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Exchange equilibria of potassium in soils, V. Effect of natural organic matter on K–Ca exchange

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ABSTRACT

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Exchange equilibria of K–Ca were studied in five soil samples (Anglberg surface, ABS; Anglberg subsurface, ABSS; Ottenhofen surface, OHS; Ottenhofen surface limid, OHSL; Buchhofen surface, BHS) from the Federal Republic of Germany. These samples had a wide difference in their clay content, clay mineralogy, CEC, K-fixation capacity, organic matter (OM), specific surface area, and surface charge density (SCD). Untreated and H_2O_2-treated samples were Ca-saturated and equilibrated with KCl+$CaCl_2$ solutions at a constant chloride concentration of 0.025 $M\,l^{-1}$ in the equilibrium solutions. The experimental results were described, using the Gaines and Thomas, and Babcock and Duckart thermodynamic approaches, and various selectivity quotients.

Out of five, two soil samples showed a decrease in the Gapon (K_G) and Vanselow (K_V) selectivity quotients in the lower K-saturation (i.e., 0–15 exchangeable potassium percentage, EPP, in ABS; 0–30 EPP in ABBS) zone on oxidation of OM. In the remaining three soil samples, K_G and K_V increased with H_2O_2-treatment for the whole exchange isotherms. The Gaines and Thomas standard free energy for K–Ca exchange (ΔG_0) decreased in all but one (i.e., ABSS) and Babcock and Duckart ($\Delta G_0'$) in all the soil samples on OM oxidation. The values of ΔG_0 were less negative than those of $\Delta G_0'$ for comparable soil samples. The positive or negative effect of OM on K-preference has been ascribed to the "resultant" of the two opposing phenomena, viz., an increase in SCD and "low K-specific adsorption sites" (causing a decrease in K-preference), and an increase in the internal:external surfaces due to organo-mineral colloids (causing an increase in K-preference).

INTRODUCTION

The role of organic manuring and the contents of natural organic matter (OM) in soils on the exchange equilibria of potassium versus calcium has been investigated by some workers. Johnston and Addiscott (1971), while studying the effect of long-term application of farmyard manure (FYM) on K-preference of soils, observed that the quantity:intensity (Q/I) parameters of potassium for soil samples taken from the control and the FYM-treated

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plots at Rothamsted and Woburn experiments (UK) were almost identical. Goulding and Talibudeen (1984), on the other hand, observed a considerable decrease in K-preference of FYM-treated soil samples from Broadbalk and Saxmundham experiments (UK). Sparks and Liebhardt (1982), and Jardine and Sparks (1984) also found lower K-preference for surface (high OM) than for sub-soil (low OM) samples from the same soil profile, and for untreated (OM 1.4%) than for NaOCl-DCB-treated soil samples. Contrary to these results, Mehta et al. (1983) observed a decrease in the K-preference of a forest soil after H_2O_2 treatment. Poonia et al. (1986) observed an increase in K-preference of soils on FYM application. It is apparent from the limited investigations cited above that there is a considerable difference in the role of OM in influencing the K-preference of soils. Based on the results of FYM application in "three soil samples having almost identical clay mineralogy and other physicochemical properties" from Haryana (India), Poonia et al. (1986) postulated that OM plays a dual role in influencing K-specificity of soils, viz., a decrease in K-preference due to an increase in surface charge density (SCD) and non-K-specific organic surfaces, and an increase in K-preference due to an increase in internal:external exchange sites. This paper reports the results on K–Ca exchange in relation to oxidation of OM from "soils widely differing in their clay content, clay mineralogy, K-fixation capacity, specific surface area, SCD, and OM contents". The results are expressed in terms of Gapon (K_G) and Vanselow (K_V) selectivity quotients, and standard free energy of K–Ca exchange.

MATERIALS AND METHODS

Four surface (0–15 cm) soil samples and one subsurface (25–40 cm) soil sample from different locations in Bavaria, Federal Republic of Germany, viz., Anglberg surface and sub-surface (ABS and ABSS), Ottenhofen unlimed and limed (OHS and OHSL), and Buchhofen (BHS), were selected for this study. The samples were air-dried and passed through a 0.5 mm sieve. A portion of the samples was treated with H_2O_2 to remove their oxidizable organic carbon. Some relevant physico-chemical and mineralogical properties of these samples before and after H_2O_2 treatment are given in Tables I and II.

For K–Ca exchange equilibria studies, salt-free Ca-saturated soil samples were prepared by repeated washings with decreasing concentrations of $CaCl_2$ (i.e., 1 to 0.005 M), distilled water and ethanol. A final washing was given with petroleum ether to obtain friable samples on drying. The samples so prepared were air-dried and ground to pass through a 0.5 mm sieve. The procedure was essentially the same as used by Mehta et al. (1983).

Sixteen different solutions, covering the whole range of equivalent ion fractions of potassium, were prepared from $KCl+CaCl_2$ at a constant total chloride concentration of 0.025 M l^{-1}. The Ca-saturated samples were equili-

TABLE I

Some physicochemical and mineralogical properties of the soils used

Sample code	pH (0.01 N $CaCl_2$)	CEC (cM/kg)	KFC (cM/kg)	OC (%)	Clay (%)	Clay mineralogy of $<2\mu$ (%)			
						7Å Kaol	10Å Ill	14Å Ver	18Å Sm
Anglberg (Typic Humaquept)									
ABS	7.1	47.6	6.91	5.10	45	13	15	19	53
$ABSH_2O_2$	–	31.3	5.57	1.04	–	–	–	–	–
ABSS	7.2	51.9	11.52	3.27	47	11	6	12	71
$ABSSH_2O_2$	–	38.5	9.21	0.95	–	–	–	–	–
Ottenhofen (Typic Agriaquoll)									
OHS	5.4	22.3	2.04	2.78	27	7	28	20	45
$OHSH_2O_2$	–	15.5	2.28	0.40	–	–	–	–	–
OHSL	5.7	22.8	0.92	3.10	27	–	–	–	–
$OHSLH_2O_2$	–	14.2	0.98	0.42	–	–	–	–	–
Buchhofen (Typic Hapludalf)									
BHS	7.3	24.5	nil	2.93	23	8	80	5	7
$BHSH_2O_2$	–	12.1	nil	0.39	–	–	–	–	–

AB = Anglberg; OH = Ottenhofen; BH = Buchhofen; S = Surface (0–15 cm); SS = subsurface (25–45 cm); H_2O_2 = sample after hydrogen peroxide treatment; L = limed; KFC = K-fixation capacity; Kaol-kaolinite; Ill = illite; Verm = vermiculite; Sm = smectite.

TABLE II

Effect of H_2O_2 treatment on external (a), total (b) and internal ($b-a$) surface area (SA), and surface charge density (SCD), and approximate per cent contribution of oxidizable organic carbon to CEC (% org. CEC)

Sample code	SA (m^2/g)				SCD (M/m^2) $\times 10^6$	Org. CEC (%)
	a	b	$(b-a)$	$(b-a)/a$		
ABS	16.1	169.1	153.4	9.5	2.81	34
$ABSH_2O_2$	27.4	158.7	131.3	4.8	1.97	–
ABSS	30.3	198.7	168.4	5.6	2.62	26
$ABSSH_2O_2$	36.6	187.5	150.9	4.1	2.05	–
OHS	15.5	109.0	93.5	6.0	2.05	31
$OHSH_2O_2$	26.9	91.0	64.1	2.4	1.70	–
OHSL	16.8	126.6	109.8	6.5	1.80	37
$OHSLH_2O_2$	26.6	103.1	76.5	2.9	1.39	–
BHS	22.8	72.5	49.7	2.2	3.38	51
$BHSH_2O_2$	22.7	76.3	53.7	2.4	1.59	–

a = external (Argon adsorption method); b = total (ethylene glycol monoethyl ether method); $(b-a)$ = internal.

brated with these solutions at a 1:25 soil–solution ratio for 24 h and analysed for K and Ca in solution and adsorbed phases as described earlier (Mehta et al., 1983). From these data, calculations were made for Gapon selectivity quotient (K_G). Vanselow selectivity quotient (K_V) and "approximate" free energies of K–Ca exchange (ΔGo, Gaines and Thomas, 1953; $\Delta Go'$, Babcock and Duckart, 1980), as follows:

For the exchange reaction:

$$Ca\,X_2 + 2K \rightleftharpoons 2K\,X + Ca$$

$$K_G = \frac{N_K}{N_{Ca}} \frac{(a_{Ca})^{0.5}}{a_K}$$

$$K_N = \frac{(N_K)^2}{N_{Ca}} \frac{a_{Ca}}{(a_K)^2}$$

$$K_V = \frac{(M_K)^2}{M_{Ca}} \frac{a_{Ca}}{(a_K)^2}$$

$$\ln K = 1 + \int_0^1 \ln K_N \, dN_K = \int_0^1 \ln K_V \, dM_K$$

$$\Delta Go = -RT \ln K$$

$$\Delta Go' = -RT \ln K'$$

where N and M stand for the equivalent and mole fractions of cations in the adsorbed phase, respectively, and a for activities ($M\,l^{-1}$) in the equilibrium solution. T is absolute (Kelvin, K) temperature and R is gas constant (8.314 J/K/M). The experiment was conducted at room temperature (i.e., 298 ± 2 K). $K' = 2K'_V$, with K'_V as the value of K_V at M_K 0.5. The maximum experimental K-saturation did not exceed 70% of CEC in any of the samples tested. As the computation of $\ln K$ needs integration of $\ln K_N$ or $\ln K_V$ for the whole range of K–Ca exchange isotherm (i.e., N_K or M_K:0–1), a best fit regression was drawn between EPP versus $\ln K_N$ or $\ln K_V$, using a third-degree polynomial equation. The coefficient of determination for the regression relationship so obtained was very high (i.e., $r^2 = 0.97$ to 0.99).

RESULTS AND DISCUSSION

The experimental results on the Gapon (K_G) and Vanselow (K_V) selectivity quotients for K–Ca exchange in relation to organic matter at the minimum and maximum experimental exchangeable potassium percentages (EPPs) are given in Table III.

The values of K_G for the surface soil sample from Anglberg (ABS) de-

TABLE III

Gapon (K_G) and Vanselow (K_V) selectivity quotients at the minimum (a) and maximum (b) experimental K-saturations, and standard free energy of K–Ca exchange by the Gaines and Thomas (ΔGio) and Babcock and Duckart ($\Delta Gio'$) approaches

Sample code	K_G $(1/M)^{0.5}$			K_V $(1/M)$			ΔGio (kJ/M)	ΔGio (kJ/M)
	a	b	a/b	a	b	a/b		
ABS	22.6 (0.5)	1.48 (52.5)	15.3	2021	2.73	740	−4.98	−6.64
$ABSH_2O_2$	9.0 (0.6)	2.93 (70.3)	3.1	318	6.02	53	−6.96	−9.49
ABSS	2172.0 (0.9)	2.27 (59.7)	957.0	$>10^6$	5.21	$>10^5$	−10.69	+10.76
$ABSSH_2O_2$	25.0 (1.0)	2.85 (67.5)	8.0	2456	6.32	389	−9.96	−12.81
OHS	12.2 (0.8)	2.31 (69.5)	5.3	586	3.85	152	−5.00	−7.02
$OHSH_2O_2$	23.4 (1.3)	2.40 (66.8)	9.8	2130	4.61	462	−7.18	−10.22
OHSL	10.0 (0.7)	0.77 (55.0)	13.0	392	0.64	568	−1.35	−5.70
$OHSLH_2O_2$	18.2 (1.1)	1.33 (70.3)	13.7	1296	1.24	1045	−5.58	−11.22
BHS	7.0 (0.8)	0.25 (22.2)	28.0	191	0.16	1191	+7.97	–
$BHSH_2O_2$	16.4 (1.5)	0.69 (44.6)	23.8	1041	0.74	1407	−1.20	−4.82

Values in ( ) in columns 2 and 3 are the minimum and the maximum experimental exchangeable potassium percentages, respectively.

creased from 22.6 at the minimum experimental K-saturation (EPP 0.5) to 1.48 $(1/M)^{0.5}$ at the maximum experimental K-saturation (EPP 52.5). The corresponding decrease in K_G for the same sample after H_2O_2 treatment ($ABSH_2O_2$) was from 9 (EPP 0.6) to 2.93 (EPP 70.3). The subsurface sample from the same location (ABSS) showed a decrease in K_G from the exceptionally high value of 2172 (EPP 0.9) to 2.27 (EPP 59.7) before H_2O_2 treatment and from 25 (EPP 1) to 2.85 (EPP 67.5) after H_2O_2 treatment ($ABSSH_2O_2$). The value of K_G for the unlimed (OHS) and limed (OHSL) samples from Ottenhofen, and a sample from Buchhofen (BHS), on the other hand, increased after peroxidation treatment throughout the entire range of K-saturation. The increase in K_G on H_2O_2 treatment was from 12.2 to 23.4, 10 to 18.2, and 7 to 16.4 at the lowest, and from 2.31 to 2.4, 0.77 to 1.33, and 0.25 to 0.69 at the highest experimental K-saturations in OHS, OHSL, and BHS soil samples, respectively. With the increase in EPP, the value of K_G decreased in all the samples. The decrease ranged from 3.1 ($ABSH_2O_2$) to 957-fold (ABBS). the decrease in K_G with the increase in K-saturation of untreated samples from Anglberg was much steeper (15.3 to 957 fold) than those treated with H_2O_2 (3.1 to 8.8-fold). In the other three pairs of soil samples, the difference in the steepness of decrease in K_G with the K-saturation of untreated and H_2O_2-treated samples, however, was inconsistent and much narrower.

The dependence of K_G on K-saturation of two representative untreated and

H_2O_2-treated soil pairs for the "whole experimental EPP range" is depicted in Fig. 1. The results for the other soil samples are omitted for brevity. The figure shows that K_G-values for the ABS were larger than those for the $ABSH_2O_2$ sample in the first 15% of K-saturation (EPP 0-15). Beyond this K-saturation level, the values of K_G for the $ABSH_2O_2$ sample, however, became larger. For ABSS (not shown in the figure), K_G-values were larger than those for the $ABSSH_2O_2$ sample for a still greater part of the exchange isotherm (i.e., EPP 0–30). Contrary to these, the values of K_G for BHS (and OTS, OTSL, not shown in the figure) were smaller than those for the $BHSH_2O_2$ (and $OTSH_2O_2$, $OTSLH_2O_2$) sample throughout the experimental K-saturation. It may be noted from Table II that the contribution of OM to CEC was only 26% in ABSS (showing a negative effect of H_2O_2 treatments on K_G in 0–30 EPP) as against 51% in BHS (showing maximum positive effect of H_2O_2 treatment on K_G throughout the experimental K-saturation).

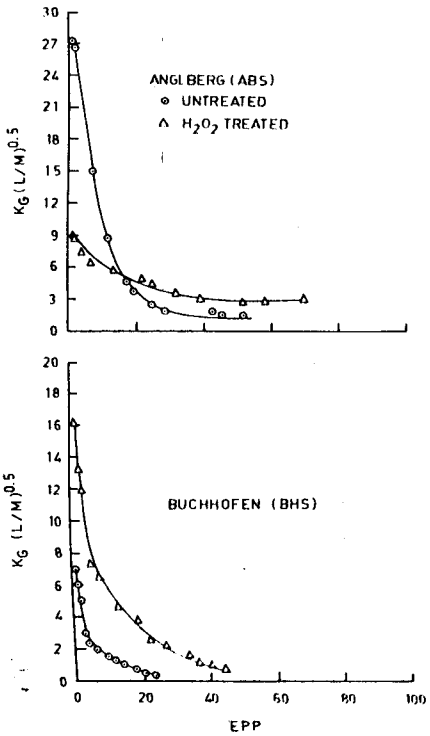

Fig. 1. Dependence of K_G on K-saturation of two untreated and H_2O_2-treated soils.

The values for K_V at the minimum experimental K-saturation decreased from 2031 to 318 in ABS, and from $> 10^6$ to 2456 l M^{-1} in ABSS on peroxidation treatment. Contrary to this, K_V for OBS, OBSL, and BHS samples increased from 568 to 2130, 392 to 1296, and 191 to 1041 l M^{-1}, respectively, on H_2O_2 treatment. Like K_G, the values for K_V at the maximum experimental K-saturation were relatively larger for the H_2O_2-treated samples from all locations. In view of the difference in the nature of equations, the increase or decrease in the magnitude of selectivity quotients in response to organic carbon oxidation or K-saturation levels, however, was more pronounced on K_V than K_G. As against a decrease of 3.1 to 957-fold in K_G, K_V decrease by 53 to $> 10^5$-fold with the increase in K-saturation.

Before dwelling on results for the thermodynamic parameters, it is important to mention that in view of the existence of different site-types, the absolute values of ΔGo (covering the entire range of exchange curves) and $\Delta Go'$ (considering the exchange preference at 0.5 mole fraction of adsorbed K) do not provide the actual information regarding the highly interesting 0–10% range of exchangeable potassium. Nevertheless, as the purpose for this study was to evaluate the influence of OM on K-preference of different soils, the "relative" values of thermodynamic parameters for the untreated and H_2O_2-treated soil samples serve the intended purpose. Further, as the adsorbed and solution phases in the experimental set-up were not in their "standard" states, the free energies of K–Ca exchange are referred to as "approximate" rather than "standard" free energies.

The "approximate" free energies of K–Ca exchange, as calculated by Gaines and Thomas (1953) (ΔGo) and Babcock and Duckart (1980) ($\Delta Go'$) approaches, are given in Table II. The results show that except for the surface sample from Anglberg (ABS), the values of ΔGo decreased (i.e., became more negative) with H_2O_2 treatment; suggesting an increase in the preference of soils for K on peroxidation treatment. The change in ΔGo on H_2O_2 treatment of different soils ranged from 0.74 (ABSS) to −9.17 (BHS) kJ M^{-1} (176 to −2191 cal M^{-1}). In general, the relative preference of different soil samples for potassium was in order ABSS ≫ OHS > ABS > OHSL > BHS. Except for the BHS sample, the values of ΔGo were negative for all the untreated as well as H_2O_2-treated samples. The value of ΔGo was minimum (−10.69 kJ M^{-1}) for the ABSS and maximum (7.97 kJ M^{-1}) for the BHS sample.

As the maximum experimental K-saturation for the BHS sample was < 0.5 M_K, $\Delta Go'$ could not be calculated for the same. Oxidation of organic matter caused a decrease in $\Delta Go'$. The decrease in $\Delta Go'$ on H_2O_2 treatment ranged from 2.05 (ABSS) to 5.5 (OHSL) kJ M^{-1}. In general, the values of $\Delta Go'$ were smaller (i.e., more negative) than those of ΔGo for the comparable samples. The results showed that the calculated values of the "approximate" free energy of K–Ca exchange for these soils by the Babcock and Duckart approach were more negative than those by the Gains and Thomas approach.

The differences between ΔGo and $\Delta Go'$ ranged from as low as 0.06 (ABSS) to as high as 5.32 ($OHSLH_2O_2$) kJ M^{-1}, depending upon the nature of the variation of K_V at different K-saturation levels.

The trend of ΔGo in relation to organic matter for the ABSS soil sample (i.e., a decrease in K-preference on oxidation of OM) is similar to that reported by Mehta et al. (1983) and Poonia et al. (1986) for some soils from Haryana (India). For other soil samples (i.e., ABS, OHS, OHSL and BHS), the trend of ΔGo in relation to organic matter (i.e., a decrease of ΔGo on peroxidation treatment), however, was in agreement to that reported by Goulding and Talibudeen (1984) for some soils of the Broadbalk and Saxmundham experiments (UK), and by Jardine and Sparks (1984) for Evesboro soil (USA).

The exchange sites on organic surfaces are known to adsorb divalent cations (Ca and Mg) more strongly than monovalent cations (K and Na). This is mainly through the local chemical bonds (i.e., liganding of divalent cations) and the Coulombic effects (i.e., preference for divalent cations due to high surface charge density, SCD, of organic soil colloids; diffuse double layer, DDL, theory: Bolt, 1955; Poonia and Talibudeen, 1977). This would mean a decrease in K-preference in response to OM. Yet it is important to mention that the generalized trend of K-specificity in different clays is: illite > vermiculite > smectite, which on the basis of SCD of these clays is in contradiction to the DDL theory. This is, however, mainly due to the geometric effects which are not accounted for by the DDL equation. While analysing the K-adsorption curves of Winsun illite, Van Schouwenburg and Schuffelen (1963) and Bolt et al. (1963) could arbitrarily divide the adsorption sites into three categories, viz., planar sites (normal preference sites for K), edge sites (very high preference sites for K), and interlattice sites (high binding energy or K-fixing sites).

Besides providing local chemical bonding and Coulombic effects to divalent cations, organic matter is known to affect the geometry of microaggregates of soils in such a way as to increase the proportion of the internal:external surfaces (Williams et al., 1967). This in turn would lead to a possible increase in the edge–interlattice sites which, as described above, are highly preferential for K-ions (Van Schouwenburg and Schuffelen, 1963). Both the above mentioned opposing phenomena operate simultaneously. The experimentally observed K-preference of soil in relation to organic matter would thus be a resultant of these effect. The relationship between the per cent contribution of H_2O_2-oxidizable OM to CEC and the change in ΔGo on oxidation of OM, as shown in Fig. 2, substantiates this contention. The results showed that when the contribution of OM to CEC was around 26%, the oxidation of OM with H_2O_2 treatment did not change the ΔGo. When this contribution exceeded 26%, the values of ΔGo became more negative on oxidation of soil OM. Contrary to this, when the contribution of OM to CEC was less than 26%, the values of ΔGo became less negative.

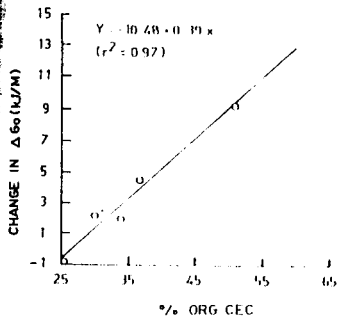

Fig. 2. Relationship of H_2O_2-oxidizable OM to CEC and charge in ΔG_o on oxidation of OM.

The results in Table II clearly show that the OM has a strong effect on the SCD and internal:external surfaces of soils. With the oxidation of OM, four out of five soil samples showed a sharp decrease in the internal:external surfaces, and all the five samples in SCD. The BHS sample, showing no effect on its internal:external surfaces, showed maximum decrease in its SCD (i.e., >50%). The increase in the K-preference on peroxidation treatment was maximum in this sample, which coincided with the "maximum decrease" in its SCD, and "maximum contribution of OM" to its CEC (i.e., >50%). A close look on the results showed that, in general, the positive effect of OM on K-specificity at low K-saturation was quite conspicuous in soils which have relatively high "K-fixation capacity". In the studies of Goulding and Talibudeen (1984), who observed a negative effect of organic manuring on the K-specificity of soils, CEC values of the FYM-treated soil samples were 37 to 59% higher than those of untreated ones. Contrary to this, in the studies of Mehta et al. (1983) and Poonia et al. (1986), where the effect of OM on K-specificity of soils was positive, the contribution of OM to CEC of the soil samples tested did not exceed 15%. These results are thus in conformity with the present findings.

From the results discussed above, it may be inferred that the effect of OM on K-specificity of soils is the "resultant" of two opposing phenomena, viz., an increase in the SCD and "low K-specific exchange sites" (causing a decrease in K-specificity), and an increase in internal:external surfaces (causing an increase in K-specificity). When the contribution of OM is less than one-fourth of the CEC of a soil, it is likely to increase the K-specificity, particularly in the low K-saturation zone. In cases where the contribution of OM to CEC of a soil is more than one-fourth, it is likely to decrease the K-specificity. Further, at a comparable contribution of OM to CEC, its positive effect towards K-specificity is likely to be more pronounced in soils which have "high K-fixation capacity" than those with "nil" or "low K-fixation capacity".

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