol Sr L^{-1} was added to the soil, the ionic strength of this solution was sufficient to buffer most of the natural soil solution salt concentration. If the total charge added to the soil (8 $mmol_c L^{-1}$) would be subtracted from the total charge content of the equilibrium solution ($M^+ + D^{2+} + Al^{3+}$ = 9.25 mmol L^{-1}, Table 3), the natural soil solution would have contained 1.25 mmol L^{-1}. If this content, for instance, were converted into divalent cations, the natural soil solution concentration would have been 0.0025 M, which is quite low but reasonable for unfertile Oxisols, according to data presented by Bohn et al. (1979, p.273) for soils of temperate regions.

CONCLUSIONS

1. Average values of cation selectivity coefficients for 14 soils of the State of Rio Grande do Sul were: $k_{Ca}^{Sr} = 0.84$, $k_{Mg}^{Sr} = 1.15$, $k_{Mn}^{Sr} = 0.78$, $k_{Ca}^{Mg} = 0.71$, $k_{Ca}^{Mn} = 1.14$, $k_{K}^{Na} = 0.48$, $k_{D_{Ca}}^{M_K} = 0.34$, $k_{Al}^{M_K} = 0.14$ and $k_{D_{Ca}}^{Al} = 3.07$.

2. Multi-element selectivity coefficients of the main cations in the soil might be estimated through routinely determined soil factors, including pH in water, pH in 0.01 M $CaCl_2$, pH in the SMP buffer solution, clay content, organic matter content, and activity ratios in the 0.004 M $Sr(NO_3)_2$ equilibrating solution.

3. Selectivity coefficients in addition to activities in the soil solution and content on the exchangeable phase of all major soil cations could be used to calculate the differential buffer power of the soil for K.

4. Estimating the activity of cations in the soil solution through the $Sr(NO_3)_2$ equilibration procedure, calculating the amounts of exchangeable cations, and estimating the selectivity coefficients might lead to a simple method for determining K diffusion parameters.

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