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EVIDENCE OF POTASSIUM FIXATION THROUGH MONO AND DIVALENT ION EXCHANGE

RIASSUNTO

Studio della potassio-fissazione attraverso lo scambio mono e divalente.

È stato studiato il comportamento di alcuni suoli dell'Algeria allo scambio eterovalente. Le isoterme di assorbimento dimostrano che il processo non è reversibile e che tutti i suoli hanno una elevata affinità per lo ione Ca^{2+} . L'equazione di Gapon non descrive in modo soddisfacente lo scambio Ca-K perché la variazione del potassio scambiabile (EKR) in funzione del potassio adsorbito (KAR) non è lineare. Questo comportamento viene interpretato in relazione alla tendenza a fissare potassio dei suoli studiati.

SUMMARY

Mono and divalent cation exchange in some algerian major soil types was studied following empirical approach. The reaction $2 \text{Na-Soil} + \text{Ca}^{2+} = \text{Ca-Soil} + 2 \text{Na}^+$ did not show complete reversibility possibly due to high Ca selectivity of soils. The soils exhibited divalent over monovalent ion affinity but for monovalent ion exchange the affinity in few cases remained almost the same. Gapon's equation did not seem to describe Ca-K exchange very satisfactorily because exchangeable potassium ratio (EKR) and potassium adsorption ratio (KAR) are not related linearly. The latter seems to be due to potassium fixing tendency of soils investigated.

INTRODUCTION

Empirical cation exchange equations are of considerable value permitting a reasonable prediction of the equilibrium between the cations in the solution and in the adsorbed phase. The relation between sodium adsorption ratio (SAR) and exchangeable sodium percentage (ESP), which «approximately» equals to exchangeable sodium ratio (ESR), developed by U.S.S.L. (United States Salinity laboratory, 1954), based on Gapon's equation (Gapon, 1933), is well known. Successively silimar relation to suit the local conditions have been reported by Bower (1959), Balba

(1963), Paliwal and Maliwal (1970). Empirical equations based on law of mass action tacitly assume that cation exchange is completely reversible (Tabikh et al, 1960; Diest and Talibudeen, 1967). If it is so, then, product of equilibrium constants K_1 and K_2 should be unity, otherwise, there is hysteresis. The object of this paper was to study: 1) the reversibility of Na-Ca exchange; 2) the empirical analysis of mono-divalent exchange in some algerian soils.

MATERIAL AND METHODS

Soil samples from 5 major soil types, Typic Xerofluvent (Reghaia), Fluventic Xerochrepts (Hadjot), Typic Torriorthents (Boudouaou), Typic Pelloxererts (Meftah) and Vertic Haplaquepts (Boufarik), were included. Their relevant physicochemical properties are enumerated in table 1.

Ion exchange equilibrium

The method was precisely the same as described by Galindo and Bingham (1977). In brief, 1 g soil samples in duplicate, to obtain homoionique Na,Ca, or K soils, were treated repeatedly with 0.2 N neutral Cl solutions and washed with 80% ethanol to remove excess of salts. Successively the samples were exchanged by a 0.05 N solution, in which M^+ / M^+ , D^{+2} ratio varied from 0 to 1, until equilibrium was reached. After washing step, as above, the exchangeable ions recovered through 0.5 N NH_4NO_3 , were determined by plasma Spectrometer spectrospan IV apparatus.

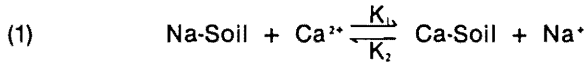
Table 1 Some important physicochemical properties of soils

Soil	Depth cm	pH 1:2.5		El. cond. mmhos/cm	O.C. %	Clay %	Cat. Exch. Cap. meq./g	
		H ₂ O	KCl				Ca or Na	K
Reghaia	-s 0-18	7.4	6.9	0.34	2.9	22.0	0.23	0.22
	-ss 18-40	7.4	6.9	0.48	1.4	22.0	0.21	0.20
Boudouaou	-s 0-10	7.4	6.1	0.42	1.3	13.0	0.14	0.13
	-ss 10-34	7.4	6.5	0.20	—	17.0	0.15	0.14
Meftah	-s 0-14	6.9	6.4	0.95	1.8	36.5	0.36	0.35
	-ss 14-40	7.9	7.1	0.47	1.4	33.5	0.44	0.42
Hadjot	-s 0-20	6.4	5.8	0.40	1.7	32.5	0.36	0.32
	-ss 20-51	7.4	6.4	0.31	0.8	25.5	0.37	0.33
Boufarik	-s 0-25	7.4	6.6	0.42	2.1	43.0	0.33	0.28
	-ss 25-45	7.8	6.7	0.61	1.5	42.0	0.35	0.29

s and ss denote surface and subsurface respectively

THEORETICAL CONSIDERATIONS

The equilibrium constant (Rao et al., 1968) for the equation,



may be calculated as follows:

$$(2) \quad \text{Na-Ca}, K_1 = \frac{\text{Ca}_s^{1/2} \text{Na}_c}{\text{Na}_s \text{Ca}_c^{1/2}}$$

$$(3) \quad \text{Ca-Na}, K_2 = \frac{\text{Na}_s \text{Ca}_c^{1/2}}{\text{Ca}_s^{1/2} \text{Na}_c}$$

where s represents the equivalent fraction adsorbed and c the cationic concentration in solution in meq/l, taking into account the activity coefficient calculated following Debye-Hückel theory.

For monovalent exchange (K-Na) selectivity coefficient (K_c) was calculated by eq (4)

$$(4) \quad K_c = \frac{K_1 \text{Na}_s}{\text{Na}_s K_2}$$

Subscripts have the same meaning as in eq (2 and 3).

The generalized form of Gapon's equation (Gapon, 1933) for mono-divalent exchange may be written as:

$$(5) \quad KG = \frac{M_s D_c^{1/2}}{D_s M_c}$$

where M and D refer to mono and divalent ions and for subscripts see eq (4). Cationic concentration is now on molar basis.

Of many empirical equations available in the literature, KG was chosen because of simplicity and common use. Recently Sposito (1977) redefined Gapon's constant and gave a new equation (6):

$$(6) \quad KG_{sp} = \frac{\text{SAR}}{2 E_{Na}} (1 - E_{Na})^{1/2}$$

where E_{Na} is the equivalent Na fraction adsorbed and SAR is based on free molar ionic concentration.

Table 2 Equilibrium constants for eq 1

Soil		K_1	K_2	$K_1 \times K_2$
Reghaia	-s	2.46	0.38	0.93
	-ss	1.87	0.34	0.64
Boudouaou	-s	1.28	1.52	1.94
	-ss	1.37	1.18	1.85
Hadjot	-s	4.29	0.26	1.12
	-ss	3.48	0.18	0.63
Meftah	-s	3.28	0.38	1.24
	-ss	1.20	0.42	1.76
Boufarik	-s	2.87	0.26	0.75
	-ss	2.75	0.28	0.77

Na-Ca exchange was also subjected to diffuse double layer analysis as modified by Bolt (1955):

$$(7) \quad T_1 / T = r / T (\beta)^{1/2} \sinh^{-1} T(\beta)^{1/2} / r + 4 Vd Ca^{1/2}$$

where T is the surface charge density of the exchanger (meq/cm^2), T_1 / T is the fraction of surface charge neutralized by the sum of excess of monovalent cation and deficit of monovalent anion, r is $\text{Na}_e/\text{Ca}_e^{1/2}$ on molar basis, β is a constant and its value at 25°C is $1.05 \cdot 10^{11}$ cm/mol . In simplified calculations Vd is assumed to be unity.

RESULTS AND DISCUSSION

Na-Ca exchange:

All the surface and subsoils manifested Ca affinity. Such affinity did not seem to depend on the cation originally present on the exchange complex as shown by fig. (1). The same figure also reveals that Na-Ca exchange is hysteretic and, therefore, exchange reaction (1) is really not reversible. Na-Ca exchange hysteresis is also manifest from table (2) since product of K_1 and K_2 (reaction 1), in all cases, is away from unity. Further proof of hysteresis is furnished by diffuse double layer equation (7).

The double layer correction factors necessary to fit the theoretical data to experimental are often higher in Ca-Na than in Na-Ca exchange (Table 3). Cation exchange hysteresis in a montmorillonite clay involving NH_4 -Ba and NH_4 -Mg was also noticed by Van Bladel and Laudelout (1967). But Tabikh et al. (1960) and Diest and Talibudeen (1967) reported that cation exchange may be reversible.

In general KG values decreased with increasing Na saturation except in few cases. Constancy of KG is generally claimed between 0-50% Na saturation (Bolt,

1955; Bower, 1959; Poonia and Talibudeen, 1977). KG_e for Ca-Na exchange varied between 23 and 76 $(\text{mol/m}^3)^{1/2}$. It should be pointed out that in the range of SAR of practical significance, i.e. 0-40, for the relation ESR-SAR identical values are given by formulations of Sposito (1977) and U.S.S.L. (1954). So, the use of recently redefined Gapon's equation by Sposito (1977) to predict ESR from SAR of irrigation waters is unnecessary indeed, at least for practical purposes. In field conditions the irrigation waters of SAR < 40 are really not used.

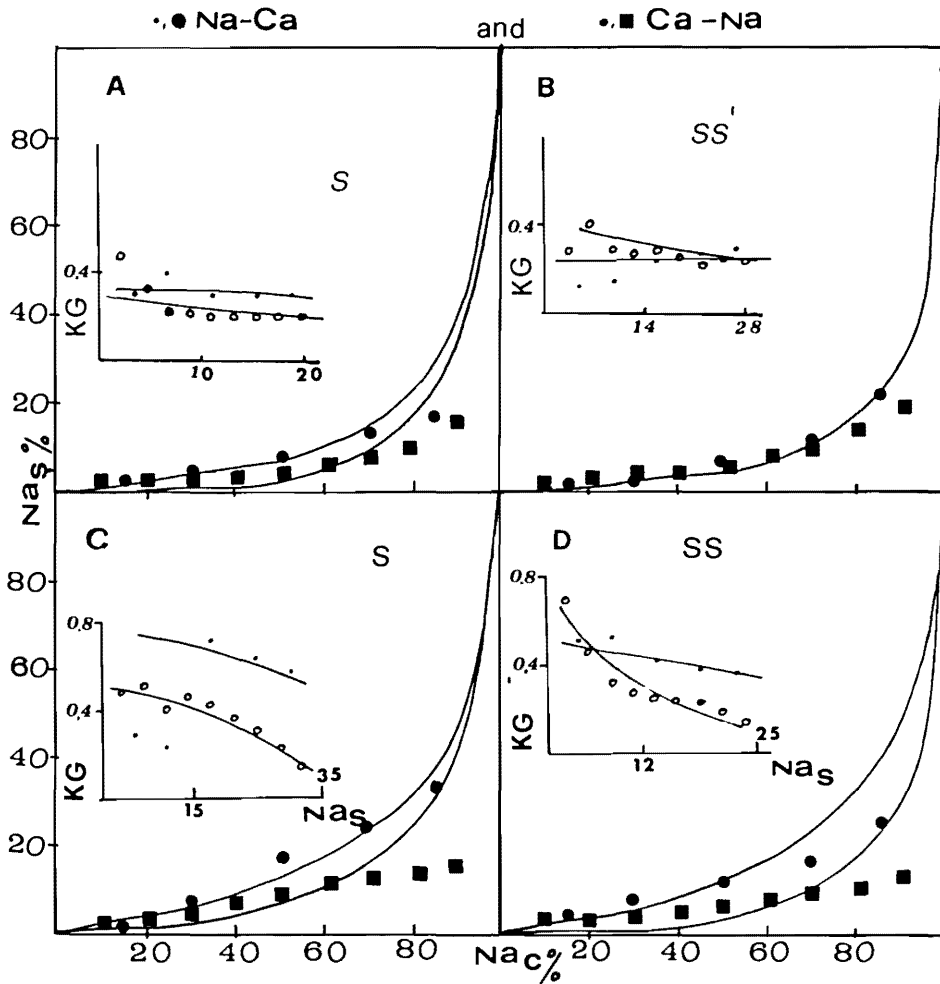


Fig. 1 - Na-Ca and Ca-Na adsorption isotherms. A. & B. Hadjot, C. & D. Meftah
 Isotherme di assorbimento Na-Ca e Ca-Na. A. & B. Hadjot, C. & D. Meftah

Table 3 Exchange constants

Soil		Na-Ca		Ca-Na			Ca-K		K-Na
		KG	DDL C.F. ¹	κ_G	$\kappa_{G,}$	DDL C.F. ¹	KG	KG, _o	Kc
Reghaia	-s	0.62	1.07	0.65	38 ± 8	1.26	2.02	16 ± 3	0.98
	-ss	0.60	1.14	0.61	27 ± 4	1.20	2.62	13 ± 3	0.89
Boudouaou	-s	1.24	—	0.93	23 ± 8	—	1.68	20 ± 5	0.93
	-ss	0.94	—	0.93	26 ± 5	—	1.42	21 ± 5	0.42
Hadjot	-s	0.31	1.88	0.24	76 ± 6	2.39	1.90	15 ± 3	0.41
	-ss	0.22	2.89	0.28	62 ± 4	2.06	2.06	14 ± 3	0.41
Meftah	-s	0.50	1.46	0.40	50 ± 9	1.64	1.68	15 ± 3	0.27
	-ss	0.45	1.27	0.32	67 ± 11	1.98	1.77	20 ± 3	0.28
Boufarik	-s	0.47	1.35	0.40	49 ± 6	1.53	1.30	20 ± 4	0.42
	-ss	0.27	1.80	0.41	46 ± 5	1.45	1.08	22 ± 4	0.52

¹ Diffuse double layer correction factors (eq 7)

Ca-K exchange:

KG values (L/mol)^{1/2} in general decreased with increasing K saturation (Knibbe and Thomas, 1972; Carson and Dixon, 1972; Bolt et al, 1963). Ca affinity of soils over K (Diest and Talibudeen, 1967; Gessa, 1970), although quite manifested, did not follow the same course over the whole range of adsorption isotherms, see and example from Reghaia and Hadjot depicted in fig. (2). In surface soils especially K selectivity was greater than Ca, until about 20% K in equilibrium solution. Mean values of KG,_o and KG for different samples, calculated using eq (6&5), are given in table (3). KG values being higher here than in Ca-Na exchange must not be interpreted as if all soils preferentially adsorb K than Na (see Na-K exchange also). Separate experiments must therefore be carried out to define the cation affinity from a given pair of cations.

If the Ca-K equilibrium data conform to Gapon's equation (4) a plot of exchangeable potassium ratio (EKR) against potassium adsorption ratio (KAR) must yield a straight line passing through the origin. The slope of this line is then Gapon's constant. Such plots were found to be curvilinear as shown by the examples depicted in fig. 3 (Gheyl and Van Bladel, 1975; Sheta et al., 1981). This figure also brings into evidence the potassium fixing tendency of these soils as, at very low values of KAR the EKR is rather high. In case of Hadjot and Boufarik some information on K fixation is given by table (1). CEC in presence of K is lower than in presence of Ca or Na. Consequently, calculation of KG from plot of fig. (3) was left out, because under such conditions Gapon's equation could not describe satisfactorily the Ca-K exchange.

The nature of clay in all soils is illitic and Boufarik soil tends to exhibit vertic cha-

racter. Selectivity of certain clays for potassium has indicated that mica minerals are the most highly selective followed by vermiculite. Under some conditions certain montmorillonites do not adsorb potassium selectively (Rich, 1968). But the small amounts of mica and vermiculite that may go undetected as impurities may exert preference for potassium ion in highly montmorillonitic soils. Carson and Dixon (1972) reported that high KG values that occur over several percent potassium saturation in coarse clay fractions indicate that this fraction is more important

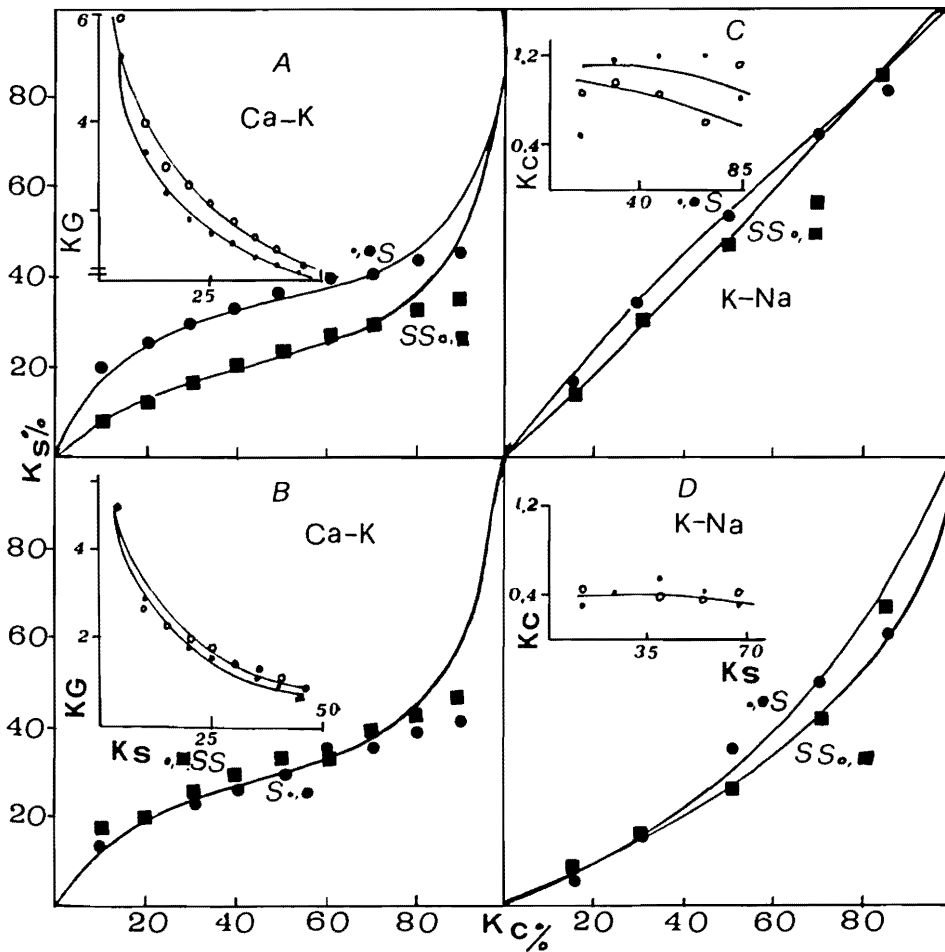


Fig. 2 - Ca-K and K-Na adsorption isotherms. A. & C. Reghala, B. & D. Hadjot
 Isotherme di assorbimento Ca-K e K-Na. A. & C. Reghala, B. & D. Hadjot

than the more abundant finer fraction in controlling KG values and presumably potassium availability to plants. This observation of these authors seems to hold for our Reghaia and Boudouaou soils as well, as they contain dominantly the coarse fraction. Relative clay fraction composition may therefore be enumerated to influence potassium affinity of soils.

The potassium fixation process was also revealed in K-Na exchange. In fact, Meftah soil (fig 2) evidences greater affinity for Na than for K. Similar behaviour was manifested by Hadjot and Boufarik soils, which were already mentioned to fix potassium. So the observation that in monovalent exchange the preferentially adsorbed ion is the one with smaller hydrated ion size (Helffrich, 1962) seems to be overshadowed by these soils potassium fixing tendency. Reghaia and Boudouaou soils, which apparently do not seem to participate in K fixing process, show no preference for either Na or K.

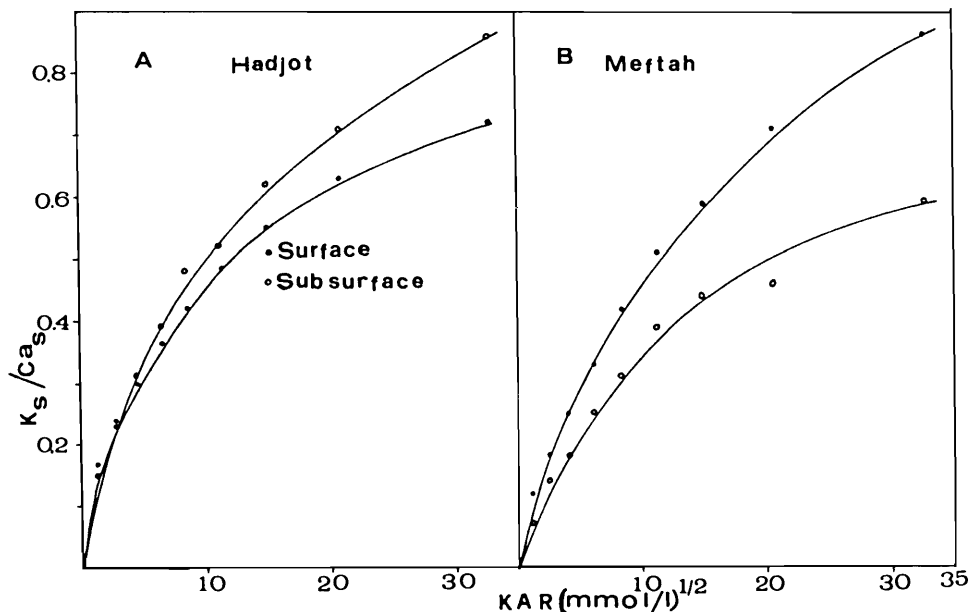


Fig. 3 - Potassium adsorption ratio vs exchangeable potassium ratio curves. A. Hadjot, B. Meftah
Relazione tra K_s/Ca e KAR

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